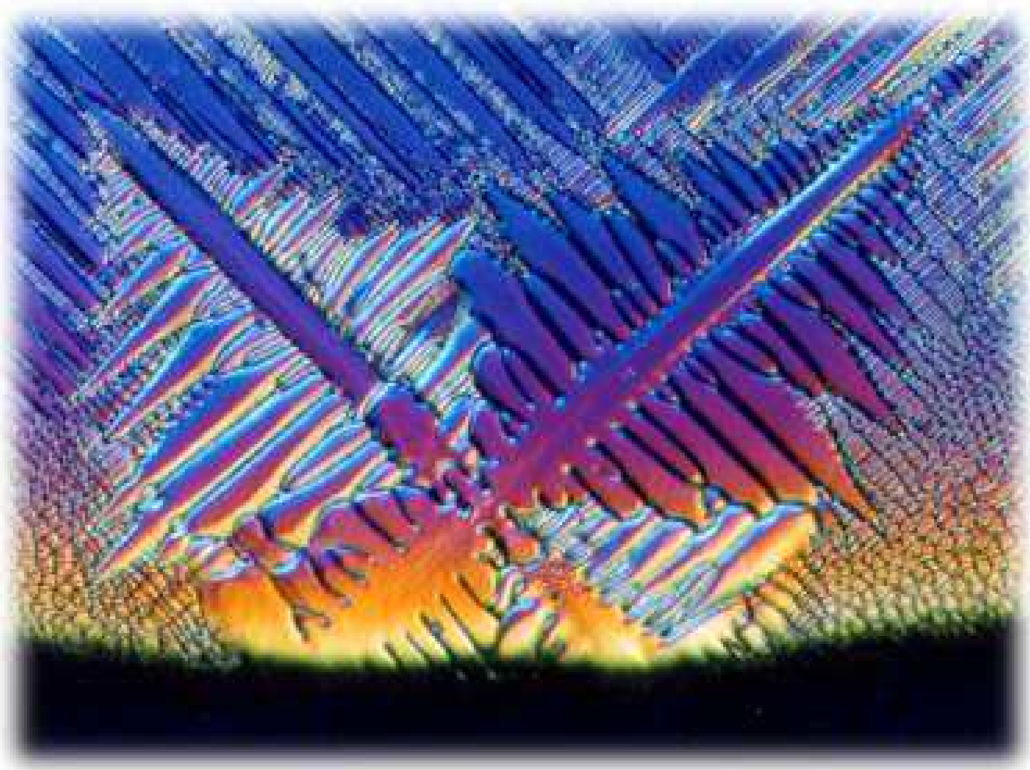
Condensed Matter Physics

- Largest subfield of physics
- Link between atoms and everyday world.
- Unity obscured by tremendous variety of topics.



Dividing the field

Historical Roots

- Atomic Structure
- Electronic Structure
- Mechanical Properties
- Electron Transport
- Optical Properties
- Magnetism

Concepts

- Self–organization
- Form and Function
- Scaling and Symmetry
- Precision Measurement
- Fabrication
- Computation

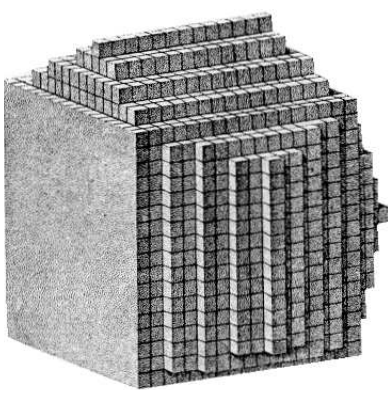
Atomic Structure

Questions:

- What is the basic structure of matter?
- How do atoms spontaneously organize?

Basic Answer:

- Scaling theory relates atom–scale units to macroscopic solids.
- Atoms form crystalline arrays.
- Idea comes from special class of solids: minerals.



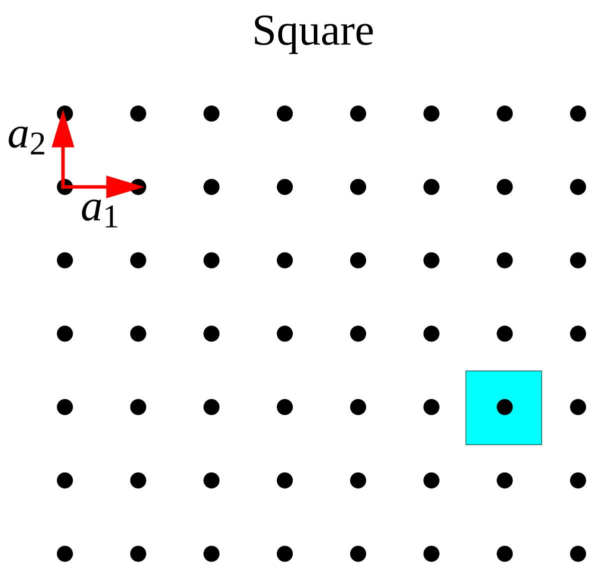
See vast numbers of minerals at http://webmineral.com/

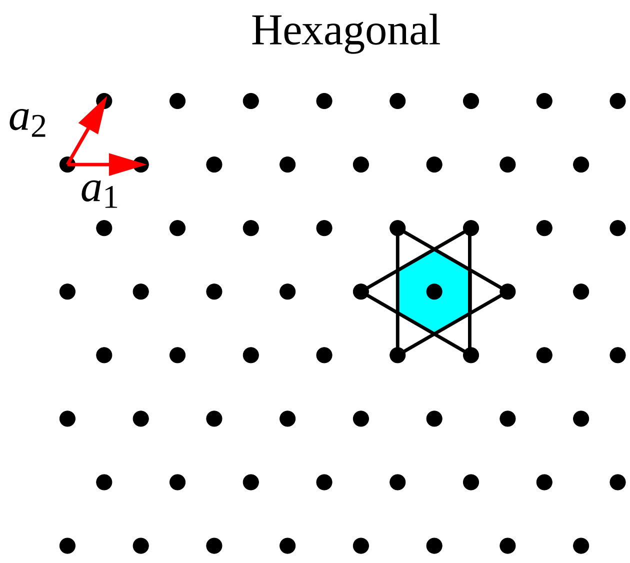
Two–Dimensional Lattices

Definitions:

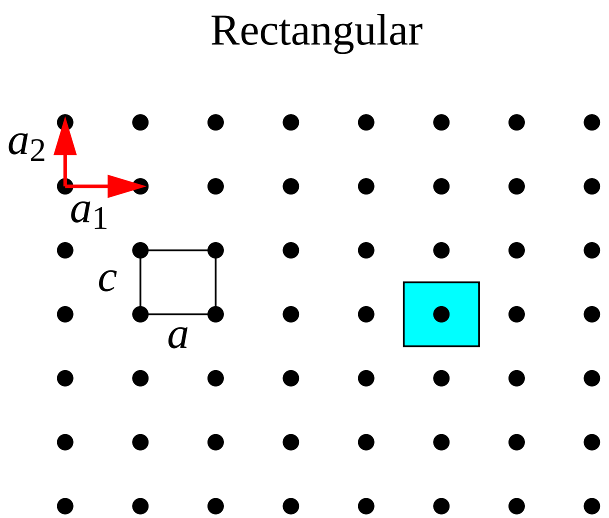
- ☞ Bravais lattice
- ☞ primitive vector
- ☞ basis vector
- ☞ unit cell (primitive or not)
- ☞ Wigner–Seitz cell (Voronoi polyhedron)
- ☞ translation, space, and point groups

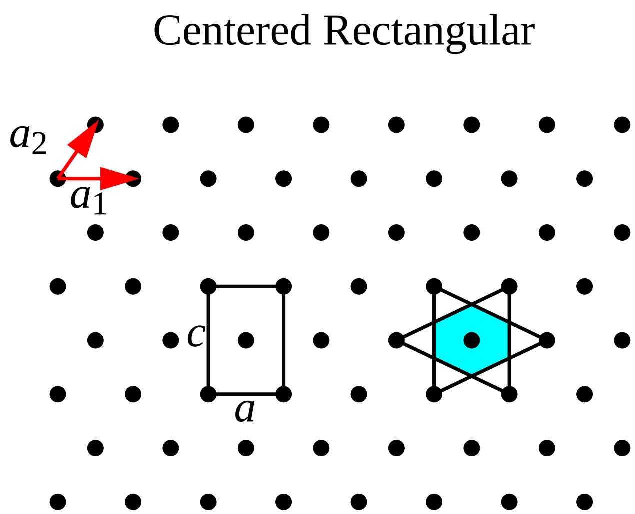
Bravais Lattices

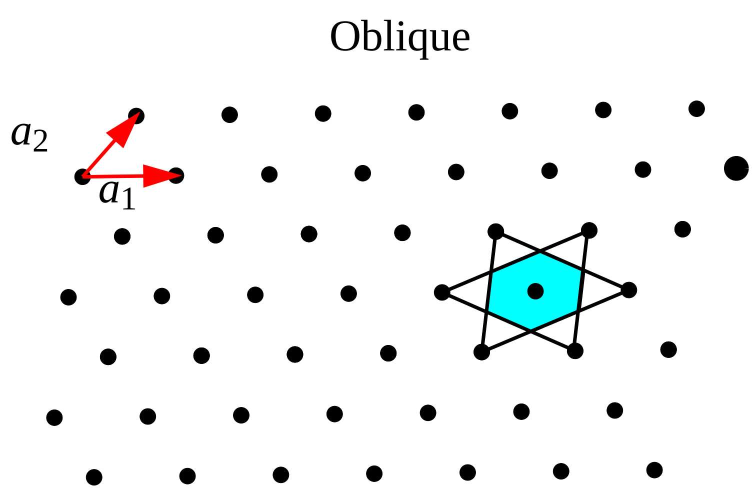




Bravais Lattices







Q: Are primitive vectors unique?

A: No..for hexagonal lattice

$$\vec{a}_1 = a(1 \;\; 0) \tag{L1a}$$

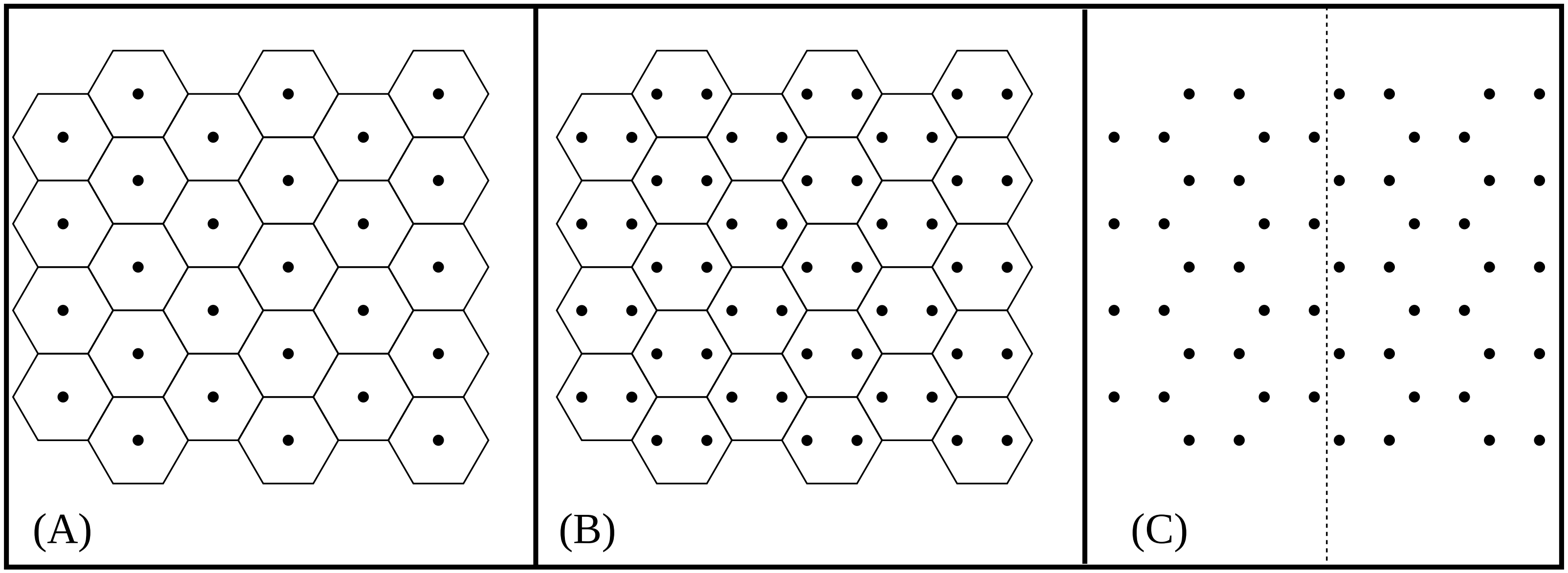
$$\vec{a}_2 = a\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \end{pmatrix}. \tag{L1b}$$

However, one could equally well choose

$$\vec{a}'_1 = a\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \end{pmatrix} \tag{L2a}$$

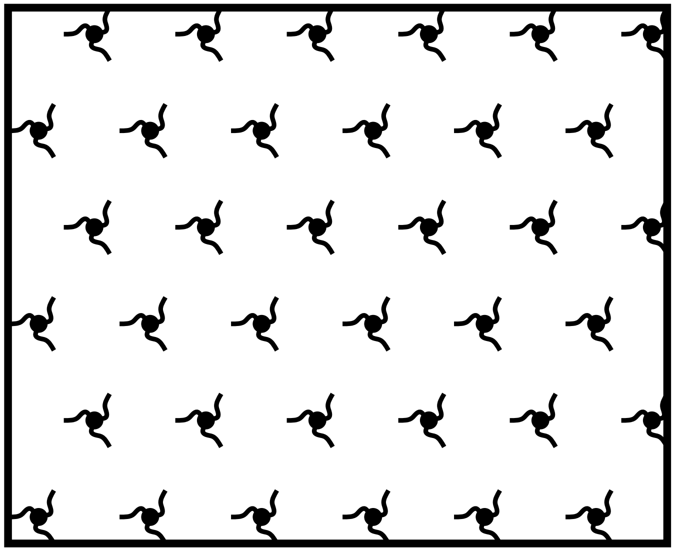
$$\vec{a}'_2 = a\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \end{pmatrix}. \tag{L2b}$$

Lattice with Basis



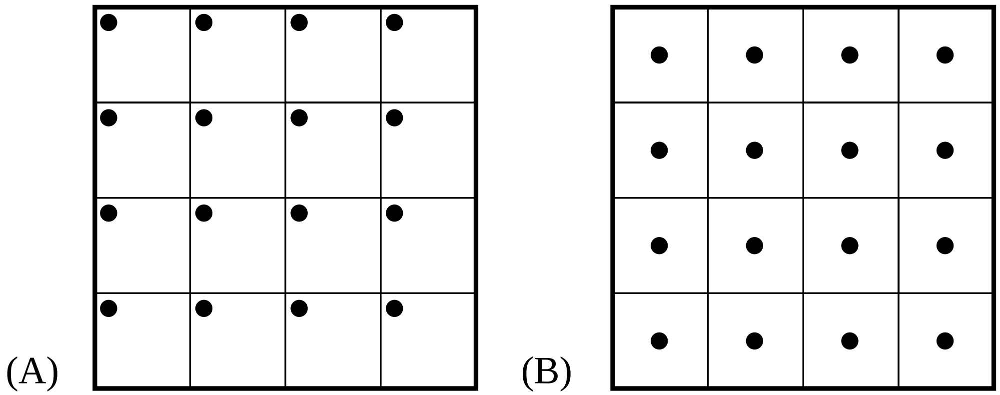
Note presence of glide plane, showing that space group is not the same as the product of translation group and point group.

Some, but not all symmetries of triangular lattice destroyed.

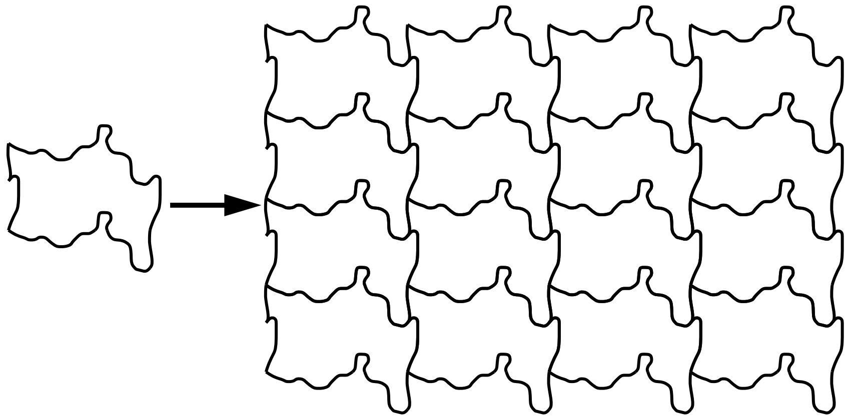


Unit cells

Unit cells are not unique.

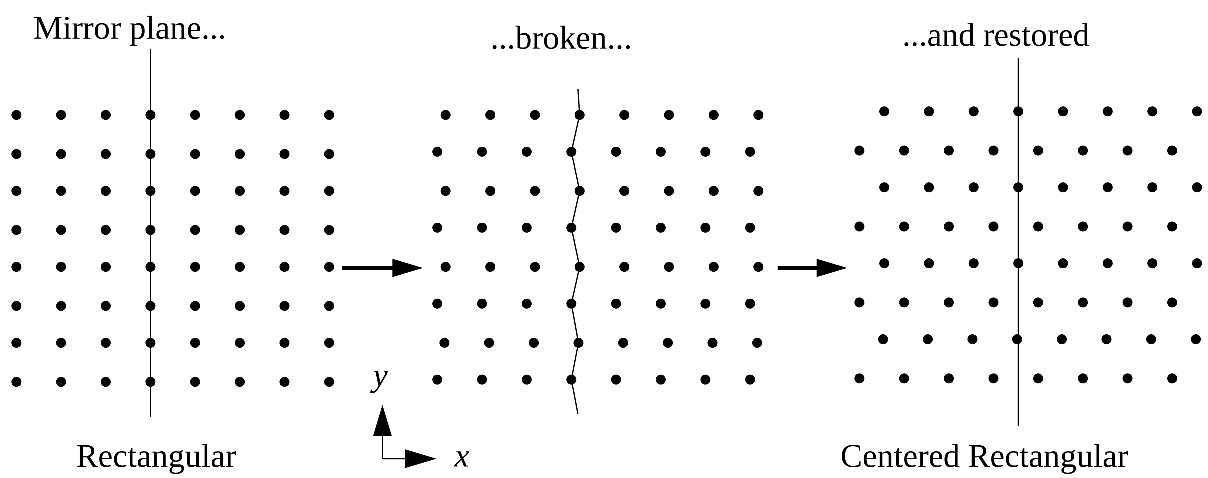


Puzzler: how does one construct bizarre–shaped cells that tile the plane?



Q: What makes lattices the same or different?

A: Two lattices are the same if one can be tranformed continuously into the other without changing any symmetry operations along the way.

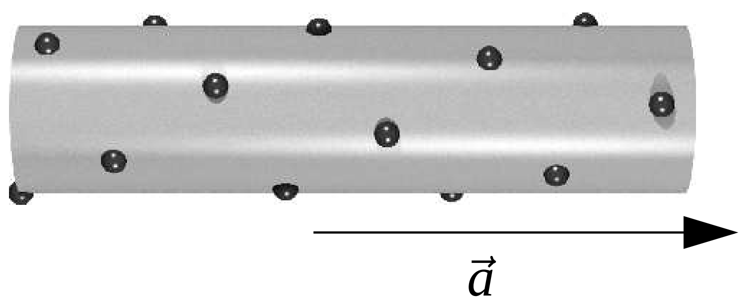


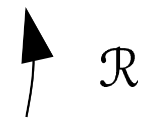
Operations

$$\mathbf{G} = \vec{a} + \mathcal{R}(\hat{n}, \theta). \tag{L3}$$

that leave lattice invariant.

Two important subgroups: translation and point groups. The full space group cannot be formed from these because of glide lines and Screw axes.





$$S\mathcal{R}S^{-1} + S^{-1}\vec{a} = \mathcal{R}' + \vec{a}'. \tag{L4}$$

$$S_t = (1-t) + St, \tag{L5}$$

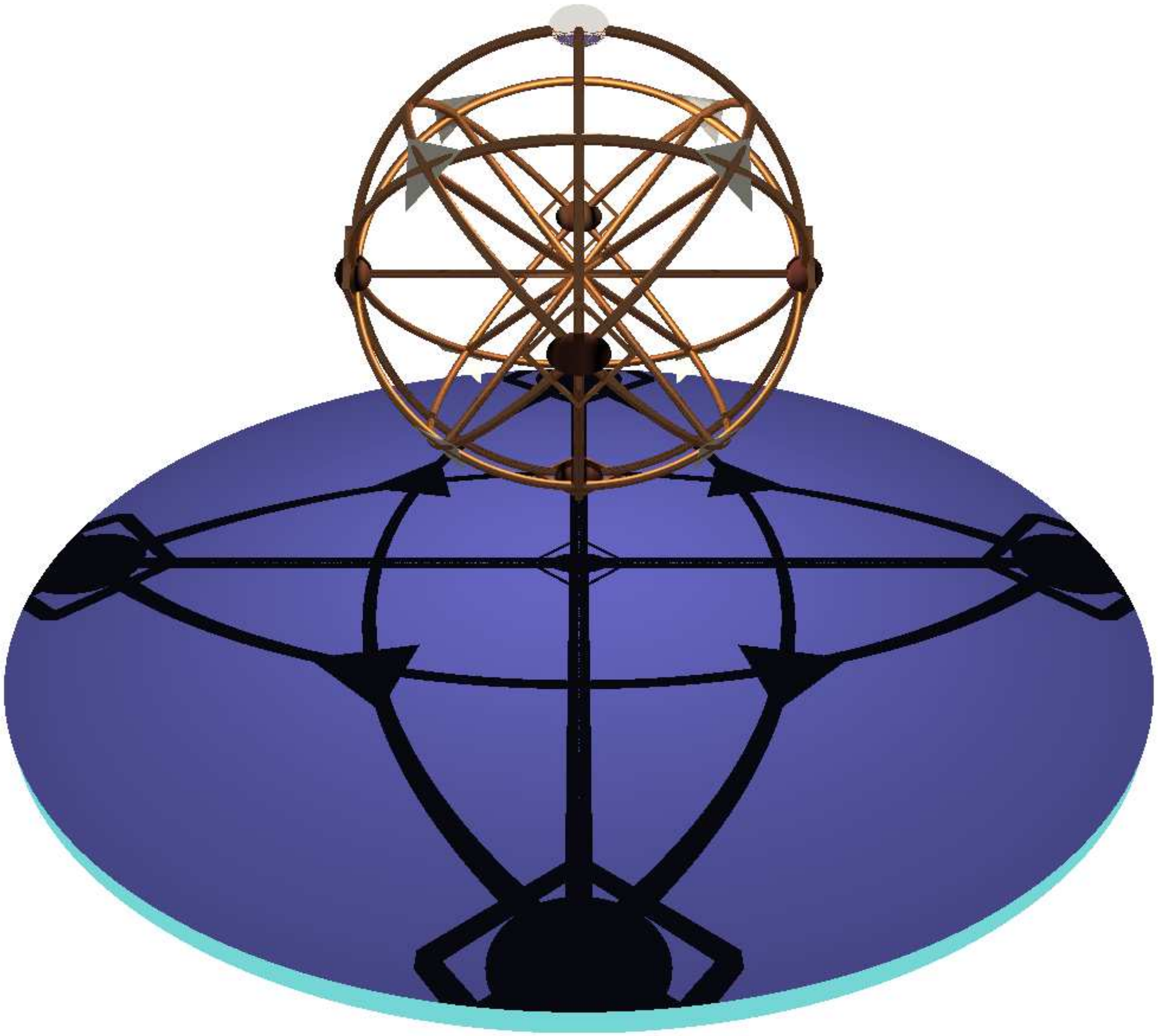
Questions

Q: How many distinct Bravais lattices are there?

A: Five

Q: How many distinct two-dimensional lattices are there?

A: Seventeen. They are enumerated at `http://www2.spsu.edu/math/tile/index.htm` or `http://www.clarku.edu/~djoyce/wallpaper/`



Topics

- Distribution of structures among elements
- A small number of popular crystal structures
- Crystal symmetries:
  - 7 crystal systems
  - 14 Bravais lattices
  - 32 point groups
  - 230 space groups

Key	Silicon (example)	Key
Atomic name Atomic number and symbol	Silicon 14 Si $u=28.09$ $n=4.99$	Atomic weight ($^{12}C=12$) Density in 10^{22} atoms cm^{-3}, at 293K or at melting
Ground state electron configuration	$[Ne]3s^23p^2$	
Melting temperature in K Crystal structure, either at 293 K, or at melting if liquid at 293 K	$T=1683$ $\rho=1\cdot 10^5$ $a=5.43$	Electrical resistivity in $\mu\Omega$ -cm at 298 K Lattice parameters

Alkali Metals

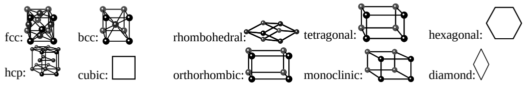
Metal	Insulator	Semiconductor	Semi-metal

Transition Metals (IIIb–VIIIb)

Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIIIb	VIIIb	VIIIb
Lithium 3 Li $u=6.94$ $n=4.63$ $1s^22s^1$ $T=454$ $\rho=8.55$ $a=4.38$	Beryllium 4 Be $u=9.01$ $n=12.36$ $1s^22s^2$ $T=1551$ $\rho=4.0$ $a=2.29$ $c=3.58$								
Sodium 11 Na $u=22.99$ $n=2.54$ $[Ne]3s^1$ $T=371$ $\rho=4.2$ $a=3.77$ $c=6.15$	Magnesium 12 Mg $u=24.31$ $n=4.31$ $[Ne]3s^2$ $T=922$ $\rho=4.45$ $a=3.21$ $c=5.21$								
Potassium 19 K $u=39.10$ $n=1.33$ $[Ar]4s^1$ $T=337$ $\rho=6.15$ $a=5.33$	Calcium 20 Ca $u=40.08$ $n=2.33$ $[Ar]4s^2$ $T=1112$ $\rho=3.43$ $a=5.59$	Scandium 21 Sc $u=44.96$ $n=4.00$ $[Ar]3d^14s^2$ $T=1814$ $\rho=61.0$ $a=3.31$ $c=5.27$	Titanium 22 Ti $u=47.88$ $n=5.70$ $[Ar]3d^24s^2$ $T=1933$ $\rho=42.0$ $a=2.95$ $c=4.68$	Vanadium 23 V $u=50.94$ $n=7.22$ $[Ar]3d^34s^2$ $T=2160$ $\rho=24.8$ $a=3.02$	Chromium 24 Cr $u=52.00$ $n=8.32$ $[Ar]3d^54s^1$ $T=2130$ $\rho=12.7$ $a=2.88$	Manganese 25 Mn $u=54.94$ $n=8.15$ $[Ar]3d^54s^2$ $T=1517$ $\rho=185.0$ $a=8.91$	Iron 26 Fe $u=55.85$ $n=8.48$ $[Ar]3d^64s^2$ $T=1808$ $\rho=9.71$ $a=2.87$	Cobalt 27 Co $u=58.93$ $n=9.09$ $[Ar]3d^74s^2$ $T=1768$ $\rho=6.24$ $a=3.54$	Nickel 28 Ni $u=58.69$ $n=9.13$ $[Ar]3d^84s^2$ $T=1726$ $\rho=6.84$ $a=3.52$
Rubidium 37 Rb $u=85.47$ $n=1.08$ $[Kr]5s^1$ $T=312$ $\rho=12.5$ $a=5.62$	Strontium 38 Sr $u=87.62$ $n=1.75$ $[Kr]5s^2$ $T=1042$ $\rho=23.0$ $a=6.08$	Yttrium 39 Y $u=88.91$ $n=3.03$ $[Kr]4d^15s^2$ $T=1795$ $\rho=57.0$ $a=3.65$ $c=5.73$	Zirconium 40 Zr $u=91.22$ $n=4.30$ $[Kr]4d^25s^2$ $T=2125$ $\rho=42.1$ $a=3.23$ $c=5.15$	Niobium 41 Nb $u=92.91$ $n=5.55$ $[Kr]4d^45s^1$ $T=2741$ $\rho=12.5$ $a=3.30$	Molybdenum 42 Mo $u=95.94$ $n=6.41$ $[Kr]4d^55s^1$ $T=2890$ $\rho=5.2$ $a=3.15$	Technetium 43 Tc $u=98.91$ $n=7.00$ $[Kr]4d^55s^2$ $T=2445$ $\rho=22.6$ $a=2.74$ $c=4.40$	Ruthenium 44 Ru $u=101.07$ $n=7.37$ $[Kr]4d^75s^1$ $T=2583$ $\rho=7.6$ $a=2.71$ $c=4.28$	Rhodium 45 Rh $u=102.91$ $n=7.26$ $[Kr]4d^85s^1$ $T=2239$ $\rho=4.51$ $a=3.80$	Palladium 46 Pd $u=106.42$ $n=6.80$ $[Kr]4d^{10}5s^0$ $T=1825$ $\rho=10.8$ $a=3.89$
Cesium 55 Cs $u=132.91$ $n=0.85$ $[Xe]6s^1$ $T=302$ $\rho=20.0$ $a=6.14$	Barium 56 Ba $u=137.33$ $n=1.57$ $[Xe]6s^2$ $T=1002$ $\rho=50$ $a=5.03$	Lutetium 71 Lu $u=174.97$ $n=k3.39$ $[Xe]4f^{14}5d^16s^2$ $T=1936$ $\rho=79.0$ $a=3.50$ $c=5.55$	Hafnium 72 Hf $u=178.49$ $n=4.49$ $[Xe]4f^{14}5d^26s^2$ $T=2503$ $\rho=35.1$ $a=3.19$ $c=5.05$	Tantalum 73 Ta $u=180.95$ $n=5.54$ $[Xe]4f^{14}5d^36s^2$ $T=3269$ $\rho=12.45$ $a=3.30$	Tungsten [Wolfram] 74 W $u=183.85$ $n=6.32$ $[Xe]4f^{14}5d^46s^2$ $T=3680$ $\rho=5.65$ $a=3.17$	Rhenium 75 Re $u=186.20$ $n=6.80$ $[Xe]4f^{14}5d^56s^2$ $T=3453$ $\rho=19.3$ $a=2.76$ $c=4.46$	Osmium 76 Os $u=190.2$ $n=7.15$ $[Xe]4f^{14}5d^66s^2$ $T=3327$ $\rho=8.12$ $a=2.73$ $c=4.32$	Iridium 77 Ir $u=192.22$ $n=7.07$ $[Xe]4f^{14}5d^76s^2$ $T=2683$ $\rho=5.3$ $a=3.84$	Platinum 78 Pt $u=195.08$ $n=6.62$ $[Xe]4f^{14}5d^{10}6s^0$ $T=2045$ $\rho=10.6$ $a=3.92$
Francium 87 Fr $u\approx 223$ $n=?$ $[Rn]7s^1$ $T=300$ $\rho=?$?	Radium 88 Ra $u=226.03$ $n\approx 1.33$ $[Rn]7s^2$ $T=973$ $\rho=100$ $a=5.15$	Lawrencium 103 Lr $u\approx 260$ $n=?$ $[Rn]5f^{14}6d^17s^2$ $T=?$ $\rho=?$?	Rutherfordium 104 Rf	Dubnium 105 Db	Seaborgium 106 Sg	Bohrium 107 Bh	Hassium 108 Hs	Meitnerium 109 Mt	

Lanthanides [Rare Earths]	Lanthanum 57 La $u=138.91$ $n=2.67$ $[Xe]5d^16s^2$ $T=1194$ $\rho=57$ $a=3.77$ $c=1.22$	Cerium 58 Ce $u=140.12$ $n=3.54$ $[Xe]4f^25d^06s^2$ $T=1072$ $\rho=73$ $a=4.85$	Praseodymium 59 Pr $u=140.91$ $n=2.89$ $[Xe]4f^35d^06s^2$ $T=1204$ $\rho=68$ $a=3.67$ $c=11.83$	Neodymium 60 Nd $u=144,24$ $n=2.93$ $[Xe]4f^45d^06s^2$ $T=1294$ $\rho=64.0$ $a=3.66$ $c=11.80$	Promethium 61 Pm $u\approx 145$ $n=3.00$ $[Xe]4f^55d^06s^2$ $T=1441$ $\rho\approx 50$ $a=?$	Samarium 62 Sm $u=150.36$ $n=3.01$ $[Xe]4f^65d^06s^2$ $T=1350$ $\rho=94.0$ $a=9.00$ $\alpha=23°13'$	Europium 63 Eu $u=151.97$ $n=2.08$ $[Xe]4f^75d^06s^2$ $T=1095$ $\rho=90.0$ $a=4.58$
Actinides	Actinium 89 Ac $u=227.03$ $n=2.67$ $[Rn]6d^17s^2$ $T=1320$ $\rho=?$ $a=5.31$	Thorium 90 Th $u=232.04$ $n=3.04$ $[Rn]5f^06d^27s^2$ $T=2023$ $\rho=13.0$ $a=5.08$	Protactinium 91 Pa $u=231.04$ $n=4.34$ $[Rn]5f^26d^17s^2$ $T=2113$ $\rho=17.7$ $a=3.93$ $c=3.24$	Uranium 92 U $u=238.03$ $n=4.79$ $[Rn]5f^36d^17s^2$ $T=1406$ $\rho=30.8$ $a=2.85$ $b=5.86$ $c=4.95$	Neptunium 93 Np $u=237.05$ $n=5.14$ $[Rn]5f^46d^17s^2$ $T=913$ $\rho=122$ $a=4.72$ $b=4.89$ $c=6.66$	Plutonium 94 Pu $u\approx 244$ $n=4.89$ $[Rn]5f^66d^07s^2$ $T=914$ $\rho=146$ $a=6.18$ $b=4.82$ $c=10.96$ $\beta=101°48'$	Americium 95 Am $u\approx 243$ $n\approx 3.39$ $[Rn]5f^76d^07s^2$ $T=1267$ $\rho=68$ $a=3.47$ $c=11.24$

The Elements



Hydrogen 1 H $u=1.008$ $n=4.54$ $1s^1$ $T=14.01$ $\rho=?$ $a=3.77$ $c=6.16$	Helium 2 He $u=4.003$ $n=3.11$ $1s^2$ At 2 K, 26 atm $a=3.53$ $c=4.24$

Halogens — Noble Gases — Noble metals

Ib	IIb	IIIa	IVa	Va	VIa	VIIa	VIIIa
		Boron 5 B $u=10.81$ $n=13.03$ $1s^22s^22p^1$ $T=2573$ $\rho=1.8\cdot 10^{12}$ $a=8.74$ $c=5.06$	Carbon 6 C $u=12.01$ $n=17.59$ $1s^22s^22p^2$ $T=3820$ $\rho=10^{19}$ $a=3.57$	Nitrogen 7 N $u=14.01$ $n=4.43$ $1s^22s^22p^3$ $T=63.29$ $\rho=?$ $a=5.64$	Oxygen 8 O $u=16.00$ $n=7.53$ $1s^22s^22p^4$ $T=54.8$ $\rho=?$ $a=6.83$	Fluorine 9 F $u=19.00$ $n=?$ $1s^22s^22p^5$ $T=53.5$ $\rho=?$ $a=6.67$	Neon 10 Ne $u=20.18$ $n=4.30$ $1s^22s^22p^6$ $T=24.5$ $\rho=?$ $a=4.45$
		Aluminum 13 Al $u=26.98$ $n=6.02$ $[Ne]3s^23p^1$ $T=934$ $\rho=2.65$ $a=4.05$	Silicon 14 Si $u=28.09$ $n=4.99$ $[Ne]3s^23p^2$ $T=1683$ $\rho=1\cdot 10^5$ $a=5.43$	Phosphorus 15 P $u=30.97$ $n=3.54$ $[Ne]3s^23p^3$ $T=317$ $\rho=1\cdot 10^{17}$ $a=18.51$	Sulfur 16 S $u=32.07$ $n=3.89$ $[Ne]3s^23p^4$ $T=386$ $\rho=2\cdot 10^{23}$ $a=10.46$ $b=12.87$ $c=24.49$	Chlorine 17 Cl $u=35.45$ $n=3.45$ $[Ne]3s^23p^5$ $T=172$ $\rho=?$ $a=6.24$ $b=4.48$ $c=8.26$	Argon 18 Ar $u=39.95$ $n=2.50$ $[Ne]3s^23p^6$ $T=83.8$ $\rho=?$ $a=5.31$
Copper 29 Cu $u=63.55$ $n=8.49$ $[Ar]3d^{10}4s^1$ $T=1357$ $\rho=1.67$ $a=3.61$	Zinc 30 Zn $u=65.39$ $n=6.56$ $[Ar]3d^{10}4s^2$ $T=693$ $\rho=5.92$ $a=2.66$ $c=4.95$	Gallium 31 Ga $u=69.72$ $n=5.10$ $[Ar]3d^{10}4s^24p^1$ $T=303$ $\rho=27$ $a=4.52$ $b=7.66$ $c=4.53$	Germanium 32 Ge $u=72.61$ $n=4.41$ $[Ar]3d^{10}4s^24p^2$ $T=1211$ $\rho=4.6\cdot 10^7$ $a=5.66$	Arsenic 33 As $u=74.92$ $n=4.64$ $[Ar]3d^{10}4s^24p^3$ $T=1090$ $\rho=26$ $a=4.13$ $\alpha=54^\circ 10'$	Selenium 34 Se $u=78.96$ $n=3.65$ $[Ar]3d^{10}4s^24p^4$ $T=490$ $\rho=1\cdot 10^6$ $a=4.37$ $c=4.96$	Bromine 35 Br $u=79.90$ $n=3.05$ $[Ar]3d^{10}4s^24p^5$ $T=266$ $\rho=?$ $a=6.74$ $b=4.55$ $c=8.76$	Krypton 36 Kr $u=83.80$ $n=2.03$ $[Ar]3d^{10}4s^24p^6$ $T=117$ $\rho=?$ $a=5.72$
Silver 47 Ag $u=107.87$ $n=5.86$ $[Kr]4d^{10}5s^1$ $T=1235$ $\rho=1.59$ $a=4.09$	Cadmium 48 Cd $u=112.41$ $n=4.63$ $[Kr]4d^{10}5s^2$ $T=594$ $\rho=6.83$ $a=2.98$ $c=5.62$	Indium 49 In $u=114.82$ $n=3.83$ $[Kr]4d^{10}5s^25p^1$ $T=429$ $\rho=8.37$ $a=3.23$ $c=4.94$	Tin 50 Sn $u=118.71$ $n=3.71$ $[Kr]4d^{10}5s^25p^2$ $T=505$ $\rho=11.0$ $a=5.83$ $c=3.18$	Antimony 51 Sb $u=121.75$ $n=3.31$ $[Kr]4d^{10}5s^25p^3$ $T=904$ $\rho=39.0$ $a=4.51$ $\alpha=57^\circ 7'$	Tellurium 52 Te $u=127.60$ $n=2.94$ $[Kr]4d^{10}5s^25p^4$ $T=723$ $\rho=4.36\cdot 10^5$ $a=4.46$ $c=5.93$	Iodine 53 I $u=126.91$ $n=2.34$ $[Kr]4d^{10}5s^25p^5$ $T=387$ $\rho=1.3\cdot 10^{15}$ $a=7.26$ $b=4.79$ $c=9.79$	Xenon 54 Xe $u=131.29$ $n=1.62$ $[Kr]4d^{10}5s^25p^6$ $T=161$ $\rho=?$ $a=6.19$
Gold 79 Au $u=196.97$ $n=5.90$ $[Xe]4f^{14}5d^{10}6s^1$ $T=1338$ $\rho=2.35$ $a=4.08$	Mercury 80 Hg $u=100.59$ $n=4.07$ $[Xe]4f^{14}5d^{10}6s^2$ $T=234$ $\rho=94.1$ $a=2.99$ $\alpha=70^\circ 45'$	Thallium 81 Tl $u=204.38$ $n=3.49$ $[Xe]4f^{14}5d^{10}6s^26p^1$ $T=577$ $\rho=18.0$ $a=3.46$ $c=5.53$	Lead 82 Pb $u=207.2$ $n=3.30$ $[Xe]4f^{14}5d^{10}6s^26p^2$ $T=601$ $\rho=20.65$ $a=4.95$	Bismuth 83 Bi $u=208.98$ $n=2.81$ $[Xe]4f^{14}5d^{10}6s^26p^3$ $T=545$ $\rho=106.8$ $a=4.75$ $\alpha=57^\circ 14'$	Polonium 84 Po $u\approx 209$ $n=2.68$ $[Xe]4f^{14}5d^{10}6s^26p^4$ $T=527$ $\rho=140$ $a=3.35$	Astatine 85 At $u\approx 210$ $n=?$ $[Xe]4f^{14}5d^{10}6s^26p^5$ $T\approx 575$ $\rho=?$?	Radon 86 Rn $u\approx 222$ $n=?$ $[Xe]4f^{14}5d^{10}6s^26p^6$ $T=202$ $\rho=?$ $a=?$

Gadolinium 64 Gd $u=157.25$ $n=3.02$ $[Xe]4f^75d^16s^2$ $T=1586$ $\rho=134$ $a=3.64$	Terbium 65 Tb $u=158.93$ $n=3.12$ $[Xe]4f^95d^06s^2$ $T=1629$ $\rho=114$ $a=3.59$ $b=6.26$ $c=5.72$	Dysprosium 66 Dy $u=162.50$ $n=3.17$ $[Xe]4f^{10}5d^06s^2$ $T=1685$ $\rho=57.0$ $a=3.59$ $c=5.65$	Holmium 67 Ho $u=164.93$ $n=3.21$ $[Xe]4f^{11}5d^06s^2$ $T=1747$ $\rho=87.0$ $a=3.58$ $c=5.62$	Erbium 68 Er $u=167.27$ $n=3.26$ $[Xe]4f^{12}5d^06s^2$ $T=1802$ $\rho=87$ $a=3.56$ $c=5.59$	Thulium 69 Tm $u=168.93$ $n=3.32$ $[Xe]4f^{13}5d^06s^2$ $T=1818$ $\rho=79.0$ $a=3.54$ $c=5.55$	Ytterbium 70 Yb $u=173.04$ $n=2.42$ $[Xe]4f^{14}5d^06s^2$ $T=1097$ $\rho=29.0$ $a=5.49$
Curium 96 Cm $u\approx 247$ $n=3.24$ $[Rn]5f^76d^17s^2$ $T=1610$ $\rho=?$?	Berklium 97 Bk $u\approx 247$ $n=3.60$ $[Rn]5f^96d^07s^2$ $T=?$ $\rho=$?	Californium 98 Cf $u\approx 251$ $n=?$ $[Rn]5f^{10}6d^07s^2$ $T=?$ $\rho=?$ $a=?$	Einsteinium 99 Es $u\approx 254$ $n=?$ $[Rn]5f^{11}6d^07s^2$ $T=?$ $\rho=?$?	Fermium 100 Fm $u\approx 257$ $n=?$ $[Rn]5f^{12}6d^07s^2$ $T=?$ $\rho=?$?	Mendelevium 101 Md $u\approx 258$ $n=?$ $[Rn]5f^{13}6d^07s^2$ $T=?$ $\rho=?$?	Nobelium 102 No $u\approx 259$ $n=?$ $[Rn]5f^{14}6d^07s^2$ $T=?$ $\rho=?$?

Web Elements

Allotropy

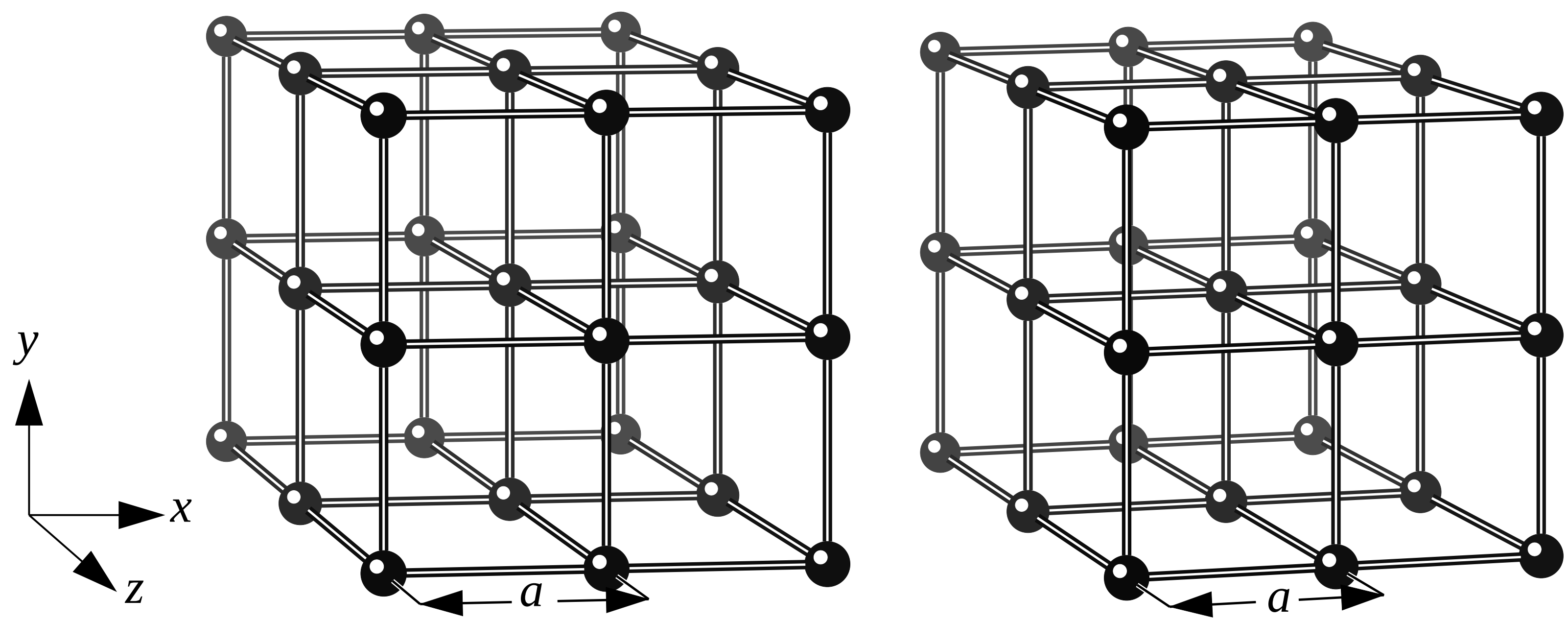
Many elements adopt multiple crystal structures between 0 K and their melting temperature. Plutonium has a particularly elaborate phase diagram:

Transformation Temp, C	Phase	Structure (atoms per unit cell)	Density (g/cc)
112	α	monoclinic (16)	19.8
185	β	fc monoclinic (34)	17.8
310	γ	fc orthorhombic (8)	17.1
450	δ	fcc (4)	15.9
475	δ'	fc tetragonal (2)	16.0
640	ϵ	bcc (2)	16.5

Table 1: Source, Atomic Weapons Establishment, Discovery Article

Popular Lattices

Simple Cubic



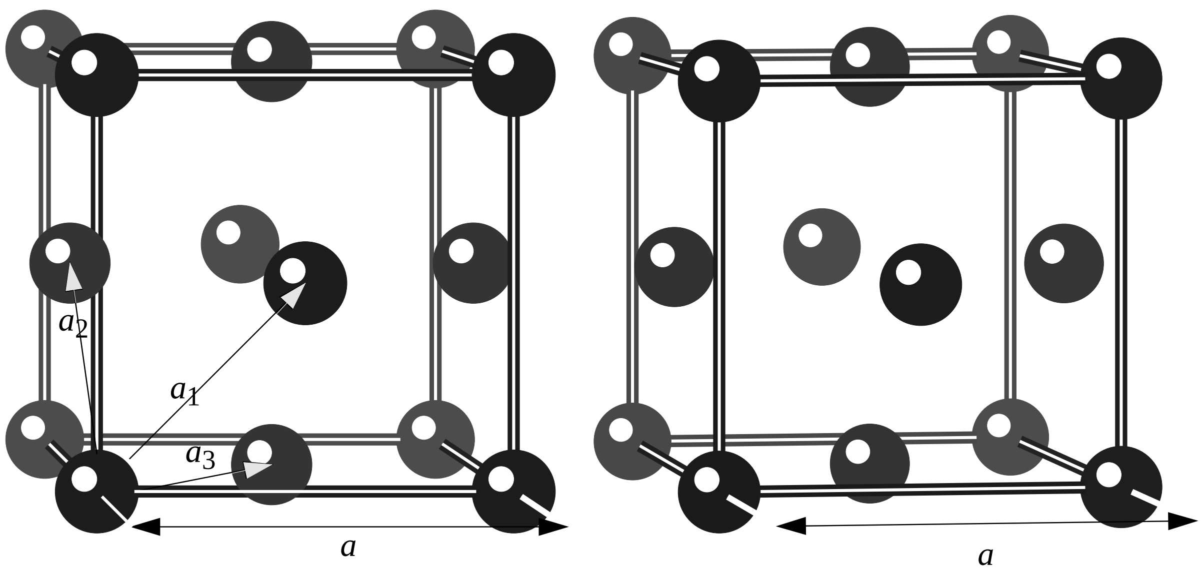
To view these crystals in 3–d, install `rasmol`. Using xpdf version 2, one can click on the name above each figure and invoke rasmol automatically. Configure rasmol with a .rasmolrc file containing

spacefill 100

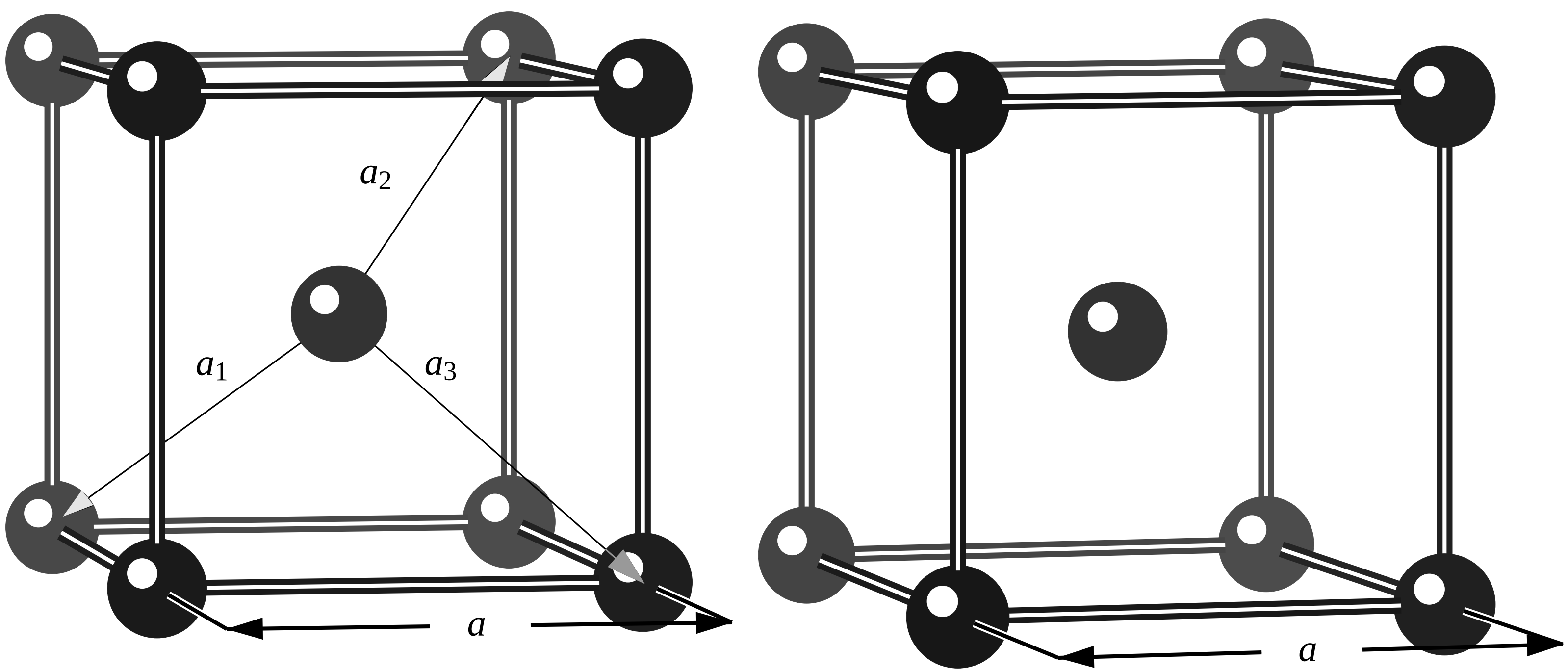
wireframe 20

Popular Lattices

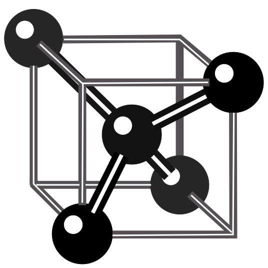
Face Centered Cubic (fcc)

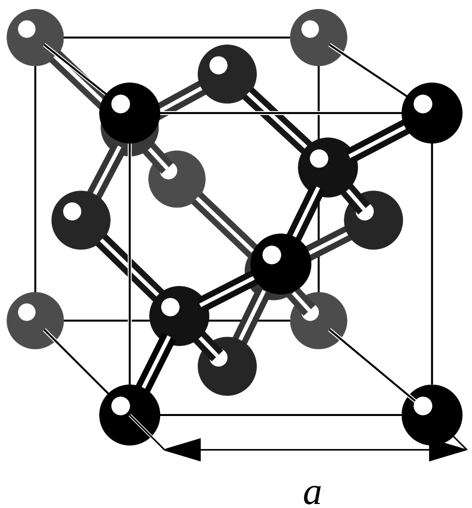


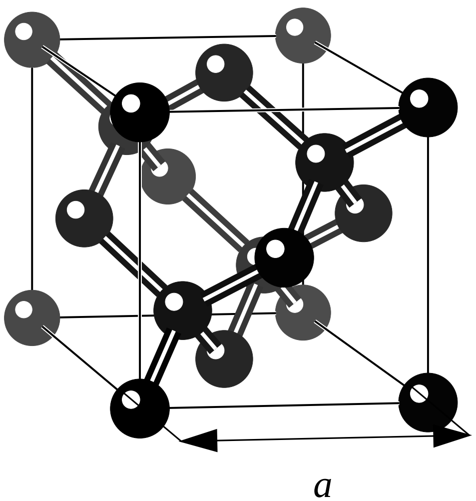
Body Centered Cubic (bcc)



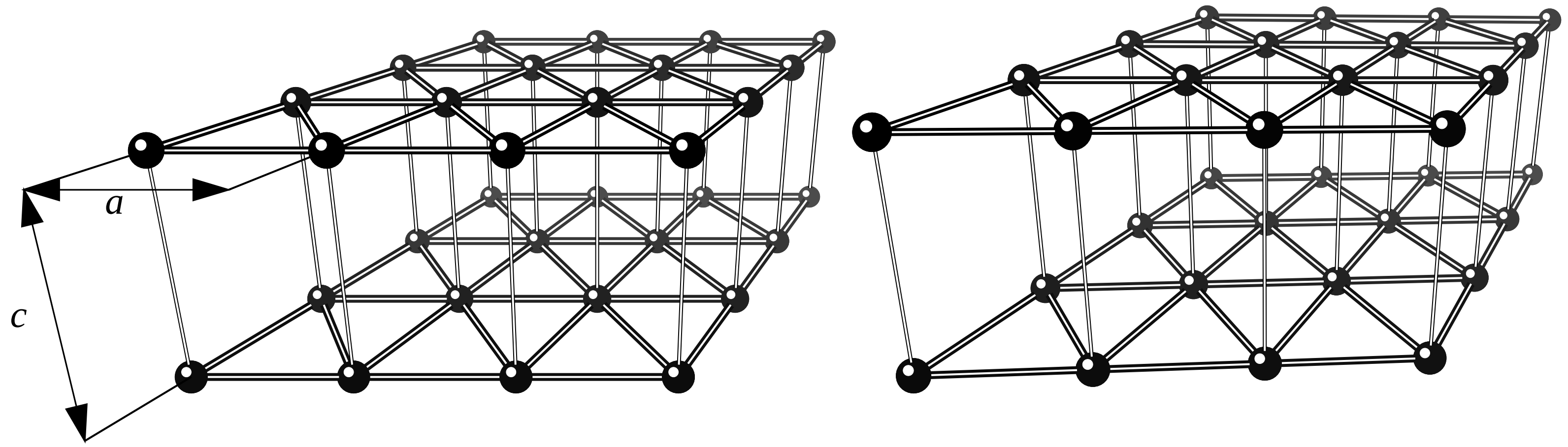
Diamond



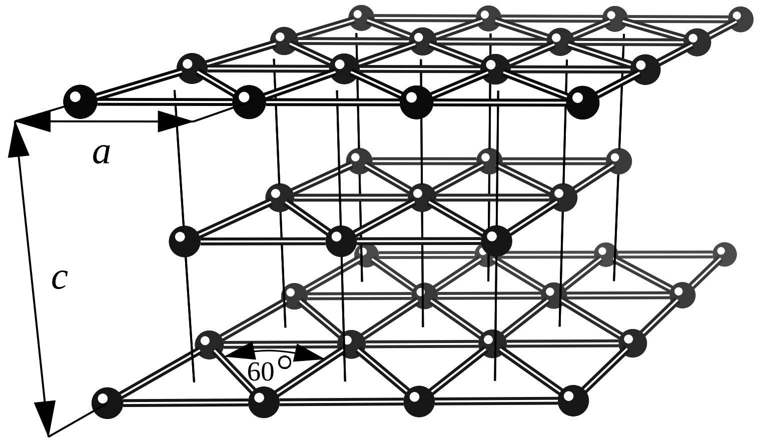


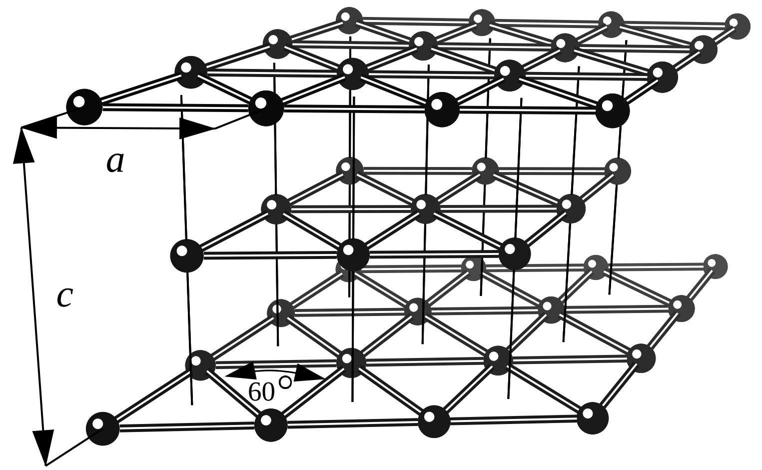


Hexagonal



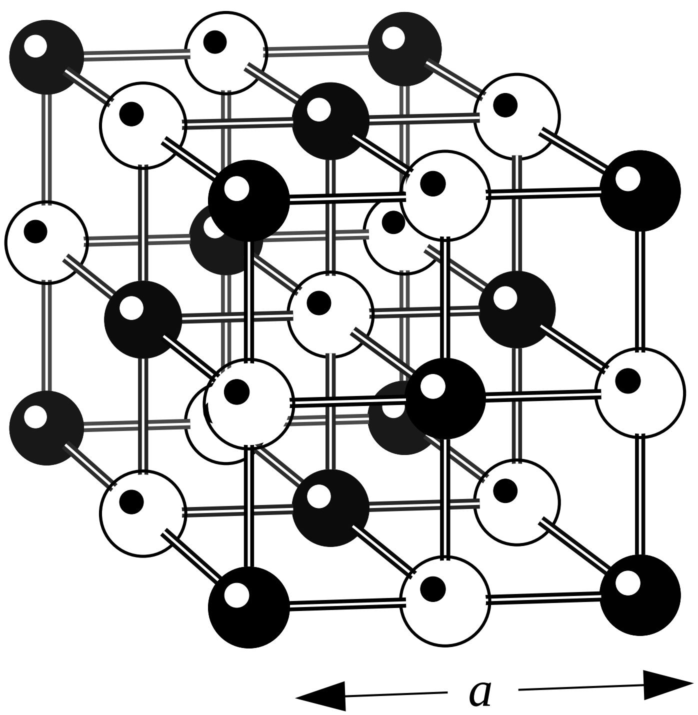
Hexagonal Close Packed (hcp)

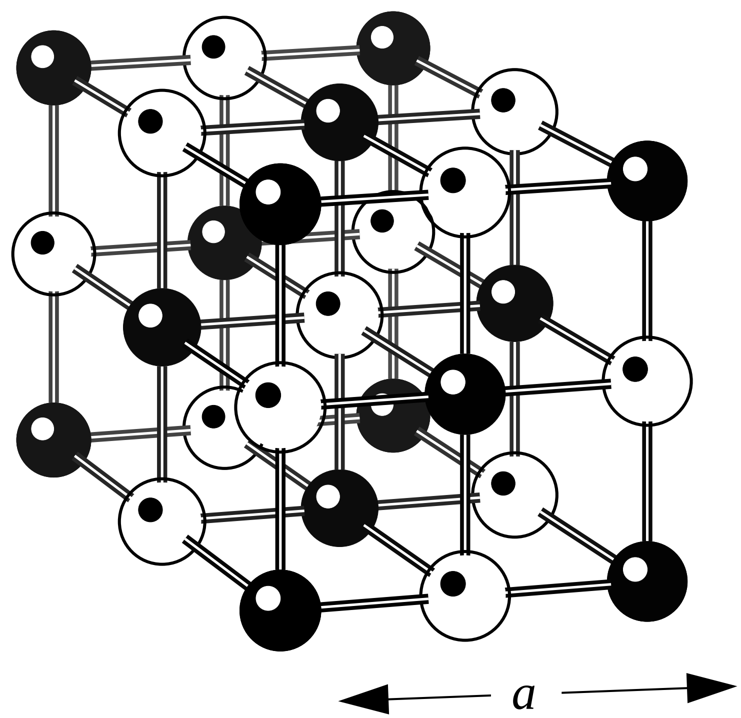




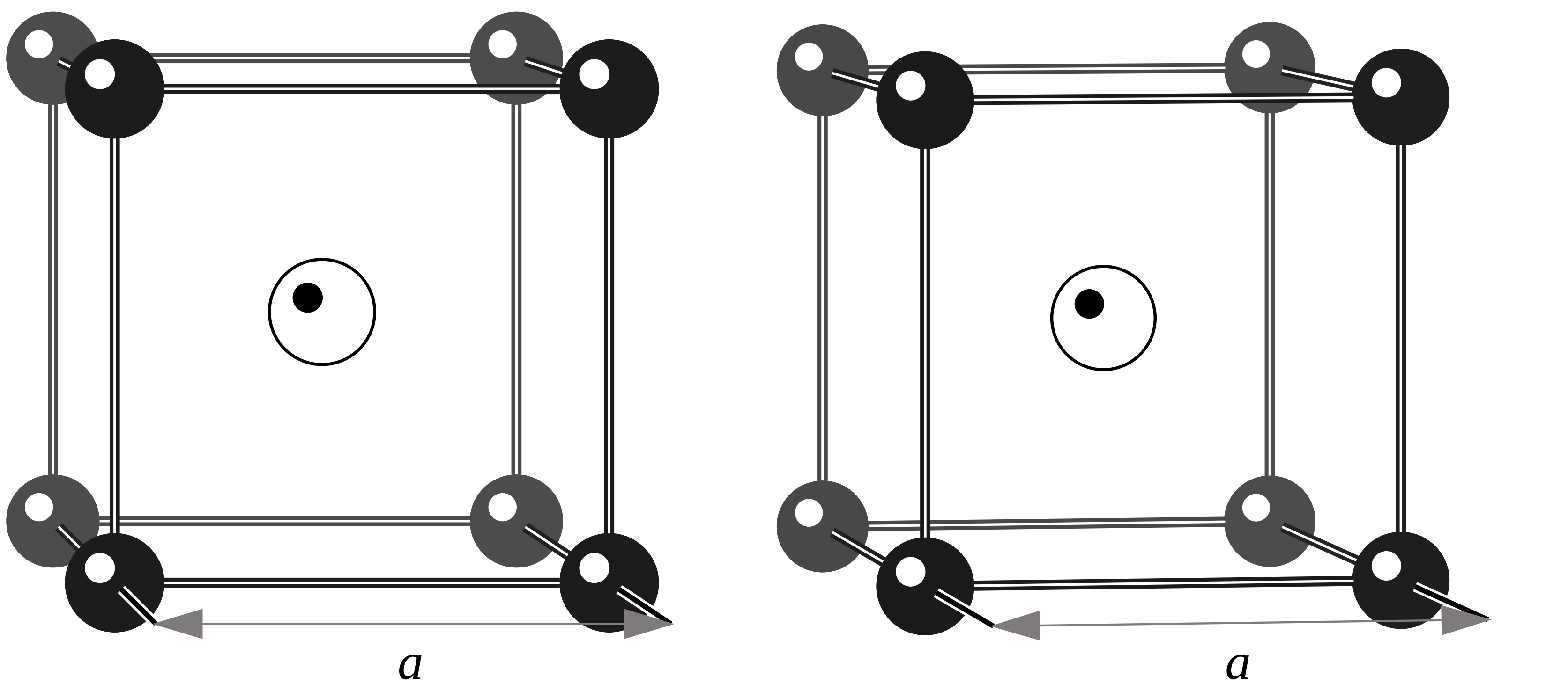
Popular Lattices

Sodium Chloride (NaCl)

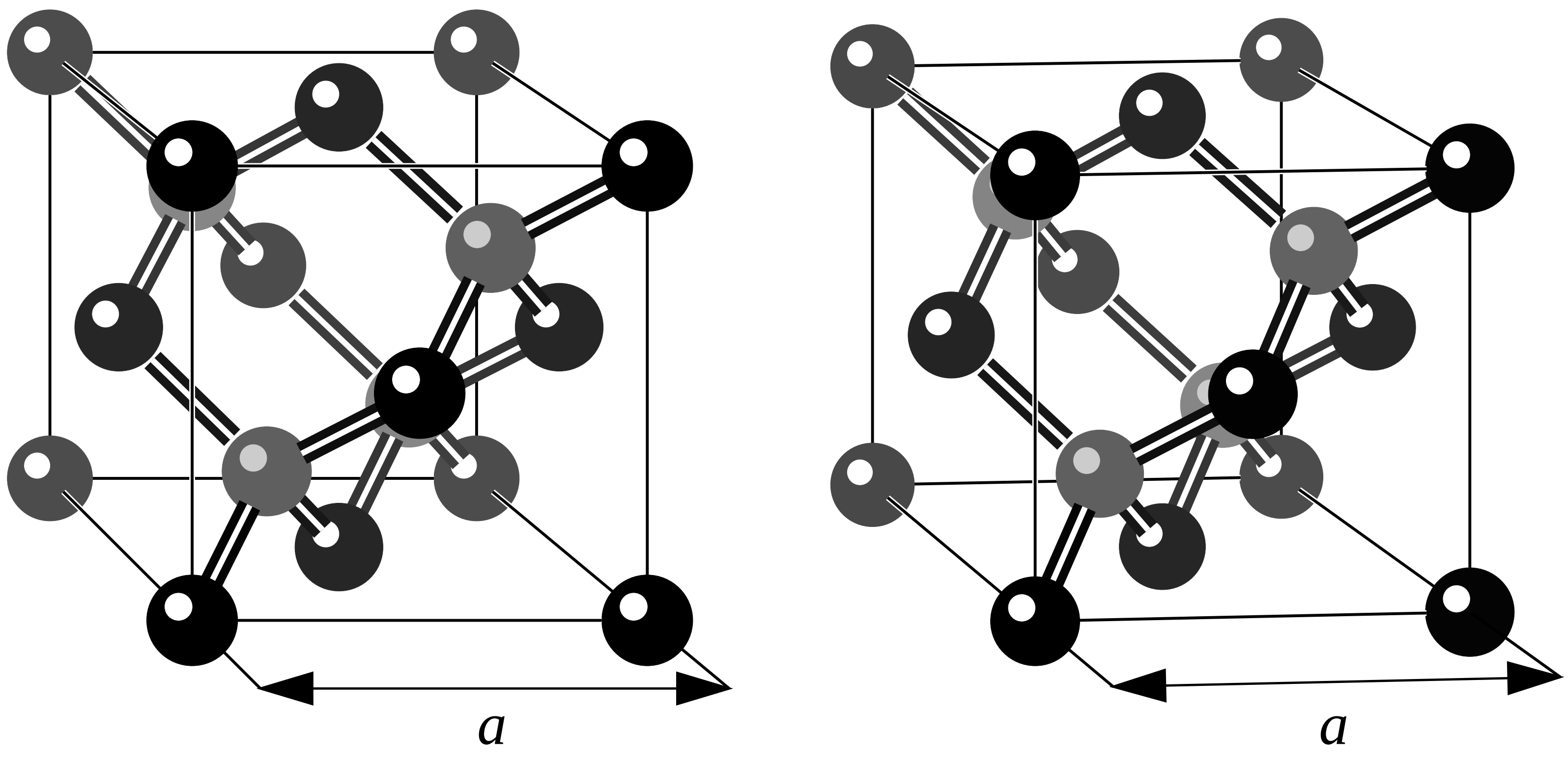




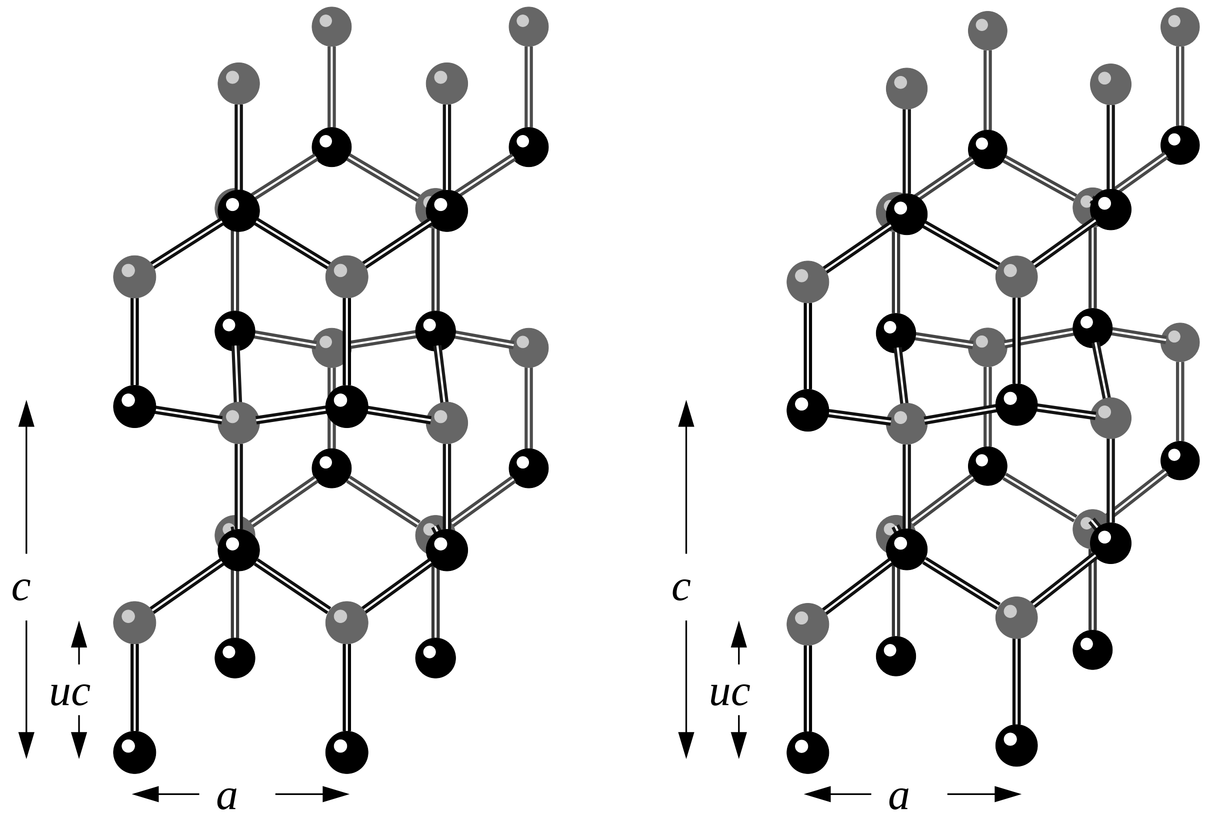
Cesium Chloride (CeCl)



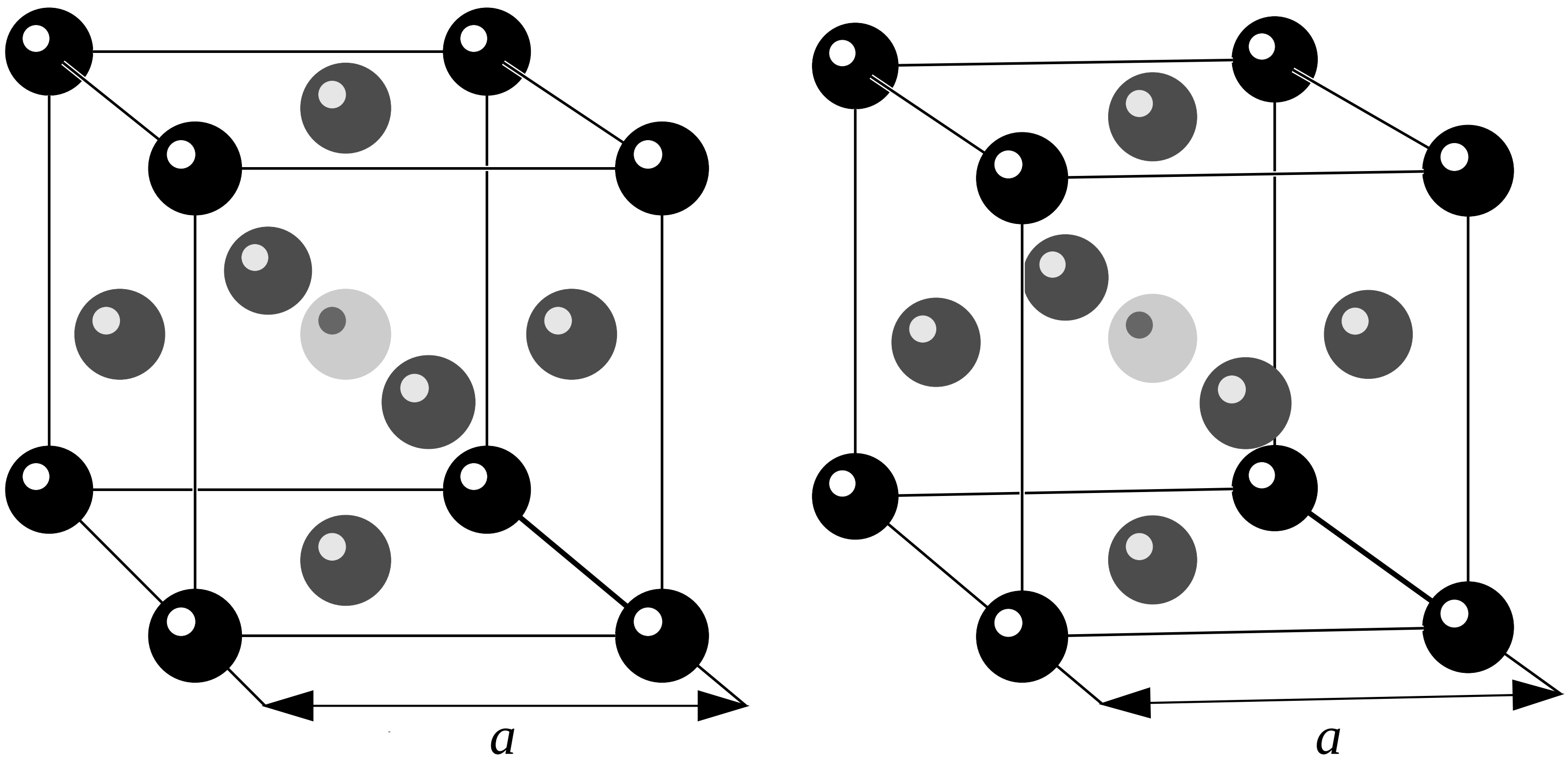
Zincblende



Wurtzite



Perovskite



Please welcome The Bravais Lattice Song

http://www.haverford.edu/physics-astro/songs/bravais.htm

Fourteen Bravais Lattices and Seven Crystal Systems

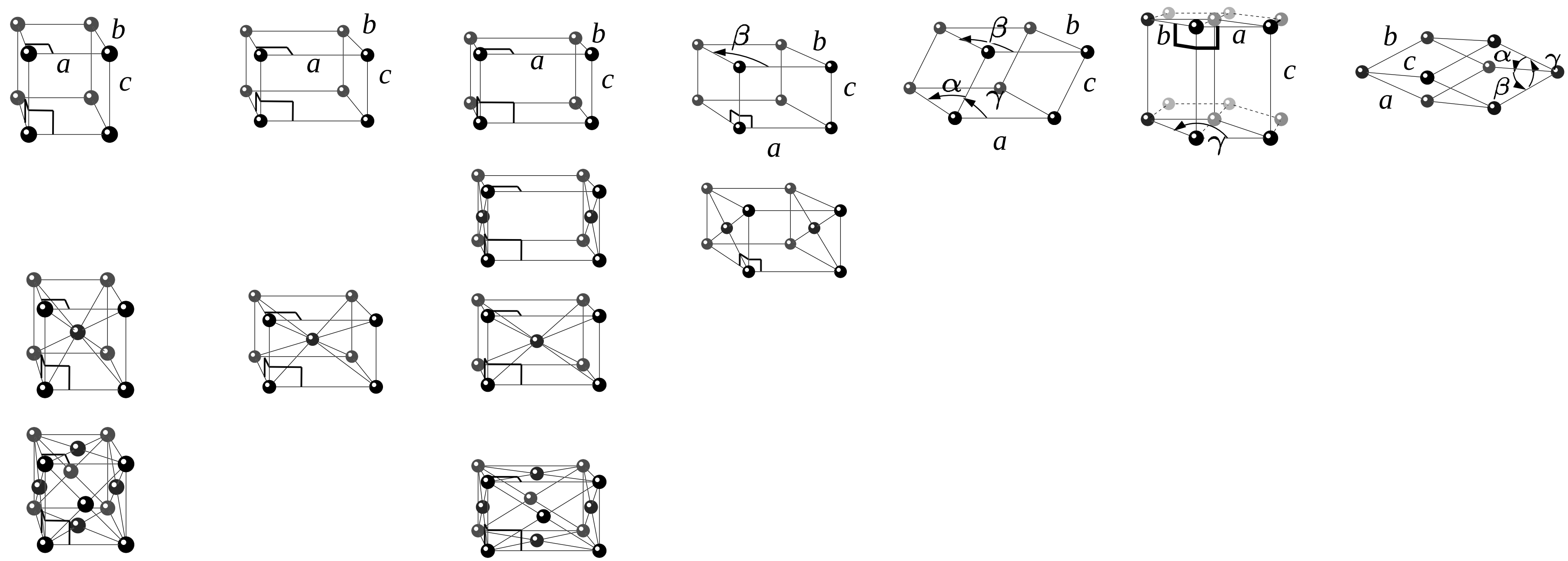
Cubic	Tetragonal	Orthorhombic	Monoclinic	Triclinic	Hexagonal	Rhombohedral
$a{=}b{=}c$	$a{=}b{\neq}c$	$a{\neq}b{\neq}c$	$a{\neq}b{\neq}c$	$a{\neq}b{\neq}c$	$a{=}b{\neq}c$	$a{=}b{=}c$
$\alpha{=}\beta{=}\gamma{=}90^\circ$	$\alpha{=}\beta{=}\gamma{=}90^\circ$	$\alpha{=}\beta{=}\gamma{=}90^\circ$	$\alpha{=}\gamma{=}90^\circ$	$\alpha,\beta,\gamma{\neq}90^\circ$	$\alpha{=}\beta{=}90^\circ$	$\alpha{=}\beta{=}\gamma{\neq}90^\circ$
			$\beta{\neq}90^\circ$		$\gamma = 120^\circ$	

Simple

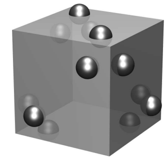
Base-Centered

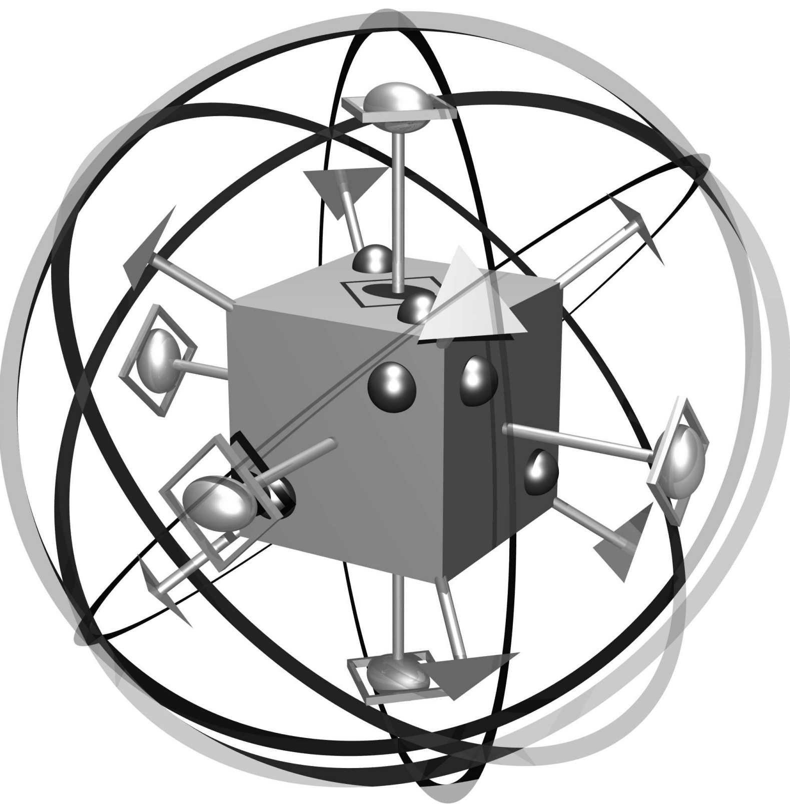
Body-Centered

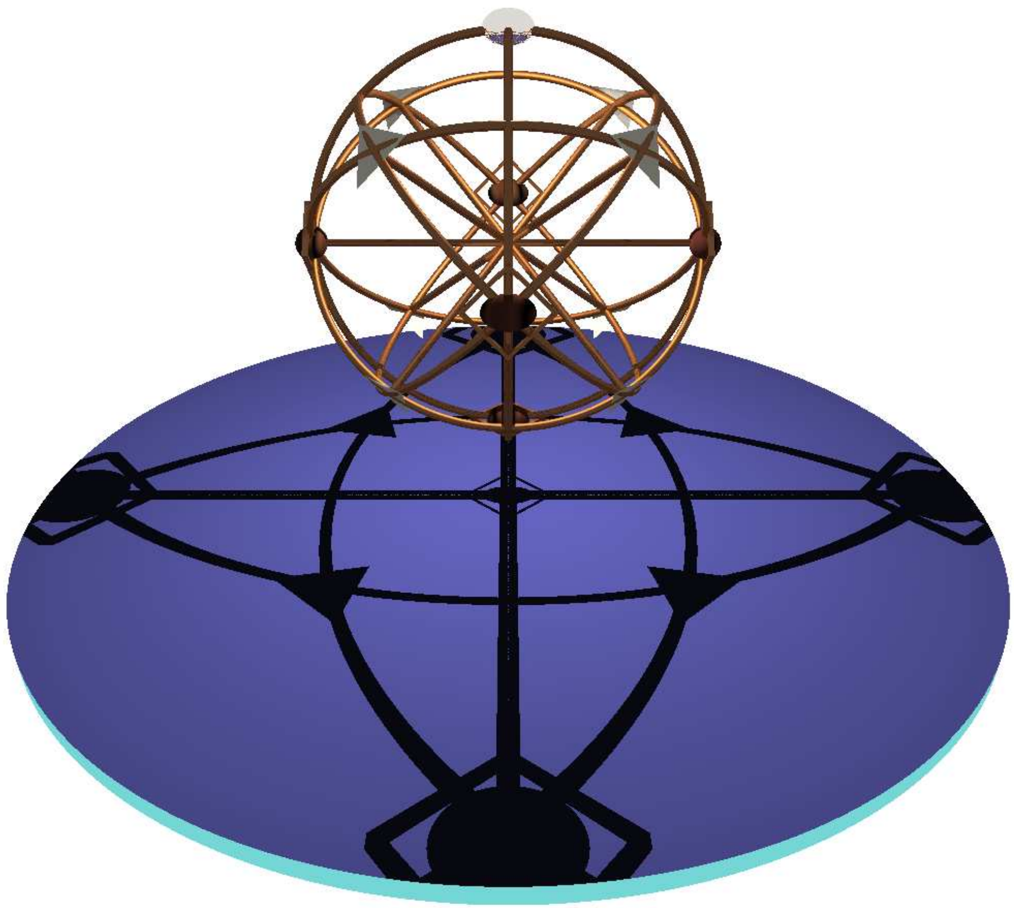
Face-Centered



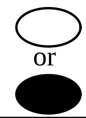
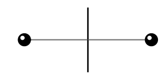
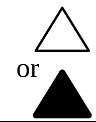
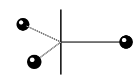
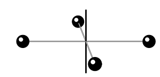
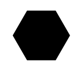
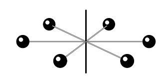
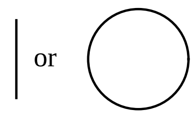
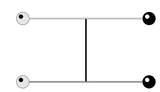
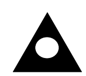
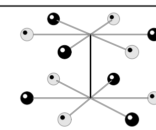
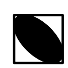
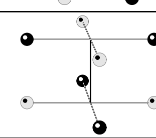
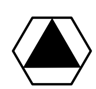
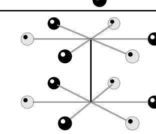
Fourteen Bravais Lattices and Seven Crystal Systems







Symmetry Axes

Axis type	Schönflies Notation	International Notation	Symbol	Operation
Inversion	$i = S_2$	$\bar{1}$	○	$\vec{r} \to -\vec{r}$
Twofold	C_2	2		
Threefold	C_3	3		
Fourfold	C_4	4		
Sixfold	C_6	6		
Twofold Rotoinversion or Mirror	σ_h, $\perp$ to axis σ_v, plane contains axis σ_d, bisects twofold axes	$\bar{2} \equiv m$		
Threefold Rotoinversion	S_6^{-1}	$\bar{3}$		
Fourfold Rotoinversion	S_4^{-1}	$\bar{4}$		
Sixfold Rotoinversion	S_3^{-1}	$\bar{6}$		

Schönflies

C = Cyclic; allows successive rotation about main axis.

D = Dihedral; contains two-fold axes perpendicular to main axis.

S = Spiegel; unchanged after combination of reflection and rotation.

T = Tetragonal.

O = Octahedral.

A subscript $n = 1 \ldots 6$ denotes the order of a rotation axis, and subscripts h, v, and d denote the three types of mirror plane on previous slide.

International

Associates each group with a list of its symmetry axes Notation such as $6m$ refers to a mirror plane containing a sixfold axis, while $\frac{6}{m}$ refers to a mirror plane perpendicular to a sixfold axis.

32 Crystallographic Point Groups

Triclinic	Monoclinic	Ortho-rhombic	Trigonal	Tetragonal	Hexagonal	Cubic
C_1 1	C_2 2		C_3 3	C_4 4	C_6 6	T 23
	C_{1h} C_s $\bar{2}$ m				C_{3h} $\bar{6}$	
	C_{2h} $\frac{2}{m}$ $2/m$			C_{4h} $\frac{4}{m}$ $4/m$	C_{6h} $\frac{6}{m}$ $6/m$	T_h $\frac{2}{m}\bar{3}$ $m\bar{3}$
		C_{2v} $2mm$ $mm2$	C_{3v} $3m$	C_{4v} $4mm$	C_{6v} $6mm$	
S_2 C_i $\bar{1}$			S_6 C_{3i} $\bar{3}$	S_4 $\bar{4}$		T_d $\bar{4}3m$
		D_2 V 222	D_3 32	D_4 422	D_6 622	O 432
			D_{3d} $\bar{3}\frac{2}{m}$ $\bar{3}m$	D_{2d} V_h $\bar{4}2m$		
					D_{3h} $\bar{6}m2$	
		D_{2h} V_h $\frac{2}{m}\frac{2}{m}\frac{2}{m}$ mmm		D_{4h} $\frac{4}{m}\frac{2}{m}\frac{2}{m}$ $4/mmm$	D_{6h} $\frac{6}{m}\frac{2}{m}\frac{2}{m}$ $6/mmm$	O_h $\frac{4}{m}\bar{3}\frac{2}{m}$ $m\bar{3}m$

230 Space Groups

Learn as much as you want at

http://cst-www.nrl.navy.mil/lattice/spcgrp/

http://www.uwgb.edu/dutchs/SYMMETRY/3dSpaceGrps/3DSPGRP.HTM

http://www-structure.llnl.gov/Xray/tutorial/spcgrps.htm

http://www.ccas.ru/galiulin/feddos1.html

Some consequences of symmetry

Sometimes it is possible to decide that some particular effect must vanish in a particular crystal simply by considering its symmetries. Magic when it works.

Example: Piezoelectricity

$$e_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha}\right). \tag{L1}$$

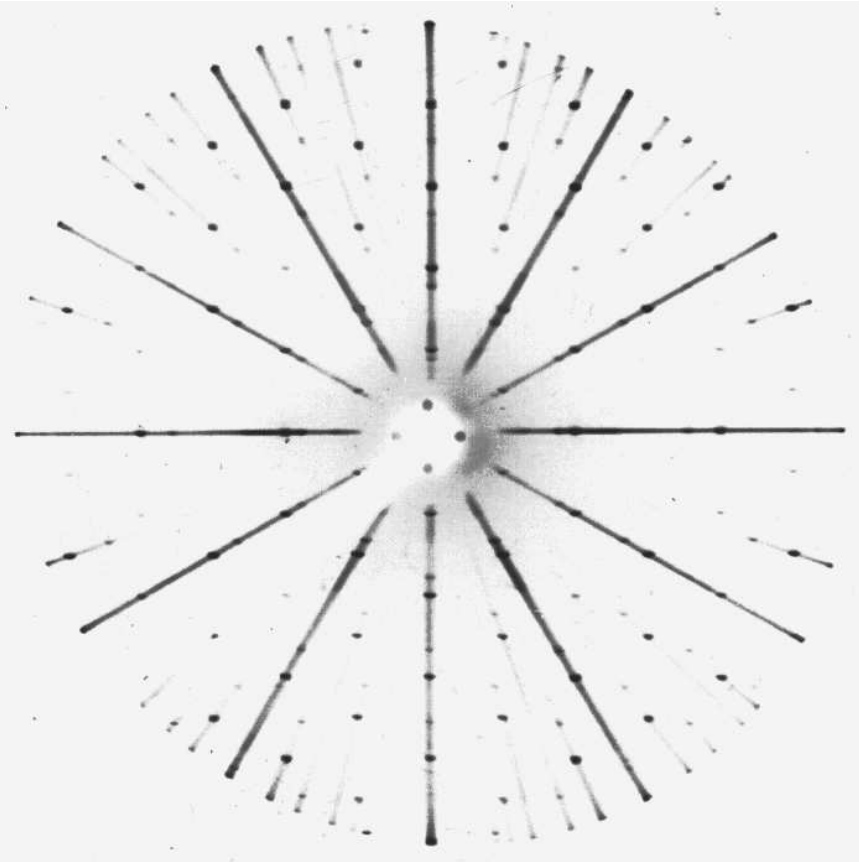
$$P_\gamma = \sum_{\alpha\beta} \mathcal{B}_{\alpha\beta\gamma} e_{\alpha\beta}, \tag{L2}$$

$\mathcal{B}$ is the most general possible tensor describing a general linear relationship between dipole moment and the strain, and is computed by considering all atoms in equilibrium.

Consider $r \to -\vec{r}$.

Crystal cannot be centrosymmetric, ruling out possibility of (large) effect in huge numbers of compounds.

Experimental Determination of Crystal Structures



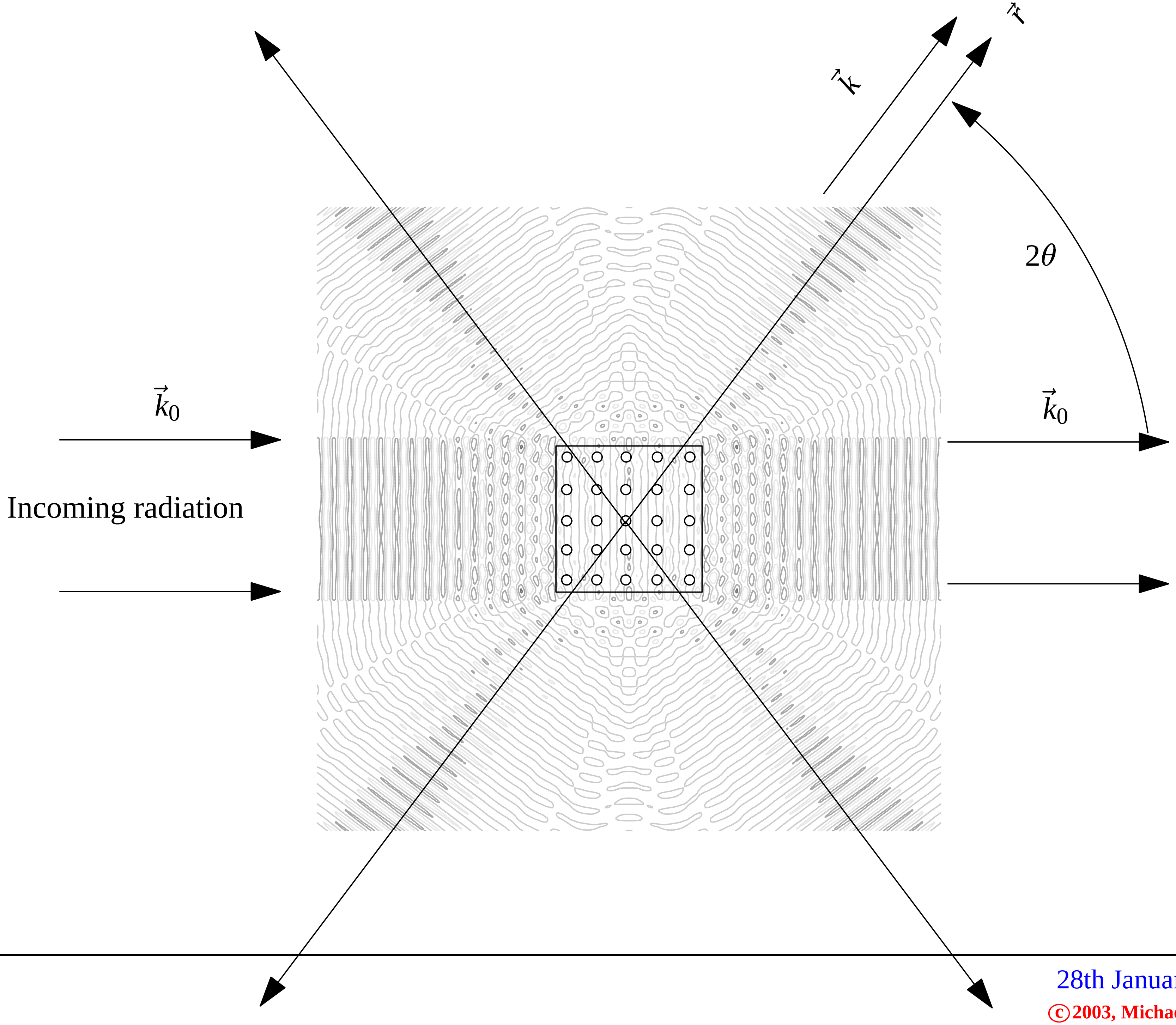
History

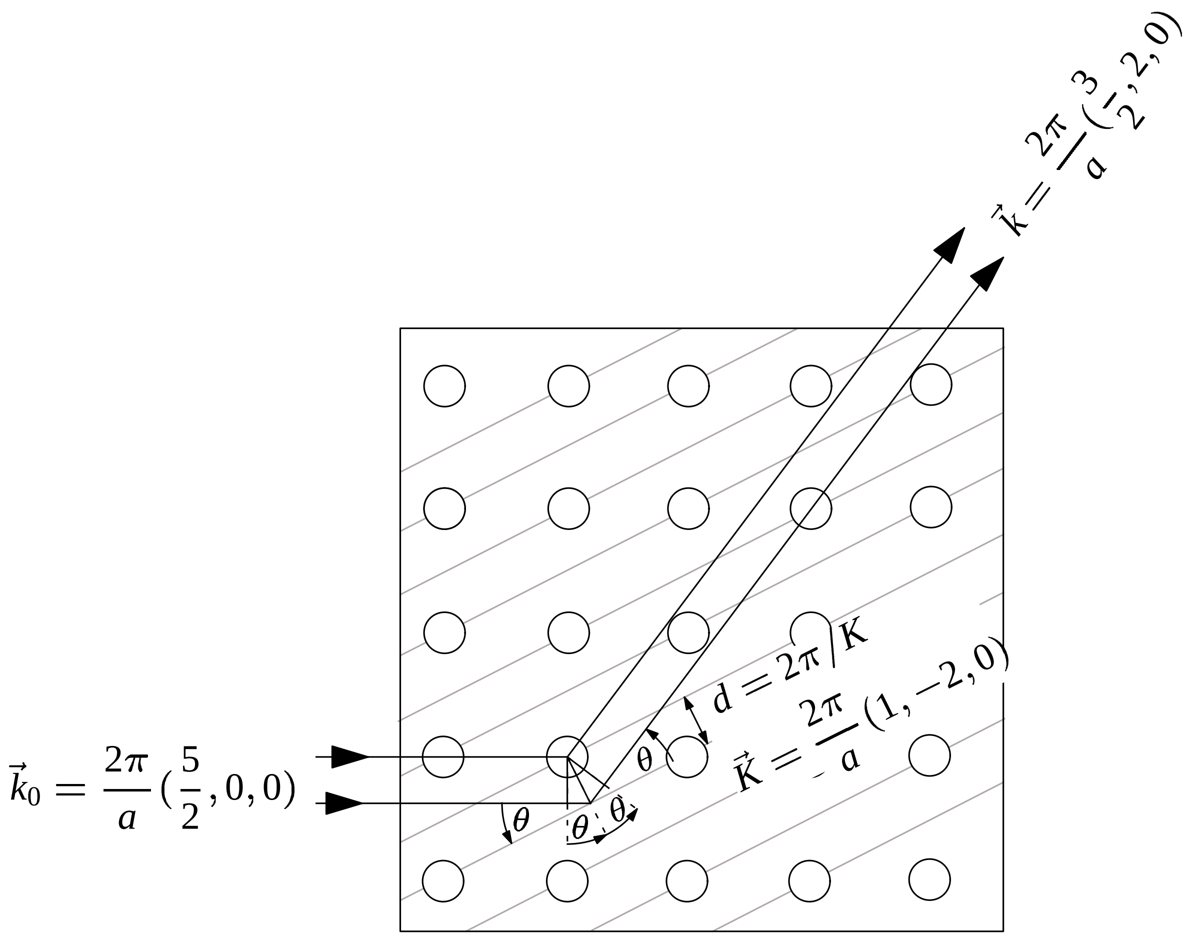
Experiments and theory in 1912 finally revealed locations of atoms in crystalline solids.
Essential ingredients:

- Theory of diffraction grating.
- Skiing, and physics table at Café Lutz.
- Willingness to disobey supervisor, and belief that “experiment was safer than theory.”
- X-ray tubes, photographic plates, and experience with their use.
- Persistence.
- Coherent experiments dragging incoherent theory along behind.

Terms

- Bragg scattering, elastic and inelastic
- Bragg angle
- Bragg peak
- Bragg planes
- Atomic form factor
- Reciprocal lattice
- Miller indices
- Structure factor
- Extinctions
- Ewald construction
- Laue method
- Debye-Scherrer method, powder diffraction


$\vec{r}$
$\vec{k}$
2θ
$\vec{k}_0$
$\vec{k}_0$
Incoming radiation



Plane wave travels toward solid, scatters off atoms. Coherent scattering pattern reveals crystalline pattern.

Schiff page 115 or Jackson Eq. 9.8

$$\psi \approx A e^{-i\omega t}[e^{i\vec{k}_0\cdot\vec{r}} + f(\hat{r})\frac{e^{ik_0 r}}{r}] \tag{L1}$$

$$I_{\text{atom}} \equiv \frac{d\sigma}{d\Omega}_{\text{atom}} = |f(\hat{r})|^2 \tag{L2}$$

f is atomic form factor.

$$\psi \sim Ae^{-i\omega t} e^{i\vec{k}_0\cdot\vec{R}}[e^{i\vec{k}_0\cdot(\vec{r}-\vec{R})} + f(\hat{r})\frac{e^{ik_0|\vec{r}-\vec{R}|}}{|\vec{r}-\vec{R}|}]. \quad \text{(L3)}$$

For sufficiently large r,

$$k_0|\vec{r}-\vec{R}| \approx k_0 r - k_0\frac{\vec{r}}{r}\cdot\vec{R}. \quad \text{(L4)}$$

Using Eq. (L4) and defining

$$\vec{k} = k_0\frac{\vec{r}}{r}, \quad \text{(L5)}$$

and $$\vec{q} = \vec{k}_0 - \vec{k} \quad \text{(L6)}$$

gives

$$\psi \sim Ae^{-i\omega t}[e^{i\vec{k}_0\cdot\vec{r}} + f(\hat{r})\frac{e^{ik_0 r + i\vec{q}\cdot\vec{R}}}{r}]. \quad \text{(L7)}$$

Note that

$$q = 2k_0 \sin\theta. \quad \text{(L8)}$$

Assume multiple scattering and inelastic scattering can be ignored

$$\psi \sim Ae^{-i\omega t}\left[e^{i\vec{k}_0\cdot\vec{r}} + \sum_l f_l(\hat{r})\frac{e^{ik_0 r + i\vec{q}\cdot\vec{R}_l}}{r}\right]. \quad \text{(L9)}$$

Look away from incoming beam

$$\psi \sim Ae^{-i\omega t}\left[\sum_l f_l(\hat{r})\frac{e^{ik_0 r + i\vec{q}\cdot\vec{R}_l}}{r}\right]. \quad \text{(L10)}$$

Intensity per unit solid angle

$$I = \sum_{l,l'} f_l f_{l'}^* e^{i\vec{q}\cdot(\vec{R}_l - \vec{R}_{l'})}. \quad \text{(L11)}$$

Eq. (L11) is true no matter how atoms are arranged.

$$I = I_{\text{atom}} |\sum_l e^{i\vec{q}\cdot\vec{R}_l}|^2. \quad \text{(L12)}$$

Laue condition: find $\vec{q}$ so that for all atom locations $\vec{R}_l$

$$\exp(i\vec{q}\cdot\vec{R}_l) = 1 \quad \text{(L13)}$$

One-Dimensional Sum

$$\Sigma_q = \sum_{l=0}^{N-1} e^{ilaq}. \tag{L14}$$

$$\Sigma_q = \sum_{l=0}^{N-1} e^{ilaq} \tag{L15}$$

$$\Rightarrow e^{iaq}\Sigma_q = \sum_{l=0}^{N-1} e^{i(l+1)aq} \tag{L16}$$

$$= \sum_{l=0}^{N-1} e^{ilaq} - 1 + e^{iNaq} \tag{L17}$$

$$= \Sigma_q - 1 + e^{iNaq} \tag{L18}$$

$$\Rightarrow \Sigma_q = \frac{e^{iNaq} - 1}{e^{iaq} - 1} \tag{L19}$$

$$= \frac{e^{iNaq/2}}{e^{iaq/2}} \frac{\sin Naq/2}{\sin aq/2} \tag{L20}$$

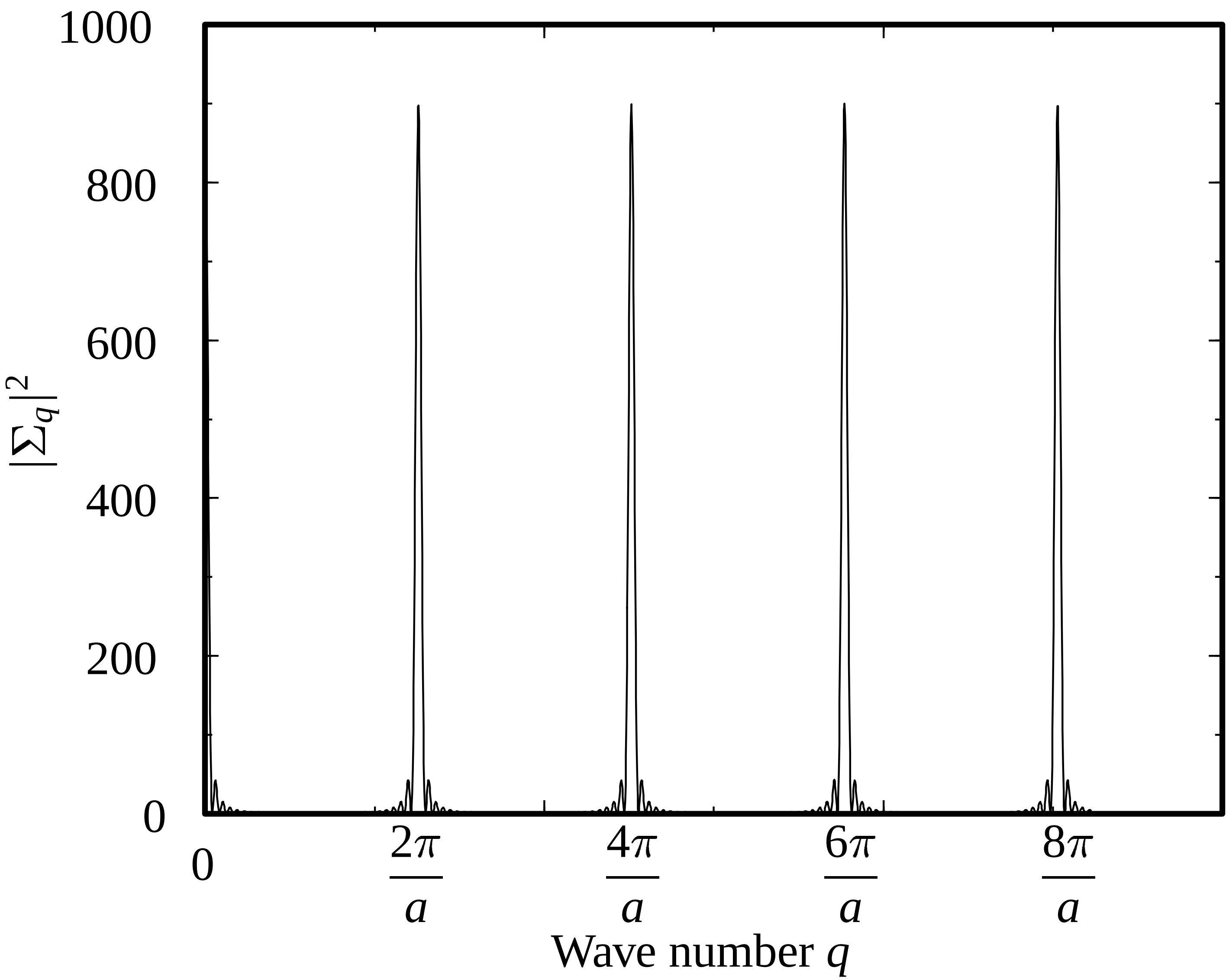
One-Dimensional Sum

$$\Rightarrow |\Sigma_q|^2 = \frac{\sin^2 Naq/2}{\sin^2 aq/2}. \quad \text{(L21)}$$

$$\Sigma_q = \frac{e^{iNaq} - 1}{e^{iaq} - 1} \quad \text{(L22)}$$

$$|\Sigma_q|^2 = \frac{\sin^2 Naq/2}{\sin^2 aq/2}. \quad \text{(L23)}$$

One-Dimensional Sum



Peaks when

$$aq/2 = l\pi \Rightarrow q = 2\pi l/a. \tag{L24}$$

View as sum of delta functions:

$$\sum_{l=0}^{N-1} e^{ilaq} = \sum_{l'=-\infty}^{\infty} N\frac{2\pi}{L}\delta(q - 2\pi l'/a). \tag{L25}$$

Main result: when $\vec{q} = \vec{k}_0 - \vec{k} = \vec{K}$ satisfies

$$\exp[i\vec{K}\cdot\vec{R}] = 1 \text{ or } \vec{K}\cdot\vec{R} = 2\pi l \quad \text{(L26)}$$

there is a strong scattering peak.

The scattering sum can be rewritten

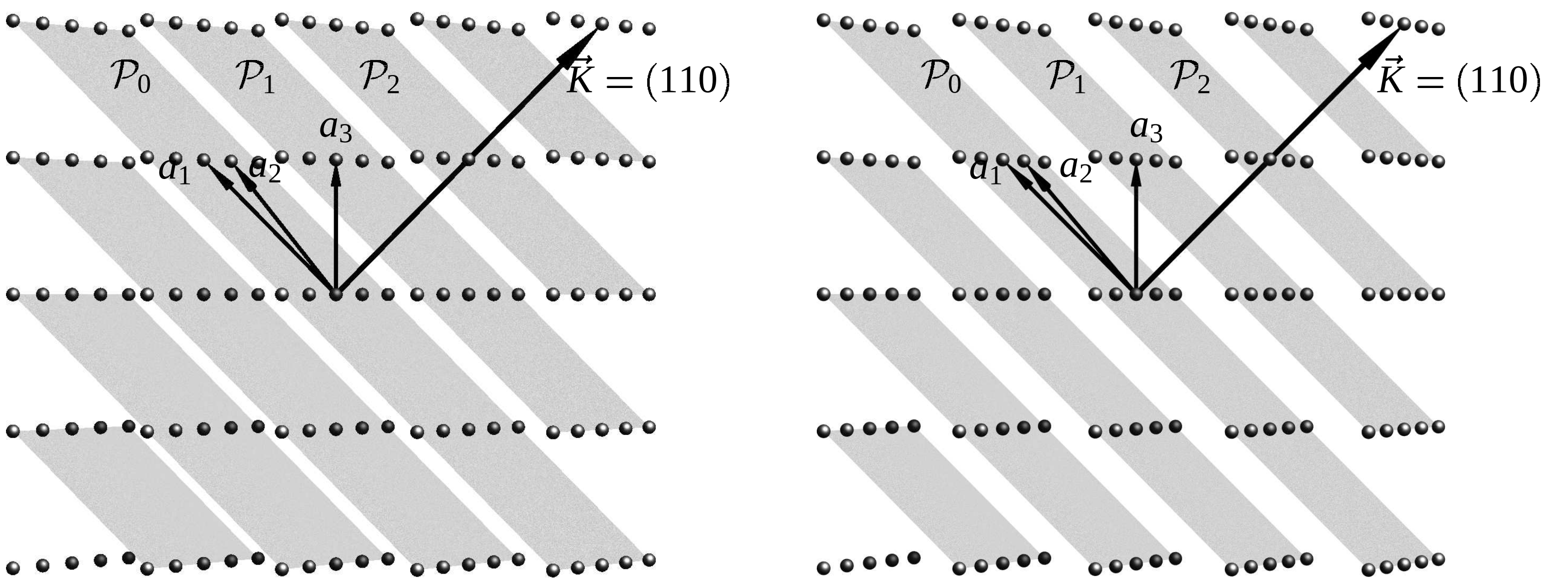
$$\sum_{\vec{R}} e^{i\vec{R}\cdot\vec{q}} = \sum_{\vec{K}} N \frac{(2\pi)^3}{\mathcal{V}} \delta(\vec{q}-\vec{K}), \quad \text{(L27)}$$

When the vectors $\vec{R}$ lie in a Bravais lattice, then vectors $\vec{K}$ satisfying Eq. (L26) also lie in a lattice— the reciprocal lattice.

First consider

$$\vec{K} \cdot \vec{R} = 0 \qquad \text{(L28)}$$

Once the direction of $\vec{K}$ is chosen, the $\vec{R}$ satisfying this condition lie in a plane passing through the origin



The magnitude of $\vec{K}$ is restricted by the need to satisfy Eq. (L28) for all Bragg planes. In the plane,

$$l_1\vec{a}_1 + l_2\vec{a}_2, \tag{L29}$$

For any $\vec{a}_3$ in an adjacent plane, suppose

$$\vec{a}_3 \cdot \vec{K} = 2\pi. \tag{L30}$$

Then

$$\vec{K} \cdot \vec{R} = \vec{K} \cdot (l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3) = 2\pi l_3. \tag{L31}$$

Explicit construction:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot \vec{a}_3 \times \vec{a}_1} \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2} \tag{L32a}$$

$$\vec{K} = \sum_{l=1}^{3} m_l \vec{b}_l. \tag{L32b}$$

Reciprocal lattice of a simple cubic lattice of lattice spacing a is another simple cubic lattice, of spacing $2\pi/a$.

The reciprocal lattice of an fcc lattice of spacing a is, however, a bcc lattice of spacing $4\pi/a$

The reciprocal lattice of a bcc lattice of spacing a is an fcc lattice of spacing $4\pi/a$.

- $[ijk]$ refers to a *direction*

$$i\hat{x} + j\hat{y} + k\hat{z} \tag{L33}$$

  in the lattice specified by the three integers i, j, and k.

- (ijk) refers to a *lattice plane* perpendicular to $[ijk]$

- $\{ijk\}$ refers to the family of lattice planes perpendicular to $[ijk]$ and related by symmetry.

$$\vec{R} = \vec{u}_l + \vec{v}_{l'} \tag{L34}$$

Regrouping of basic sum first carried out by Laue

$$\sum_{\vec{R}} e^{i\vec{q}\cdot\vec{R}} = \sum_{ll'} e^{i\vec{q}\cdot(\vec{u}_l+\vec{v}_{l'})} \tag{L35}$$

$$= \left(\sum_{l} e^{i\vec{q}\cdot\vec{u}_l}\right)\left(\sum_{l'} e^{i\vec{q}\cdot\vec{v}_{l'}}\right) \tag{L36}$$

$$\Rightarrow I \propto \left(\sum_{jj'} e^{-i\vec{q}\cdot(\vec{u}_j-\vec{u}_{j'})}\right)\left(\sum_{ll'} e^{i\vec{q}\cdot(\vec{v}_l-\vec{v}_{l'})}\right). \tag{L37}$$

Structure factor for the unit cell is

$$F_{\vec{q}} \equiv |\sum_{l} e^{i\vec{q}\cdot\vec{v}_l}|^2. \tag{L38}$$

When $F_{\vec{q}}$ vanishes, have an extinction: Laue overlooked this possibility, leading to years of confusion interpreting patterns.

Example: Diamond

$$\vec{v}_1 = (0\ \ 0\ \ 0), \quad \vec{v}_2 = \frac{a}{4}(1\ \ 1\ \ 1). \tag{L39}$$

$$\vec{K} = l_1 \frac{4\pi}{2a}(1\ \ 1\ \ -1) + l_2 \frac{4\pi}{2a}(-1\ \ 1\ \ 1) + l_3 \frac{4\pi}{2a}(1\ \ -1\ \ 1). \tag{L40}$$

Therefore,

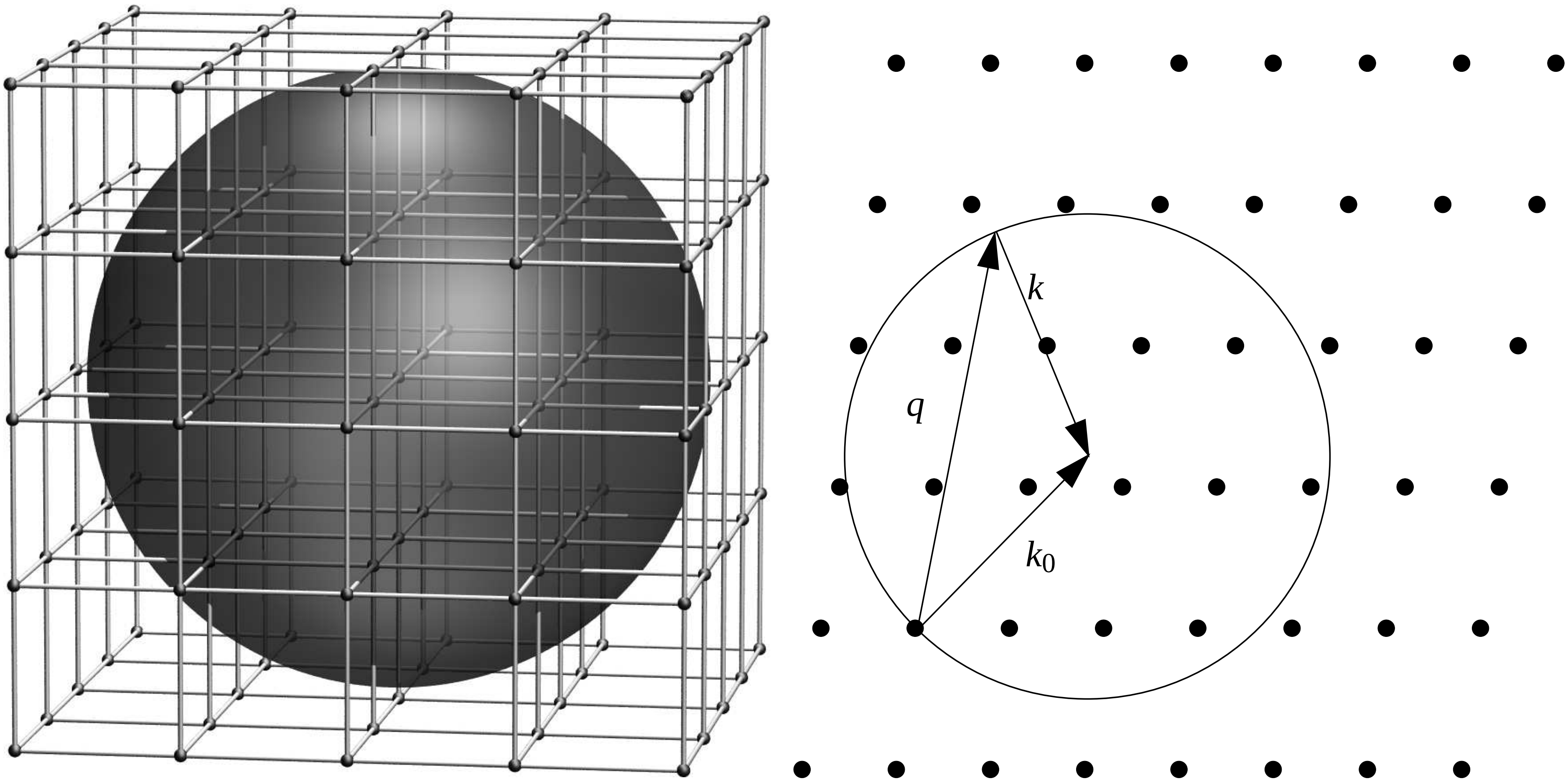
$$\vec{v}_2 \cdot \vec{K} = \frac{\pi}{2}(l_1 + l_2 + l_3), \tag{L41}$$

$F_{\vec{K}}$ is

$$F_{\vec{K}} = |1 + e^{i\pi(l_1+l_2+l_3)/2}|^2 \tag{L42}$$

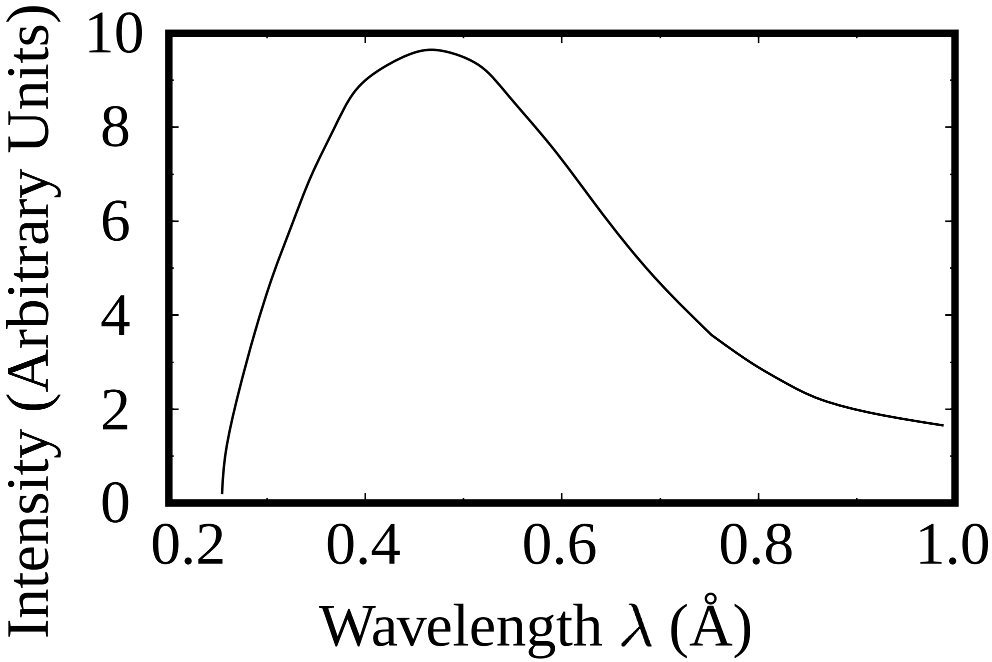
$$= \begin{cases} 4 & \text{if } l_1 + l_2 + l_3 = 4, 8, 12, \ldots \\ 2 & \text{if } l_1 + l_2 + l_3 \text{ is odd} \\ 0 & \text{if } l_1 + l_2 + l_3 = 2, 6, 10, \ldots. \end{cases} \tag{L43}$$

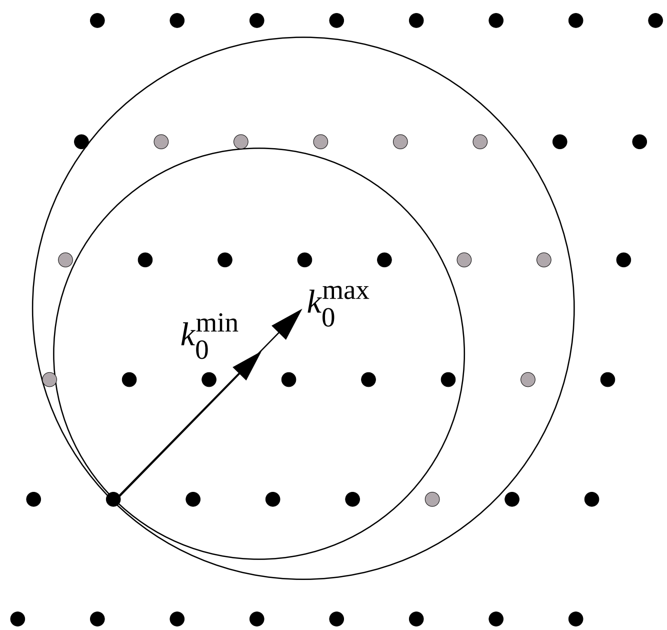
Ewald construction



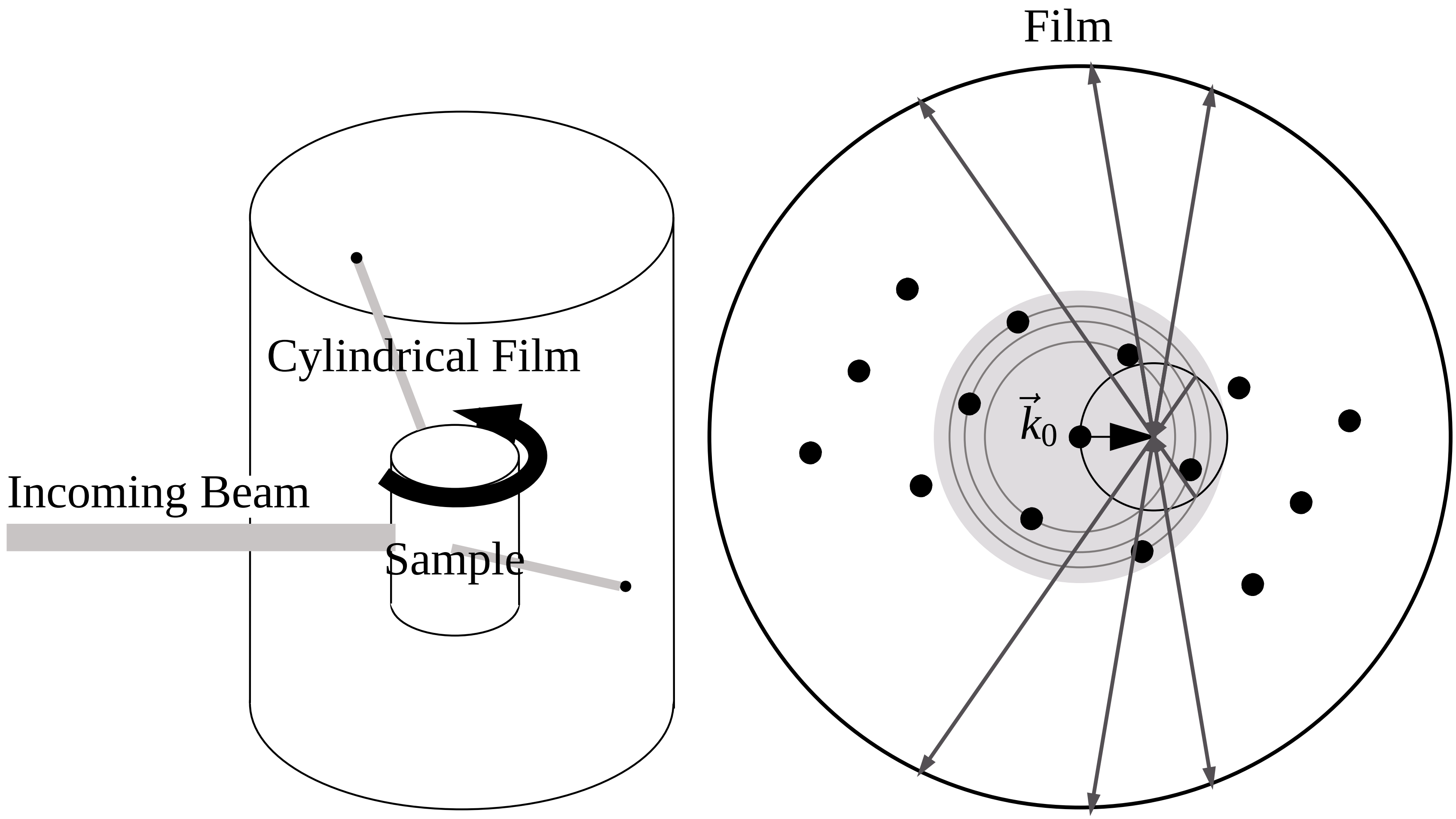
Shining generic monochromatic X-ray upon crystal gives **no scattering peaks**

Laue Method

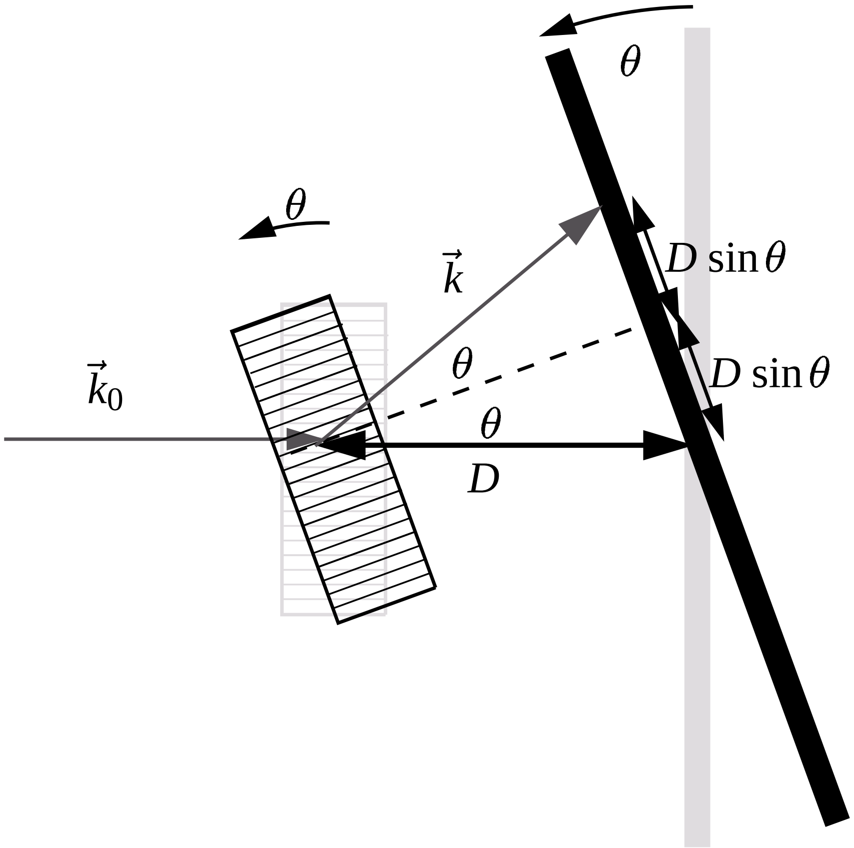

Intensity (Arbitrary Units)
10
8
6
4
2
0
0.2
0.4
0.6
0.8
1.0
Wavelength λ (Å)

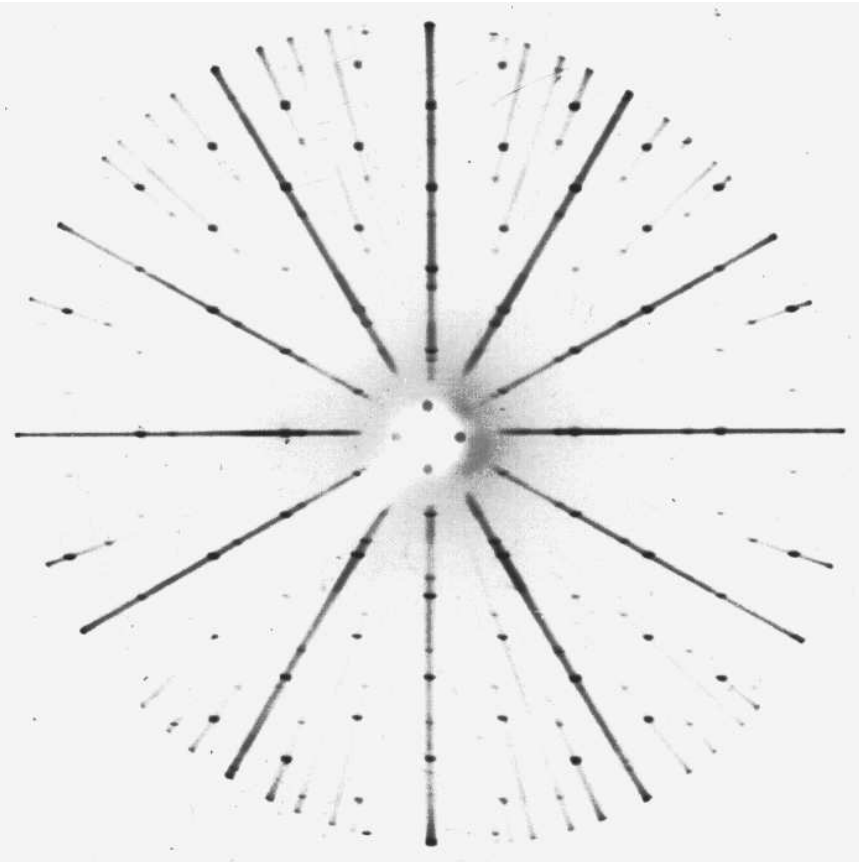

k_0^{min}
k_0^{max}

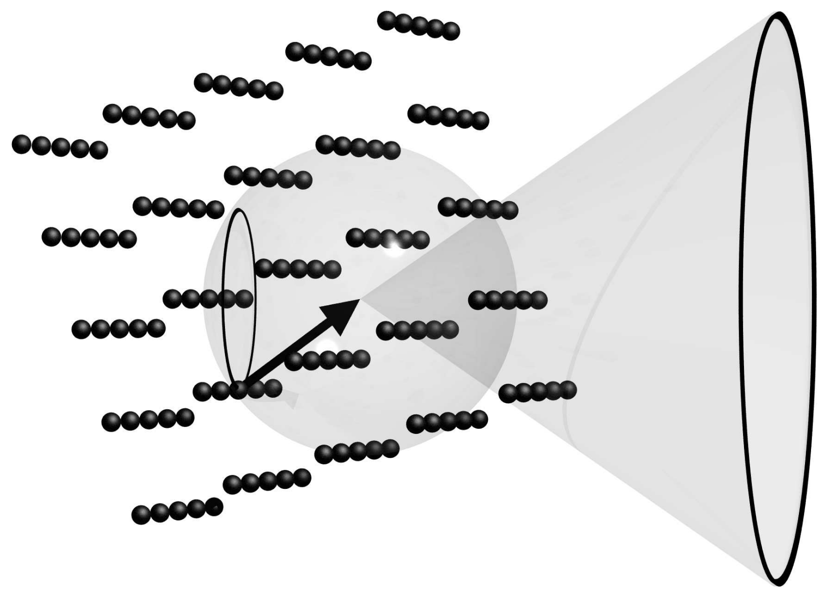
Rotating Crystal Method



Rotating Crystal Method







$$\theta = \sin^{-1}(K/2k_0) \quad \text{(L44)}$$

and the radius r on film of the scattering ring due to reciprocal lattice vector $\vec{K}$ is

$$r = D\tan(2\theta). \quad \text{(L45)}$$

More on Scattering Experiments

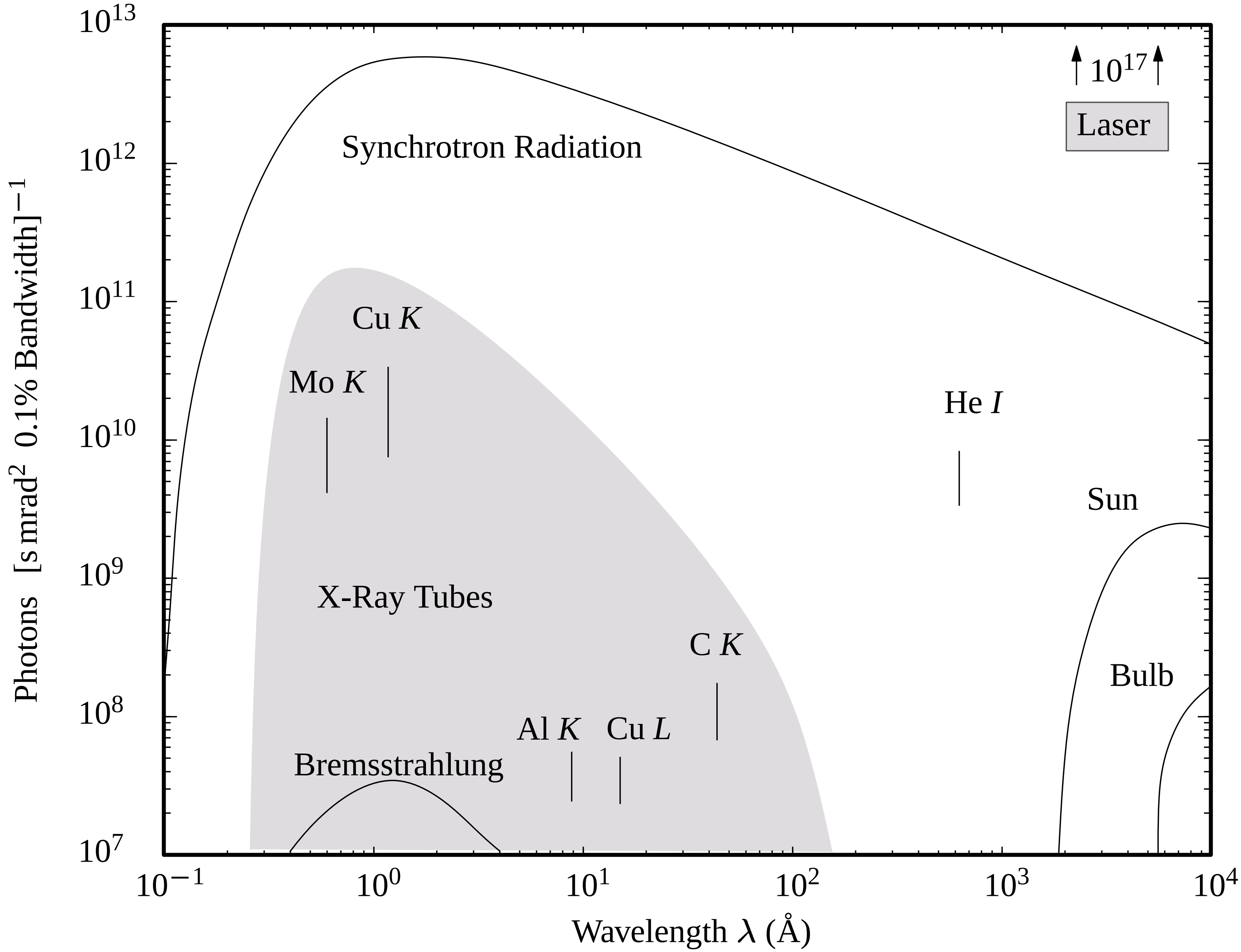
	X-rays	Neutrons	Electrons
Charge	0	0	$-e$
Mass	0	$1.67{\cdot}10^{-27}$ kg	$9.11{\cdot}10^{-31}$ kg
Typical energy	10 keV	0.03 eV	100 keV
Typical wavelength	1Å	1 Å	0.05Å
Typical attenuation length	100 μm	5 cm	1 μm
Typical atomic form factor, f	10^{-3} Å	10^{-4} Å	10 Å

Interactions of X–rays with matter

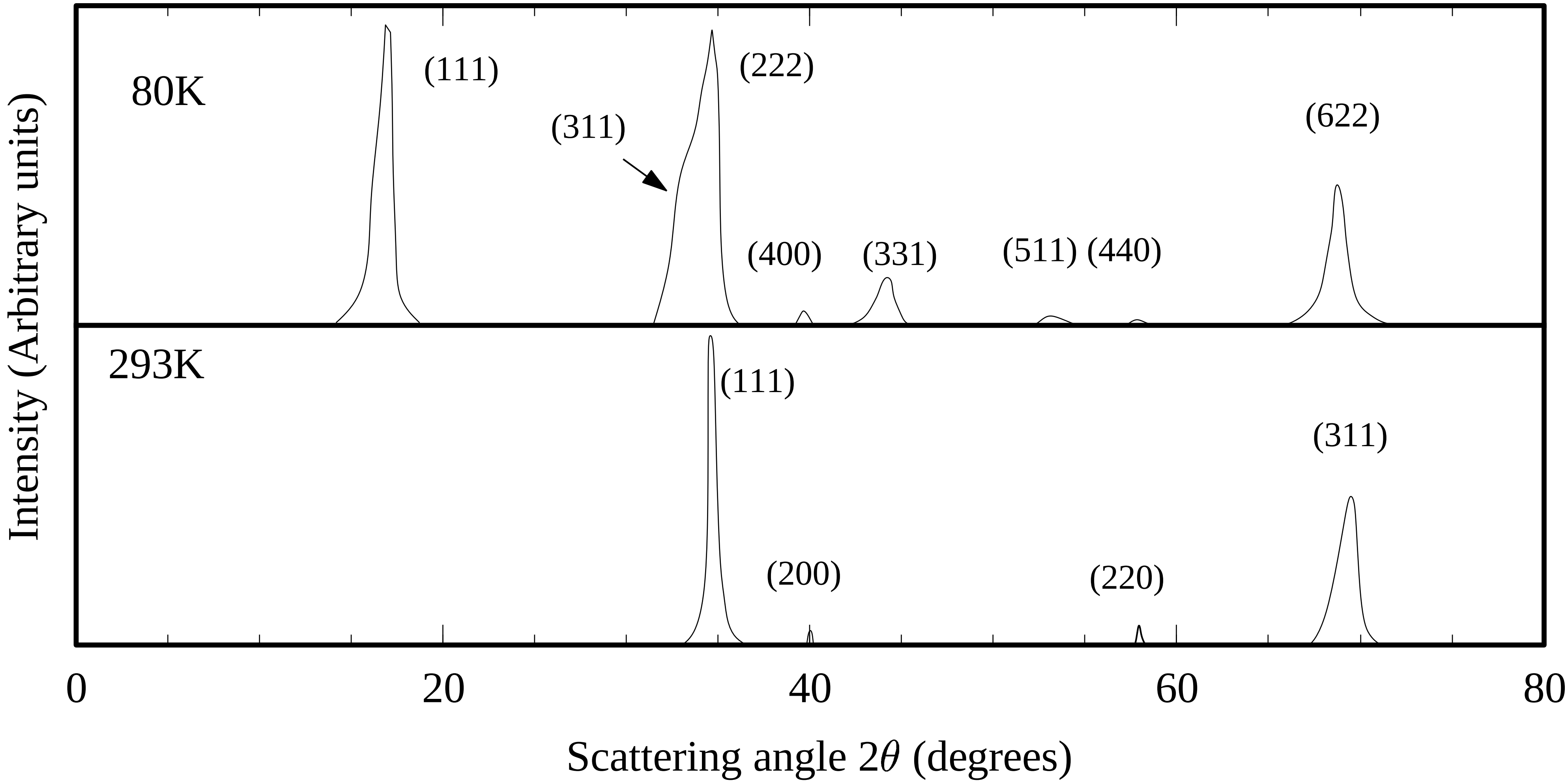
$$I_{\text{atom}}(\hat{r}) = \frac{e^4}{m^2c^4}\frac{(1+\cos^2 2\theta)}{2} \equiv \frac{e^4}{m^2c^4}P(\hat{r}) \quad \text{(L46)}$$

$$\Rightarrow f(\hat{r}) = \frac{e^2}{mc^2}\sqrt{P(\hat{r})} = 2.82\cdot 10^{-15}\sqrt{P(\hat{r})}\ \text{m} \quad \text{(L47)}$$

More on Scattering Experiments



Neutrons are almost completely isotropic. Elastic scattering (neutrons lose no energy) gives very precise information about static structure. Inelastic scattering gives very precise information about mechanical excitations. Neutrons are sensitive to the spins of the nuclei from which they scatter.



Information on a neutron detector

75 years of further advances...

Insertion of heavy atoms allows extremely complex crystals to be deciphered.

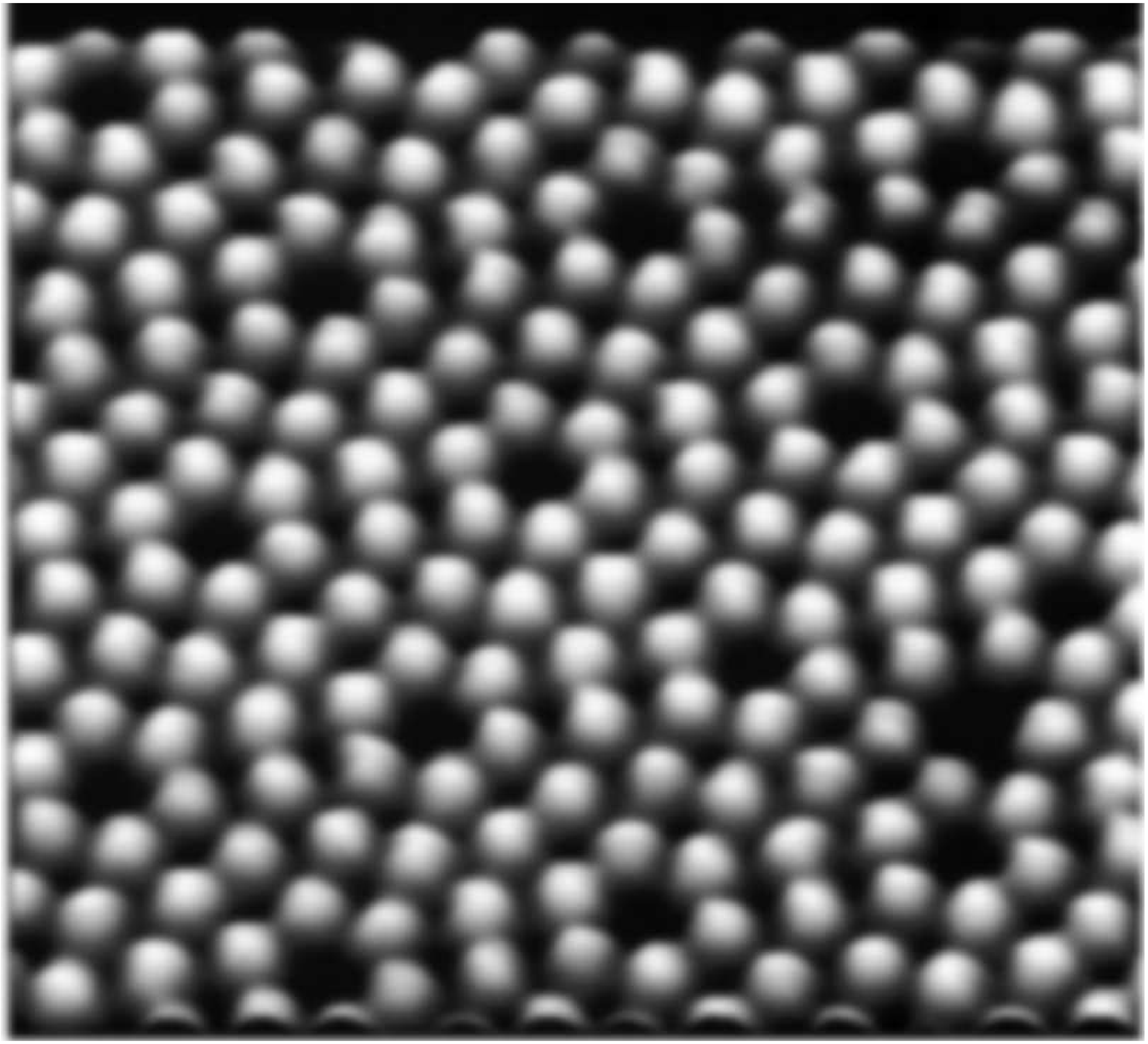
Crystallography Online

Structure of Hemoglobin

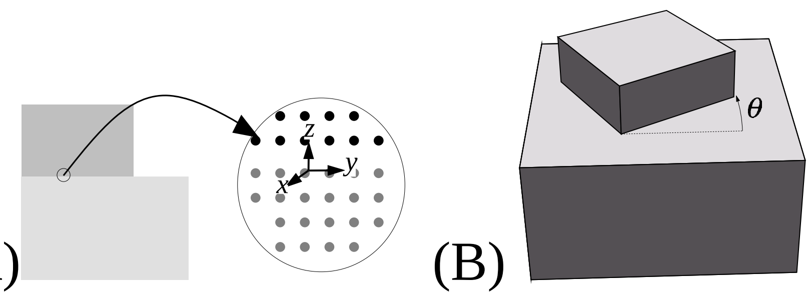
rasmol viewer for molecules

Computers do most of the work now (for better or worse)

Surfaces and Interfaces



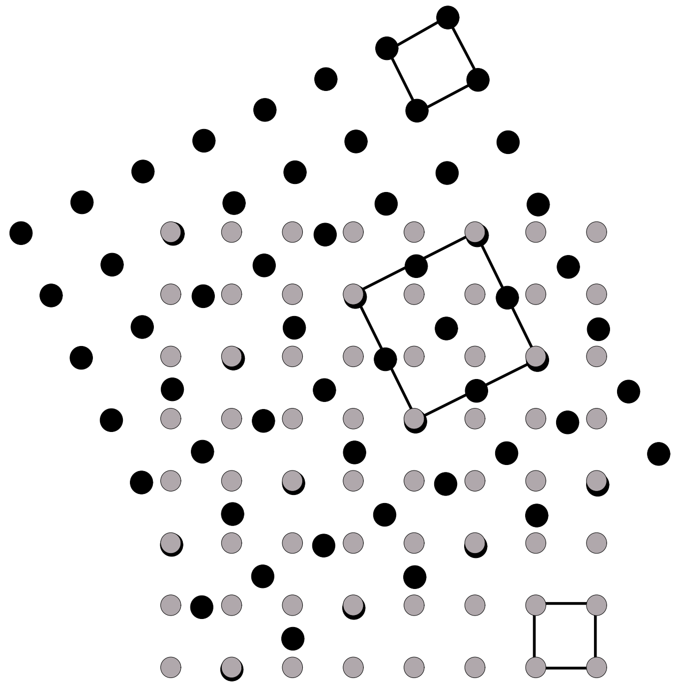
Counting up ways to align two surfaces

(A) 

(B)

Commensuarate and Incommensurate Interfaces

$$n_1\vec{a}_1 + n_2\vec{a}_2 = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} (m_1\vec{b}_1 + m_2\vec{b}_2). \tag{L1}$$

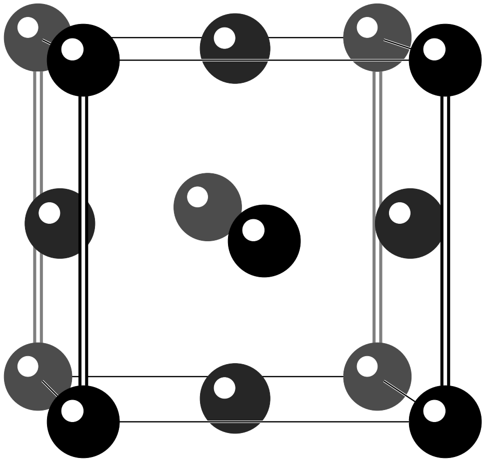


Lattice constants differ by $\sqrt{5}/2$: commensurate but incoherent.

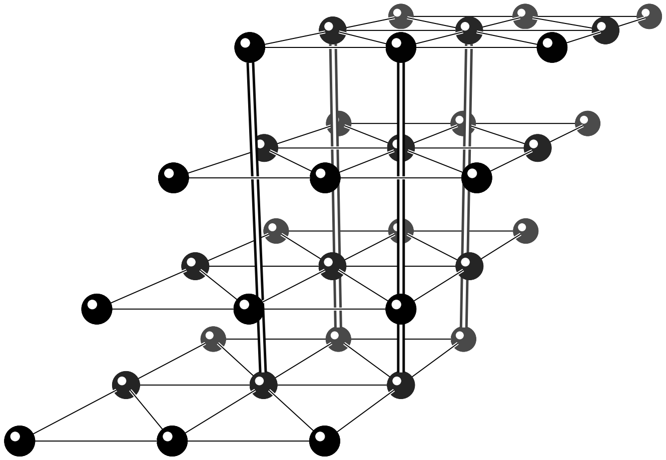
Stacking Period and Interplanar Spacing

$$P = \delta(i^2 + j^2 + k^2), \text{where } \delta \text{ equals 1 or 2.} \tag{L2}$$

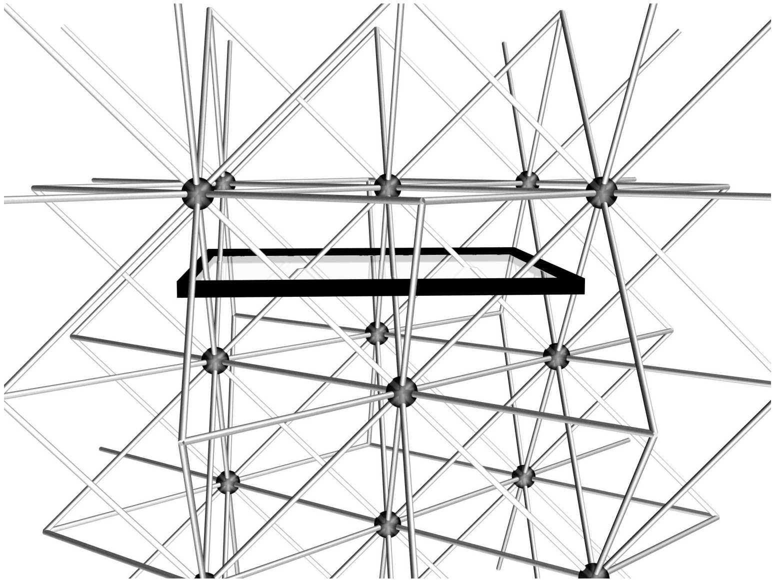
$$d = \epsilon a / \sqrt{i^2 + j^2 + k^2}, \tag{L3}$$



fcc (100) surface, $P = 2$



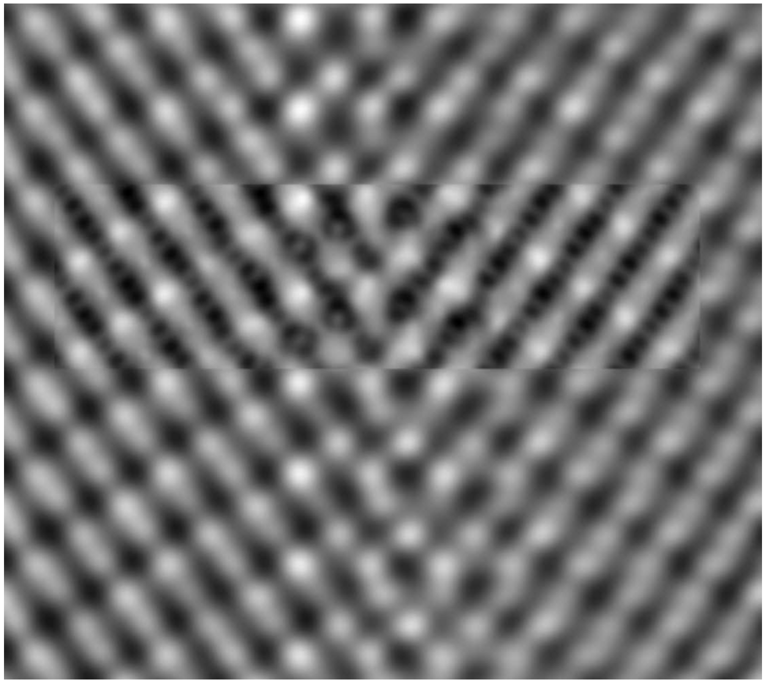
fcc (111) surface, $P = 3$

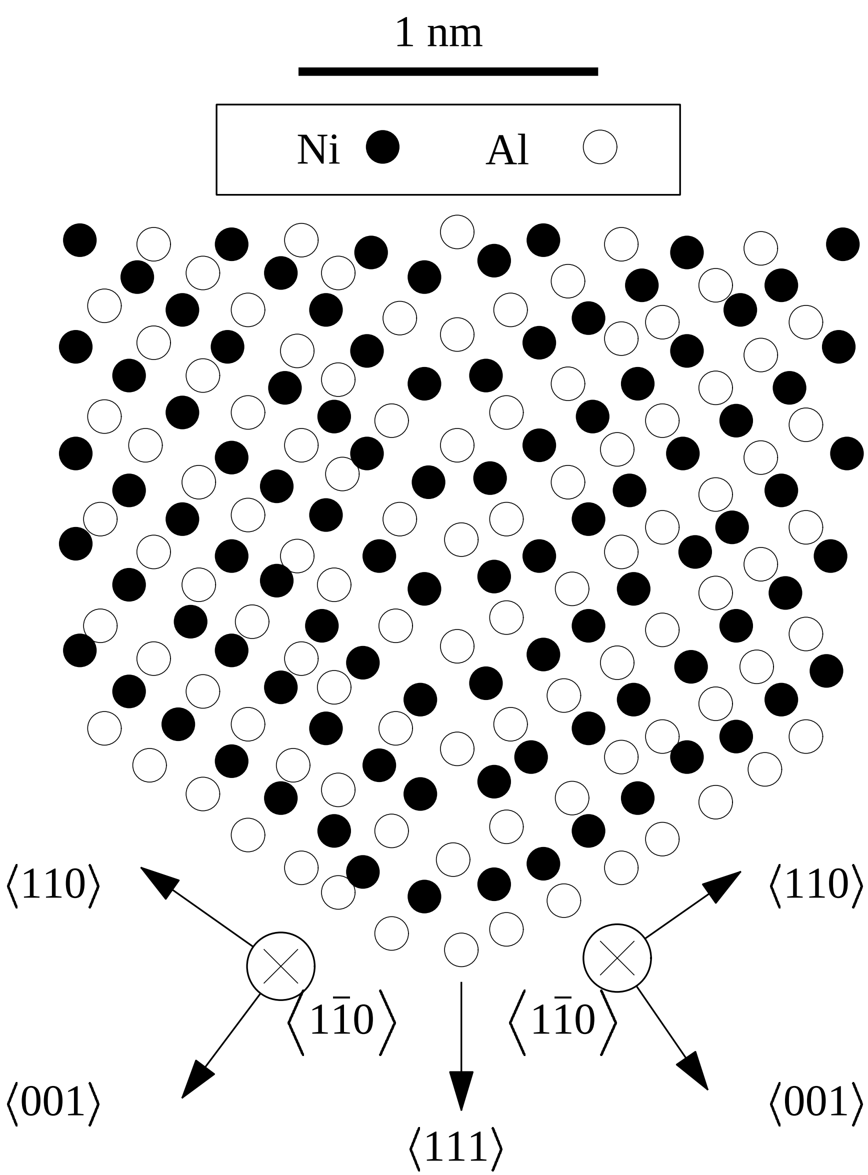


Nomenclature

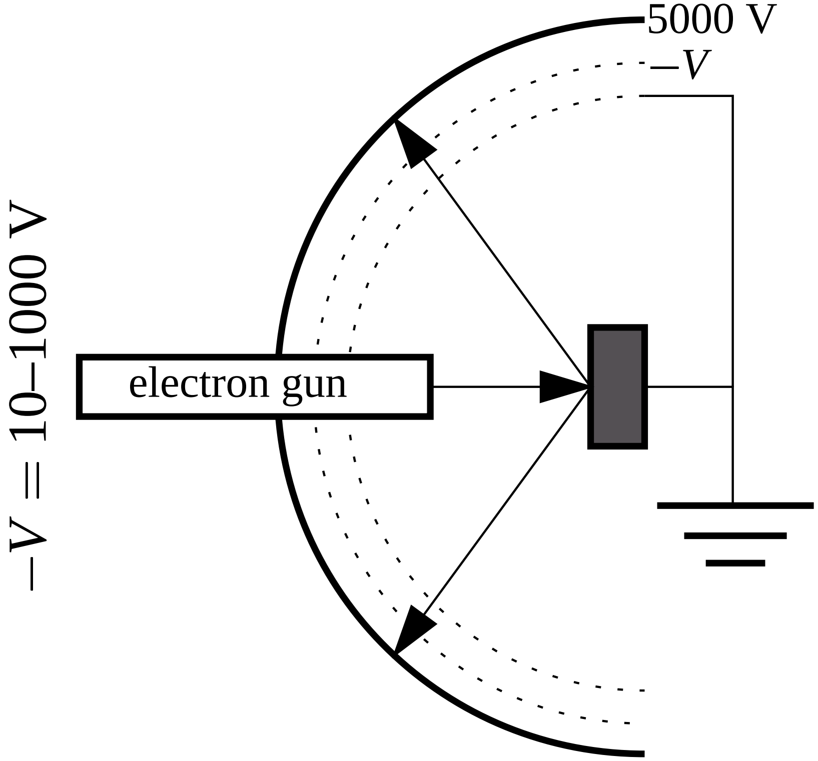
- Twin boundary
- Twist boundary
- Tilt boundary
- Stacking fault
- And here come the acronyms
- LEED—Low energy electron diffraction
- RHEED—Reflection high energy electron diffraction
- MBE—Molecular beam epitaxy
- FIM—Field ion microscopy
- STM—Scanning tunneling microscopy
- AFM—Atomic force microscopy
- HREM—High resolution electron microscopy

Twin Boundary



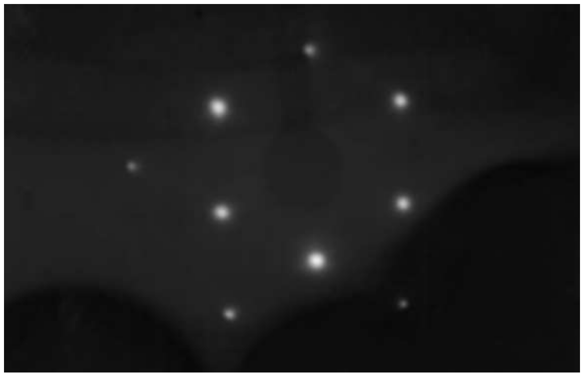


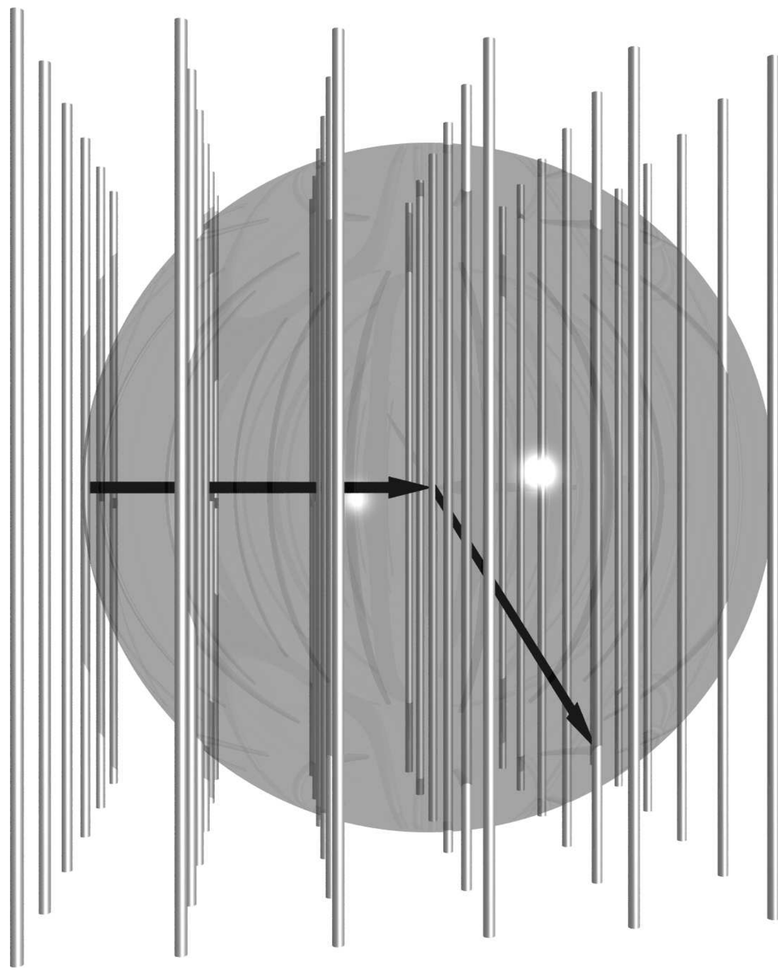
Technique used by Davisson and Germer to find wave nature of electron.



(A)

(B)



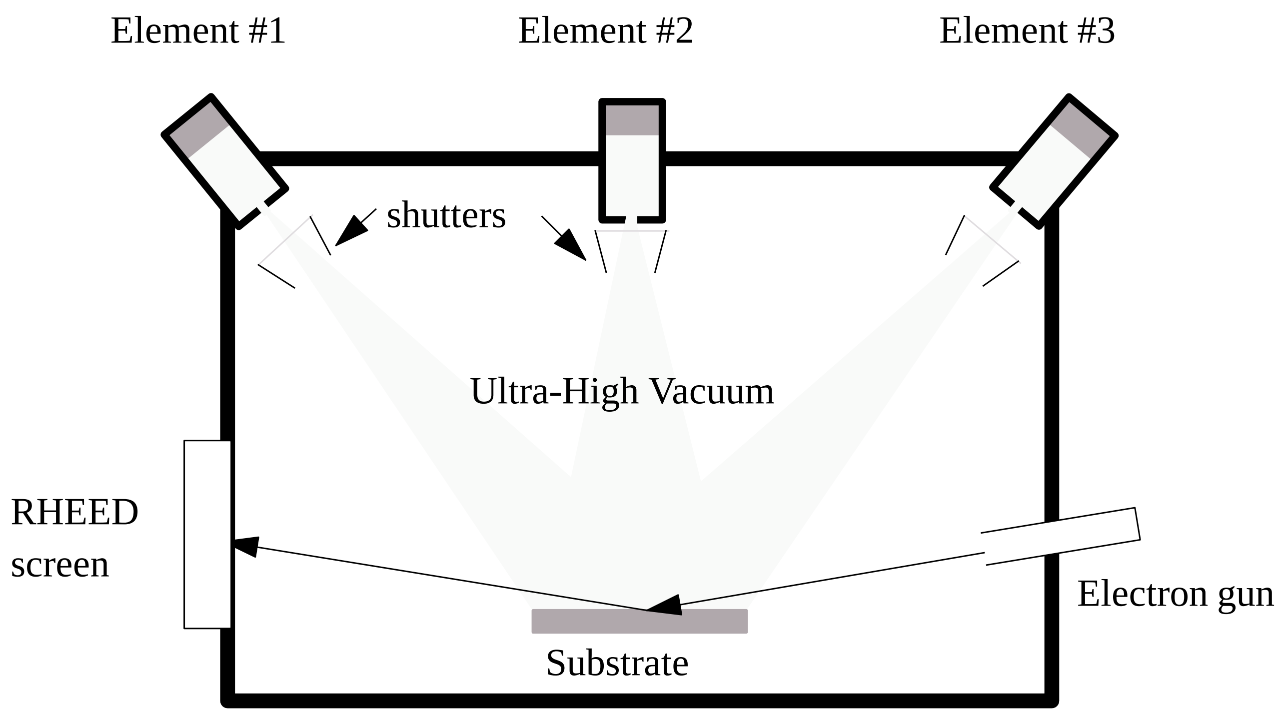


$$\lambda = 12.2\ [\text{energy}/\text{eV}]^{-1/2}\ \text{Å} \tag{L4}$$

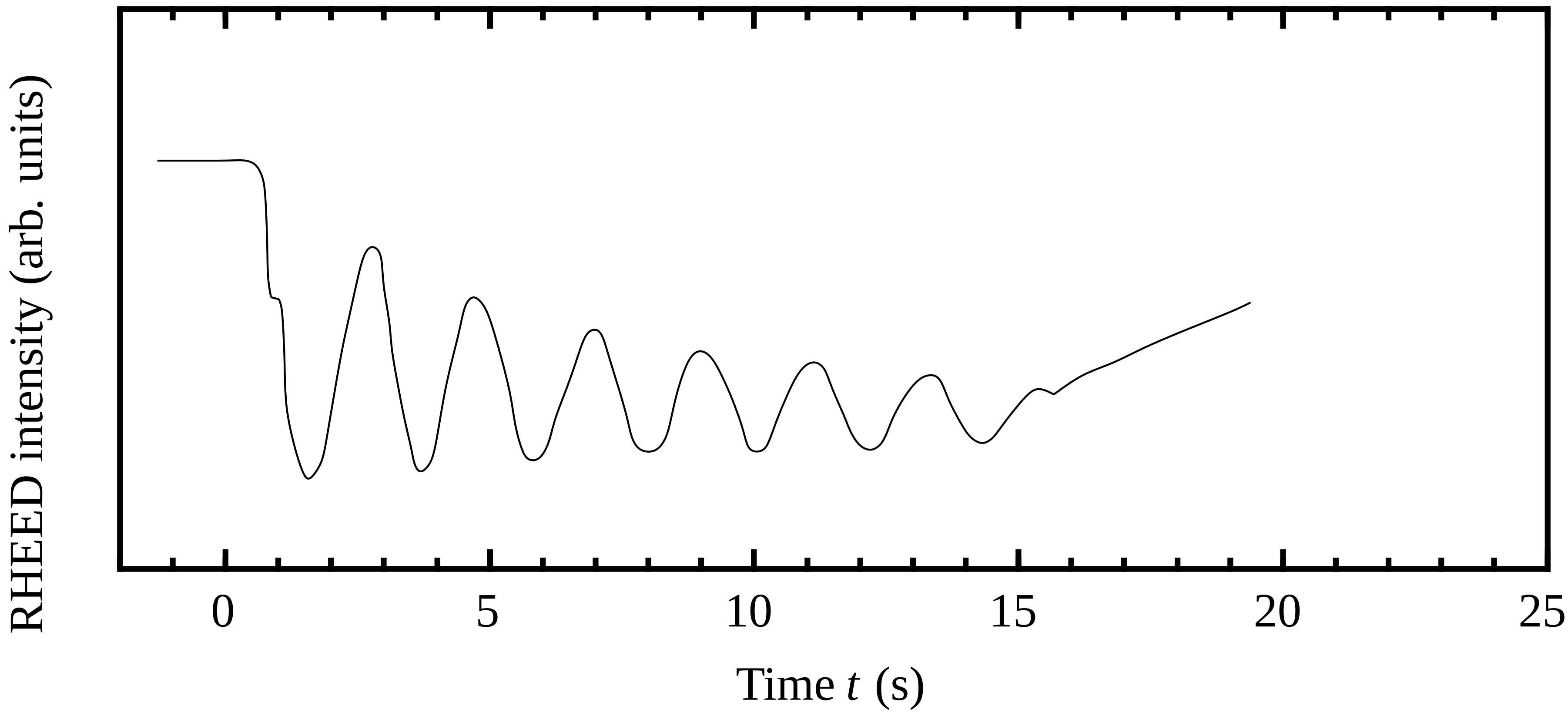
$$\vec{q}\cdot\vec{R} = 2\pi l \quad \vec{q} = (K_x, K_y, q_z). \tag{L5}$$

Molecular Beam Epitaxy (MBE) and Reflection High-Energy Electron Diffraction (RHEED)

Electrons of energy on the order of 100 keV reflected off a surface at a grazing angle. The wave vectors associated with such energies are on the order of 200 Å^{-1}, much larger than the spacing between reciprocal lattice vectors.



Molecular Beam Epitaxy (MBE) and Reflection High-Energy Electron Diffraction (RHEED)



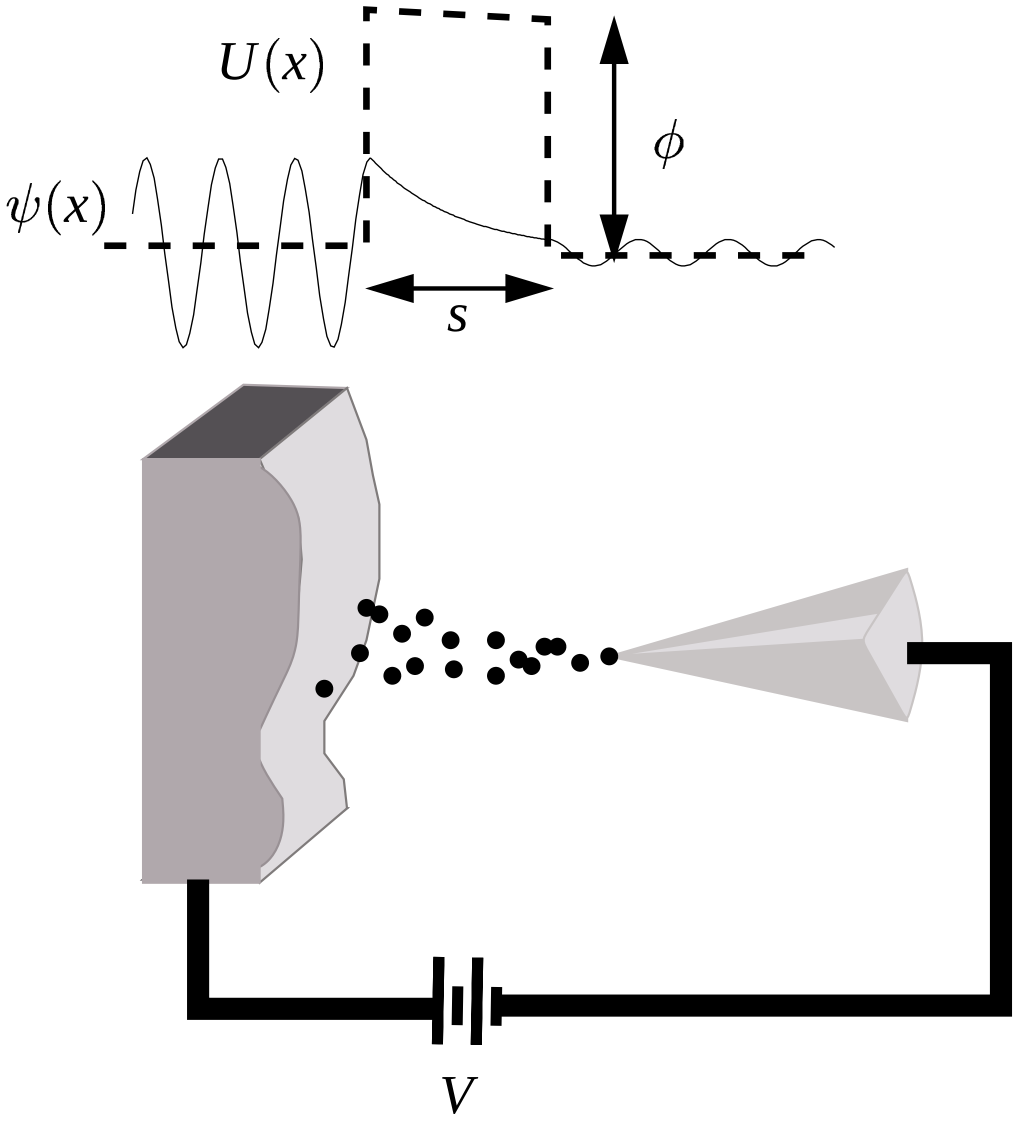
Oscillations in RHEED intensity, (001) GaAs surface monitoring the $[\bar{2}10]$ reflection as electrons reflect off the surface at an angle of 0.91°. Braun et al. (1998)

Oppenheimer and tunneling

$$i \sim \exp \frac{-C}{E} \tag{L6}$$

$$\psi \sim \exp[-x\sqrt{2mU/\hbar^2}]. \tag{L7}$$

$$\phi = \frac{1}{2}(\mu_1 + \mu_2). \tag{L8}$$



U(x)
ψ(x)
φ
s
V

$$\psi(x) \sim \exp\left[(i/\hbar)\int^{x} dx' \sqrt{2m(\mathcal{E} - U(x'))}\right]. \tag{L9}$$

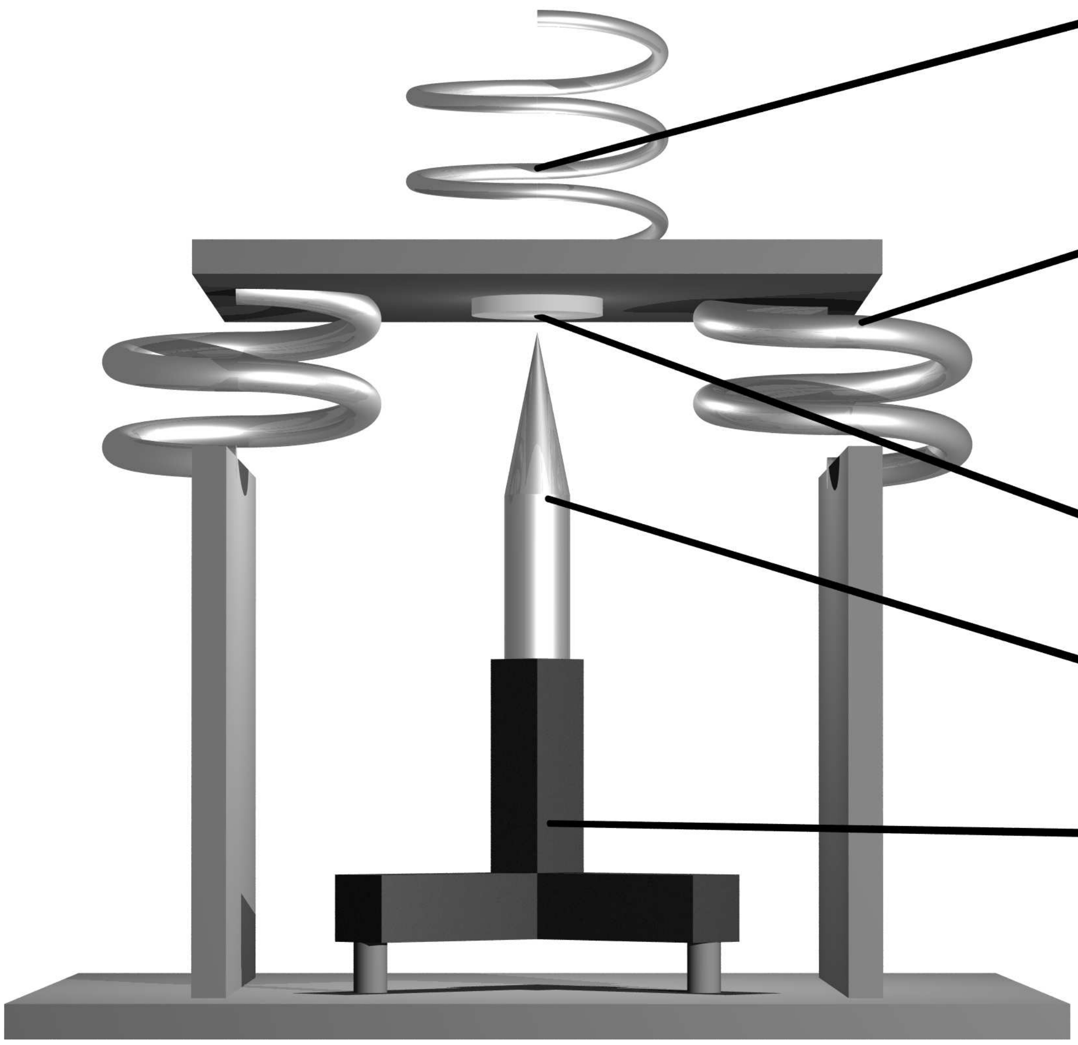
Amplitude drops by

$$\exp\left[-s\sqrt{2m\phi/\hbar^2}\right] \tag{L10}$$

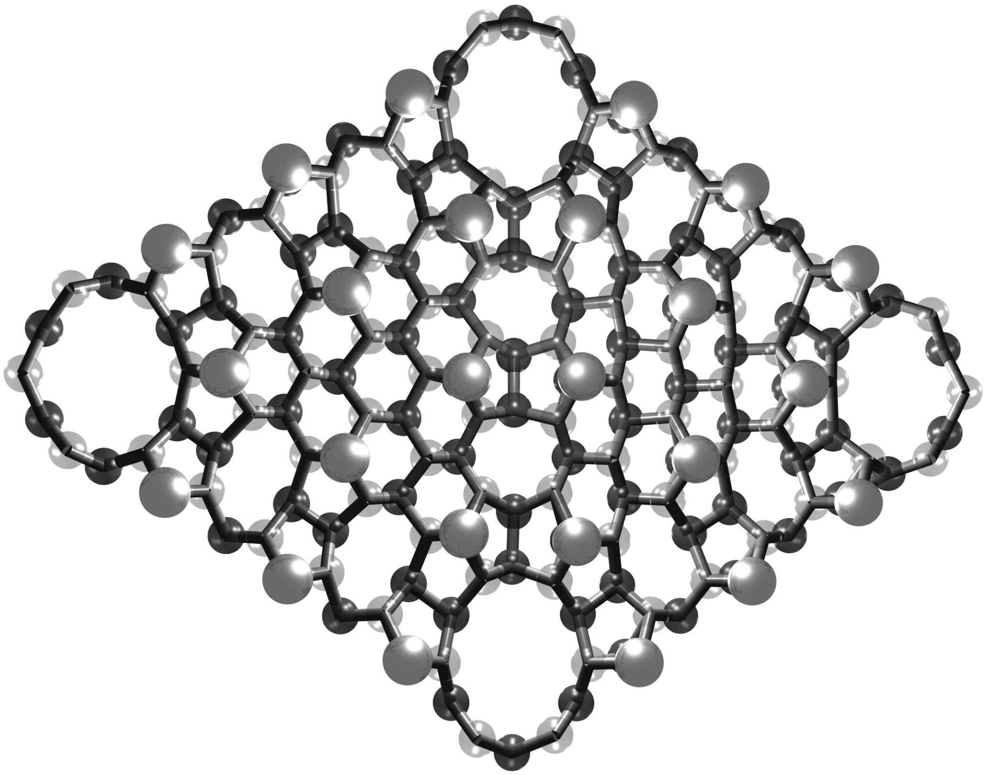
$$J \propto n_\mathrm{i} n_\mathrm{f} V \exp[-2s\sqrt{2m\phi/\hbar^2}] \tag{L11}$$

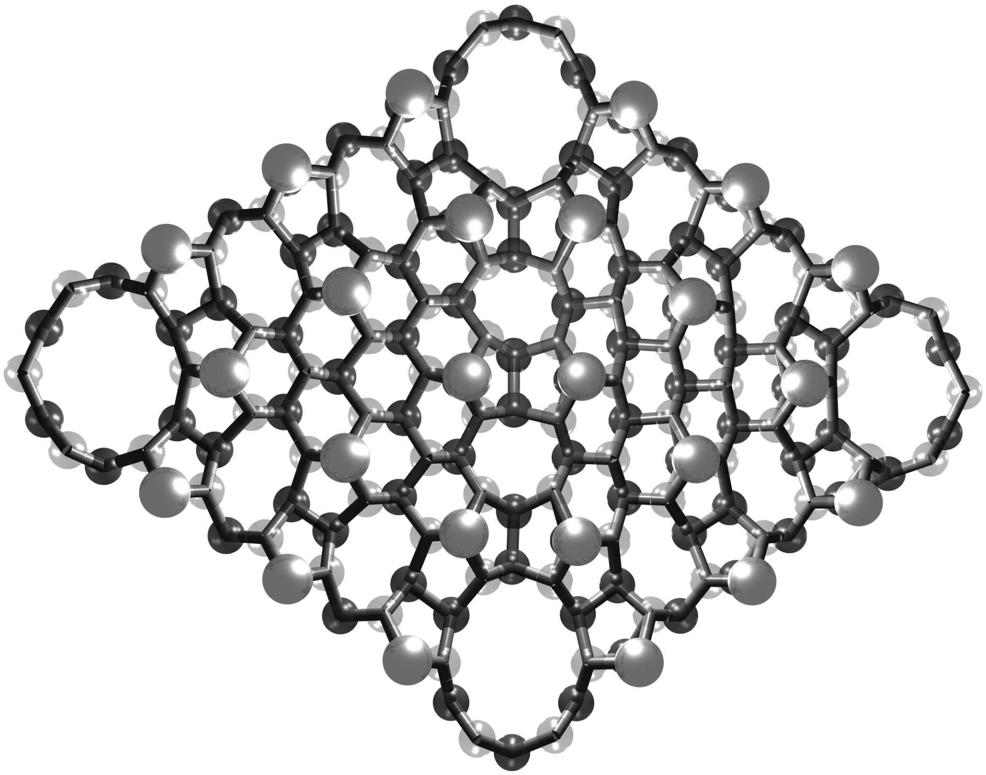
$$\propto \exp\left[-1.02[s/\text{Å}]\sqrt{[\phi/\mathrm{eV}]}\right]. \tag{L12}$$

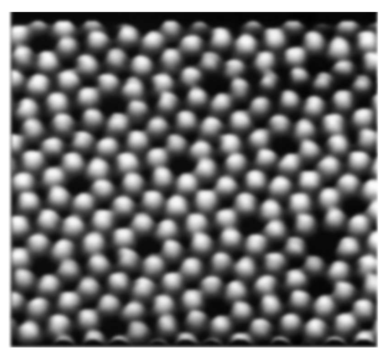
Scanning Tunneling Microscopy (STM)



Scanning Tunneling Microscopy (STM)

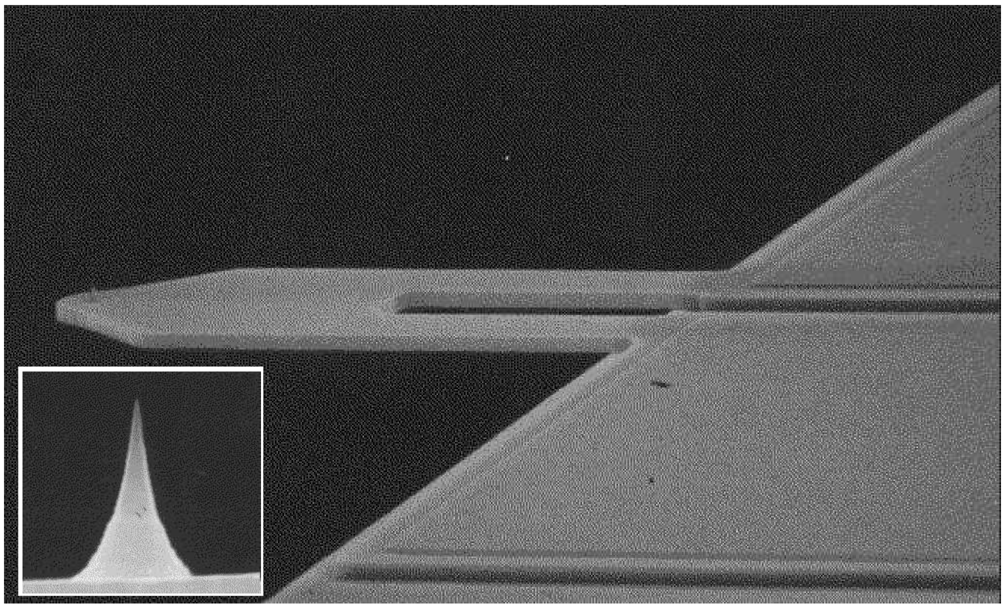


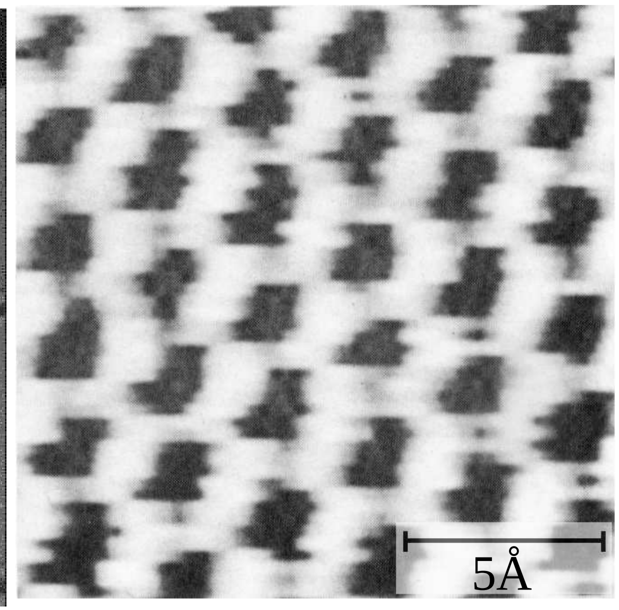




Wolkow and Avouris (1988)

Atomic Force Microscopy (AFM)





M. Tortonese

See Atomic Probe Microscope galleries at

IBM STM Image Gallery

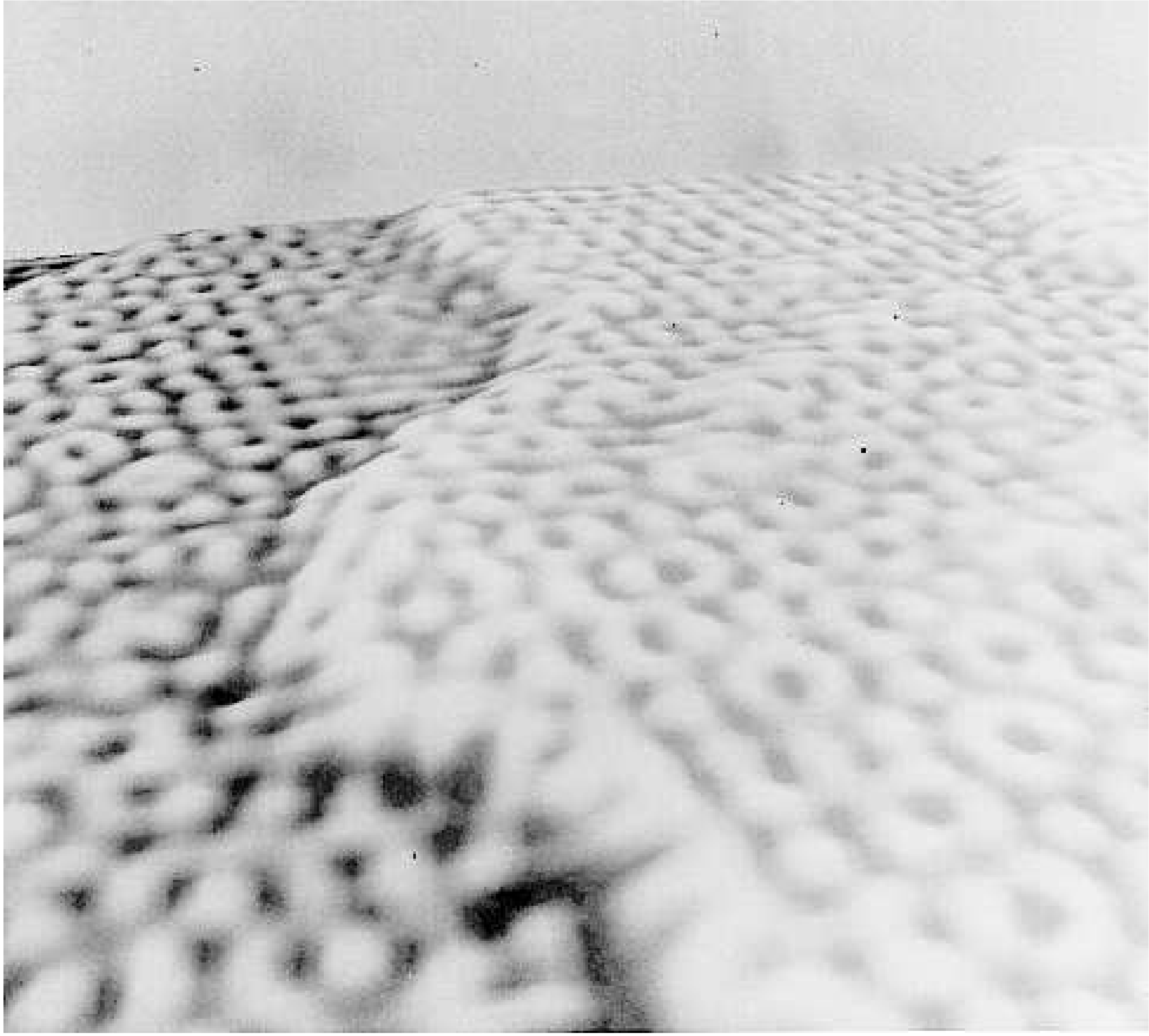
Digital Instruments/Veeco

DLA—Diffusion Limited Aggregation

Witten and Sander

Java simulator of DLA

Complex Structures



Entropy always favors mixing things together:

$$\binom{N}{M} = \frac{N!}{M!(N-M)!} \approx \frac{N^M}{M!}, \tag{L1}$$

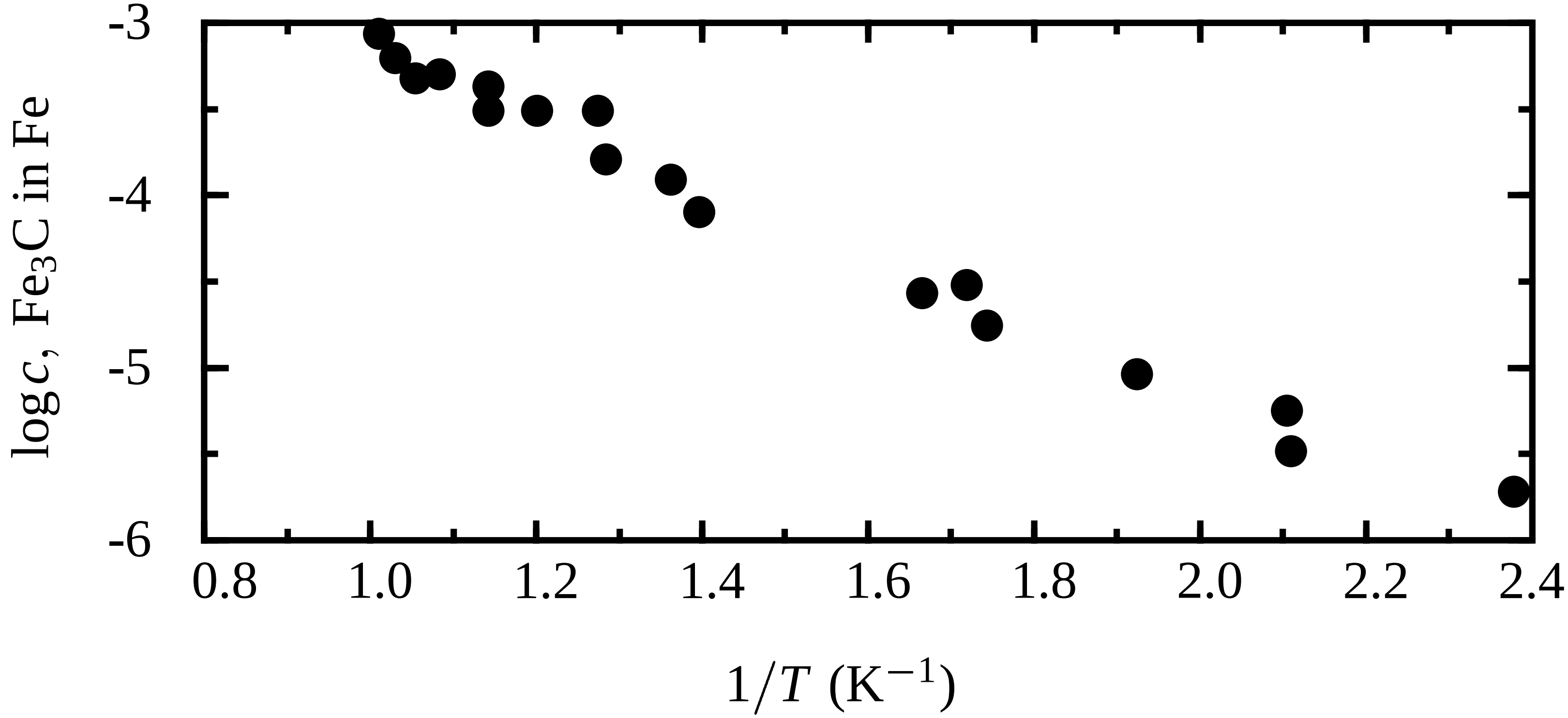
$$c = M/N, \tag{L2}$$

is

$$k_B \ln(N^M/M!) \approx -k_B N(c \ln c - c). \tag{L3}$$

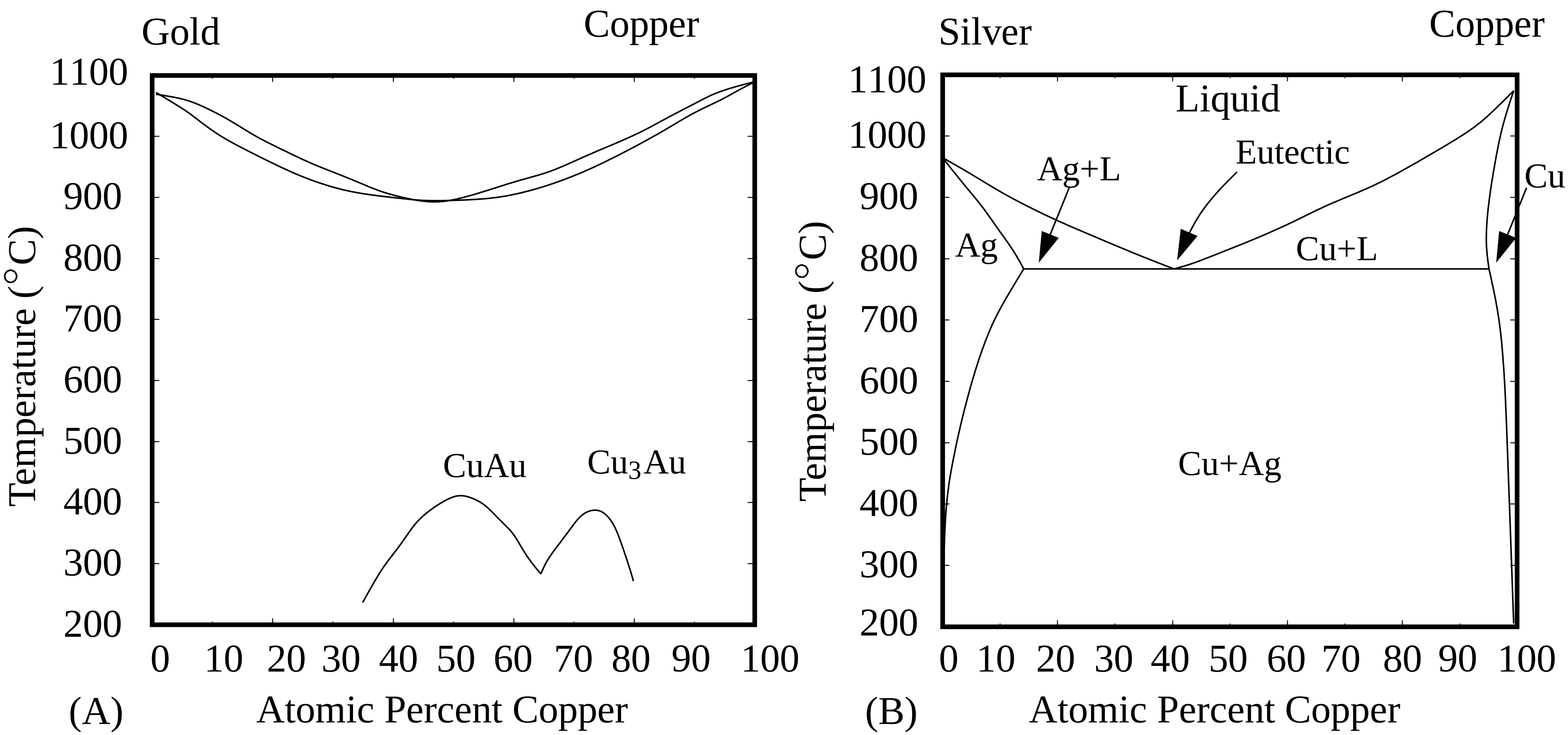
$$\mathcal{F} = \mathcal{E} - TS = N[c\epsilon + k_B T c \ln c - k_B T c], \tag{L4}$$

$$c \sim e^{-\epsilon/k_B T}. \tag{L5}$$



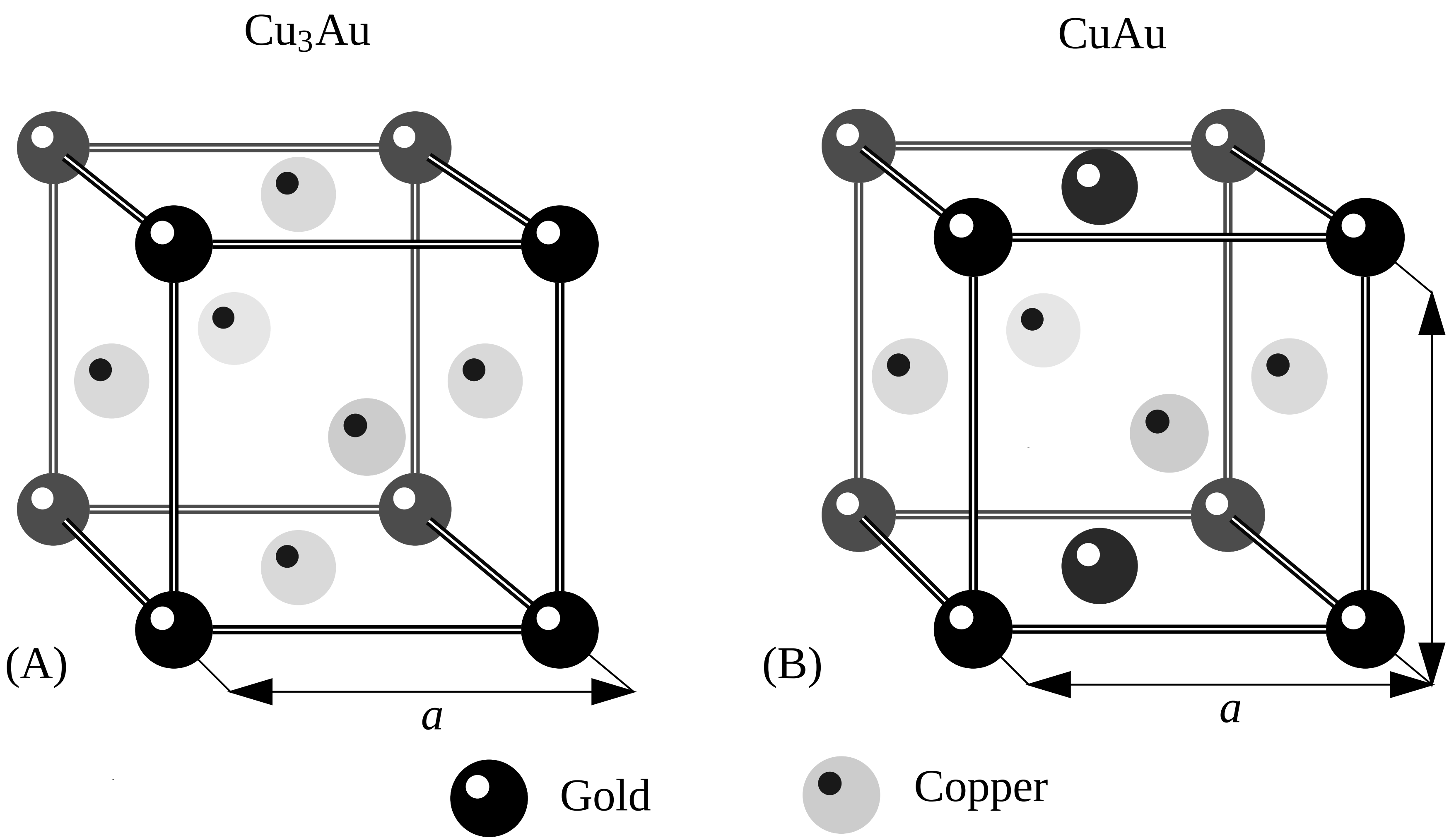
Flynn (1972)

Alloys

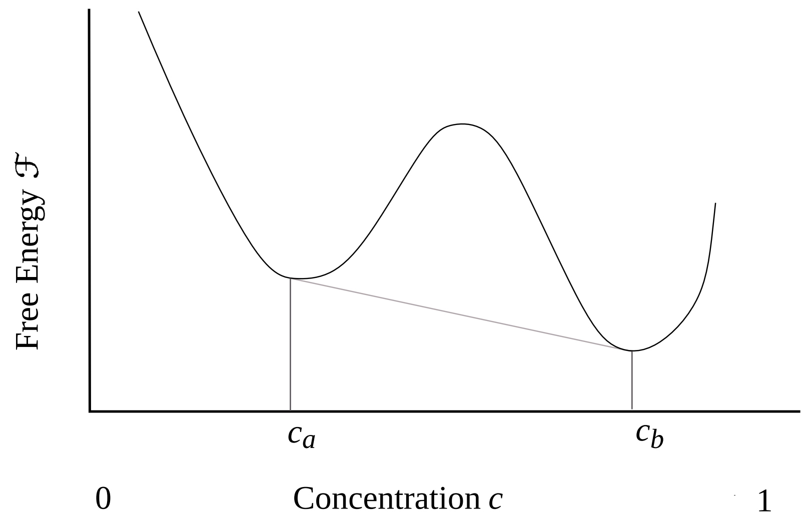


Hansen (1958)

Superlattices



(A) A 3:1 mixture of copper and gold (B) Equal mixtures. Lattice constant *c* is 7% smaller than *a*.

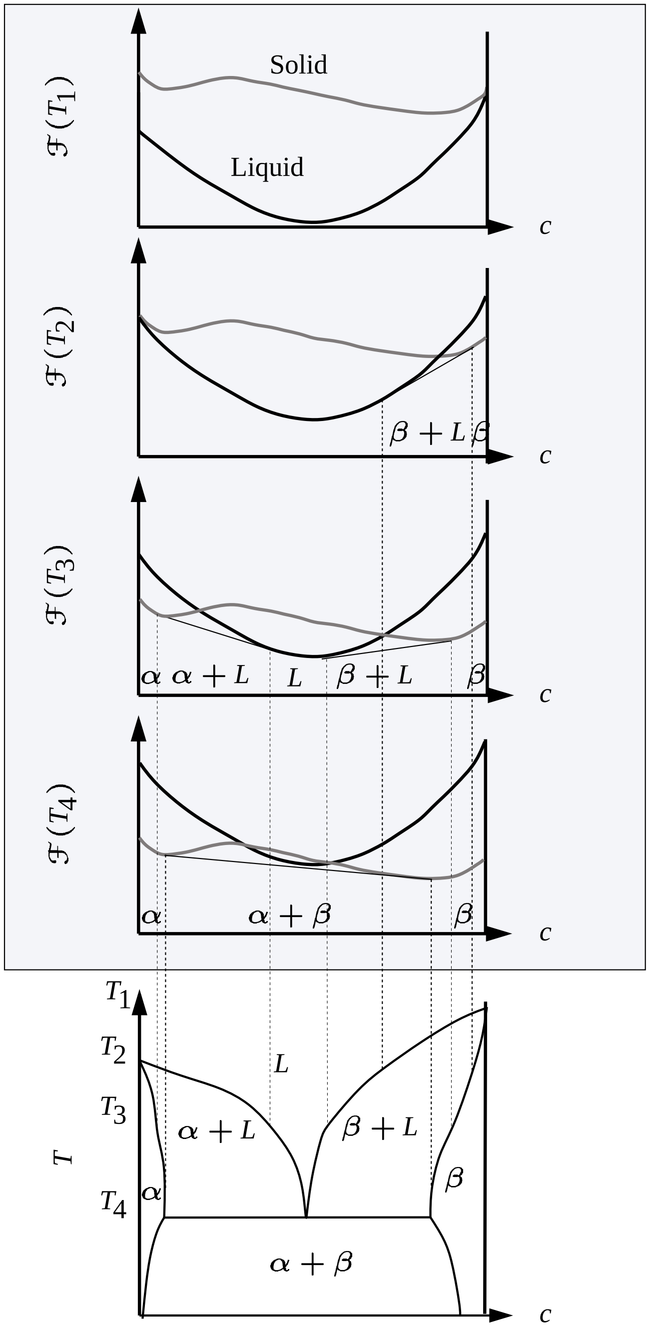


$$\mathcal{F}_{\text{ps}} = f\mathcal{F}(c_a) + (1-f)\mathcal{F}(c_b), \quad \text{(L6)}$$

$$\text{(L7)}$$

$$\Rightarrow \mathcal{F}_{\text{ps}} = \frac{c-c_b}{c_a-c_b}\mathcal{F}(c_a) + \frac{c_a-c}{c_a-c_b}\mathcal{F}(c_b). \quad \text{(L8)}$$

Phase Separation



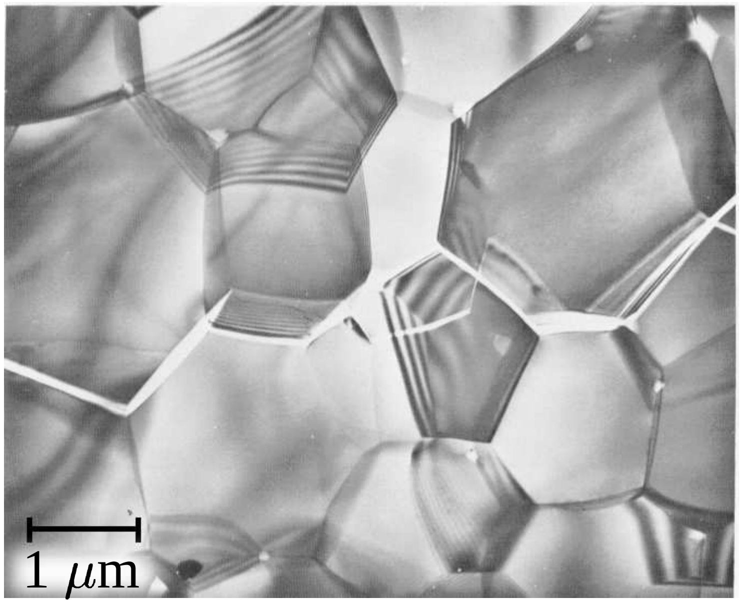
At sufficiently high temperatures, the liquid phase is of lower free energy at all concentrations c than the solid.

At this temperature, the liquid L is lower in energy to the left, but coexists with solid of type β towards the right, and β is stable for sufficiently high concentrations.

Now solid of type α is stable for low values of c, β is stable for high values, liquid is stable for a small range in the middle, and there are two coexistence regions.

Only solid phases are stable. These can be pure α, pure β, or mixtures $\alpha + \beta$ of the two.

Grains



Due to B. Hockey, attributed to E. Fuller, and published by R. Thomson (1986)

$$\vec{j} = -\mathcal{D}\vec{\nabla}c. \tag{L9}$$

$$\frac{\partial c}{\partial t} = \mathcal{D}\nabla^2 c \tag{L10}$$

$$\vec{F}_l = -\frac{\partial \mathcal{E}}{\partial \vec{R}_l}, \tag{L11}$$

$$m_l \frac{d^2\vec{R}_l}{dt^2} = \vec{F}_l. \tag{L12}$$

$$\vec{R}_l^{n+1} = 2\vec{R}_l^n - \vec{R}_l^{n-1} + \frac{\vec{F}_l^n}{m_l} dt^2 \tag{L13}$$

with

$$\vec{F}_l^n = \vec{F}_l(\vec{R}_1^n \vec{R}_2^n \ldots \vec{R}_N^n) \tag{L14}$$

Order parameters

$$n_2(\vec{r}_1,\vec{r}_2;t) = \left\langle \sum_{l\neq l'} \delta(\vec{r}_1 - \vec{R}_l(0))\delta(\vec{r}_2 - \vec{R}_{l'}(t)) \right\rangle. \tag{L15}$$

$$S(\vec{q}) \equiv \frac{I}{NI_{\text{atom}}} \tag{L16}$$

$$= 1 + \frac{1}{N}\int d\vec{r}_1\, d\vec{r}_2\, n_2(\vec{r}_1,\vec{r}_2;0)e^{i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)} \tag{L19}$$

where

$$n_2(\vec{q}) = \frac{1}{\mathcal{V}}\int d\vec{r}d\vec{r}'\, n_2(\vec{r}+\vec{r}',\vec{r};0)e^{i\vec{q}\cdot\vec{r}'}. \tag{L20}$$

Long–range order in crystals...

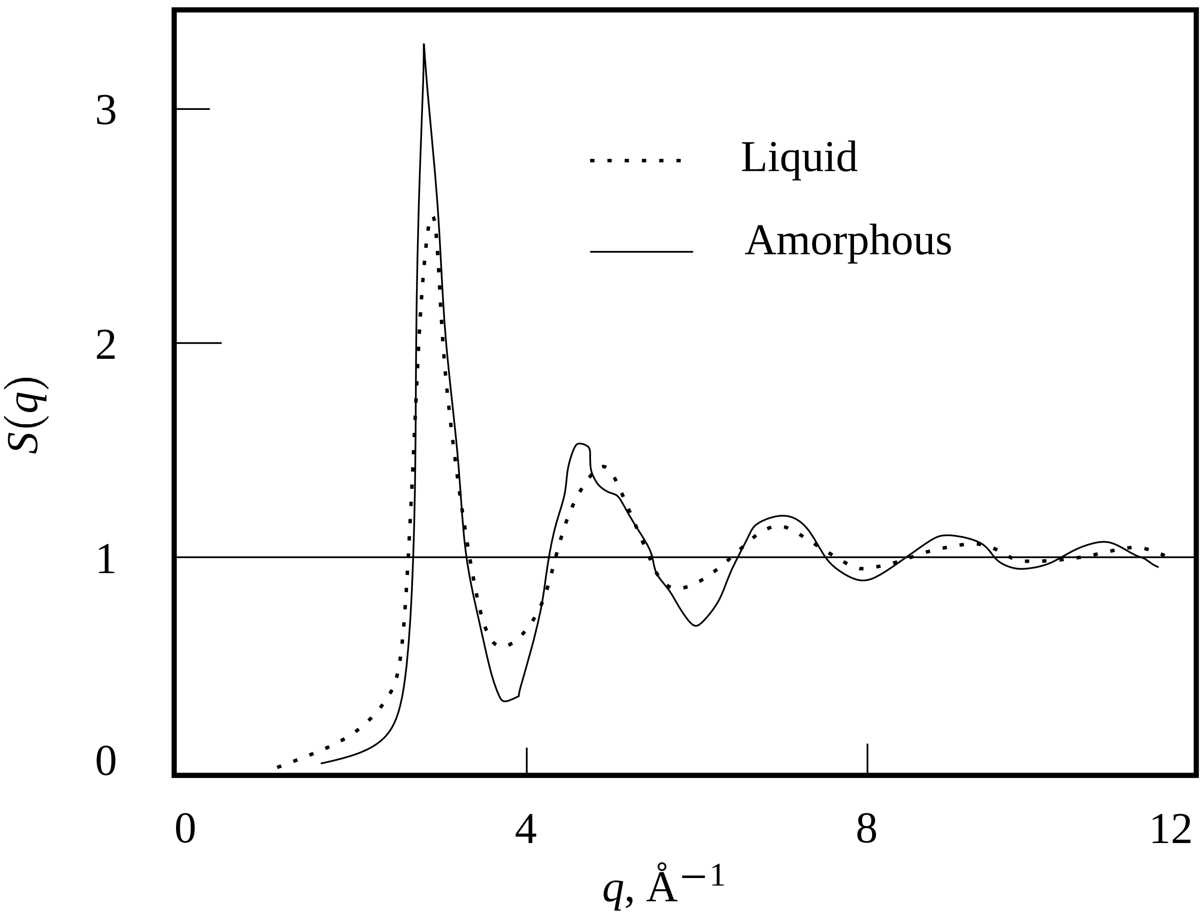
$$\mathcal{O}_{\vec{K}} = \frac{\mathcal{V}}{N^2} n_2(\vec{K}). \quad \text{(L21)}$$

Short–range order in liquids...

$$g(r) \equiv \frac{n_2(r)}{n^2}. \quad \text{(L22)}$$

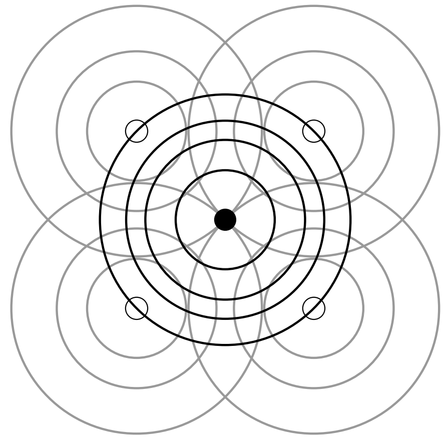
$$\begin{aligned} S(\vec{q}) &= 1 + n \int d\vec{r}\, g(r) e^{i\vec{q}\cdot\vec{r}} && \text{(L23)} \\ &= 1 + n \int d\vec{r}\, (g(r) - 1) e^{i\vec{q}\cdot\vec{r}} + n \int d\vec{r}\, e^{i\vec{q}\cdot\vec{r}} && \text{(L24)} \\ &\approx 1 + n \int d\vec{r}\, e^{i\vec{q}\cdot\vec{r}} (g(r) - 1). && \text{(L25)} \end{aligned}$$

Long- and Short-Range Order



$$z = n \int_0^{\text{first peak}} dr\, 4\pi r^2 g(r), \qquad \text{(L26)}$$

Extended X-Ray Absorption Fine Structure (EXAFS)



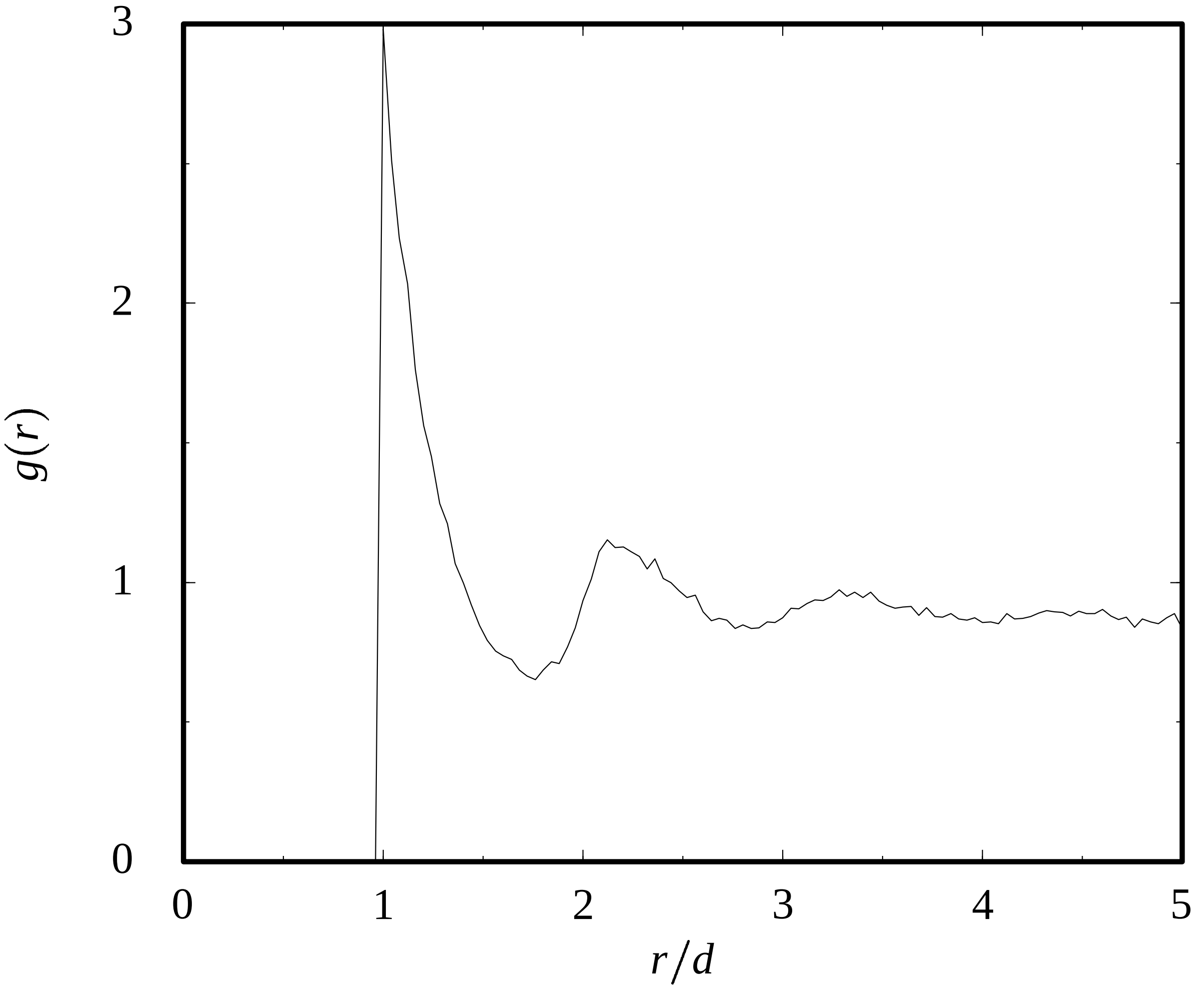
Incoming radiation whose energy $\mathcal{E}$ lies above the onset of absorption at $\mathcal{E}_a$. Receiving atom emits an electron of energy $\mathcal{E}-\mathcal{E}_a$ and wave vector $\hbar k = \sqrt{2m(\mathcal{E}-\mathcal{E}_a)}$.

$$\alpha(\mathcal{E}) \propto \sum_j |1+[e^{-R_j/l_T} e^{ikR_j} f/R_j]^2|^2 \quad \text{(L27)}$$

$$\sim \left\langle \int ds\, g(s) e^{-2s/l_T} \cos(2ks) \right\rangle . \quad \text{(L28)}$$

l_T is the mean free path of electrons in the solid.

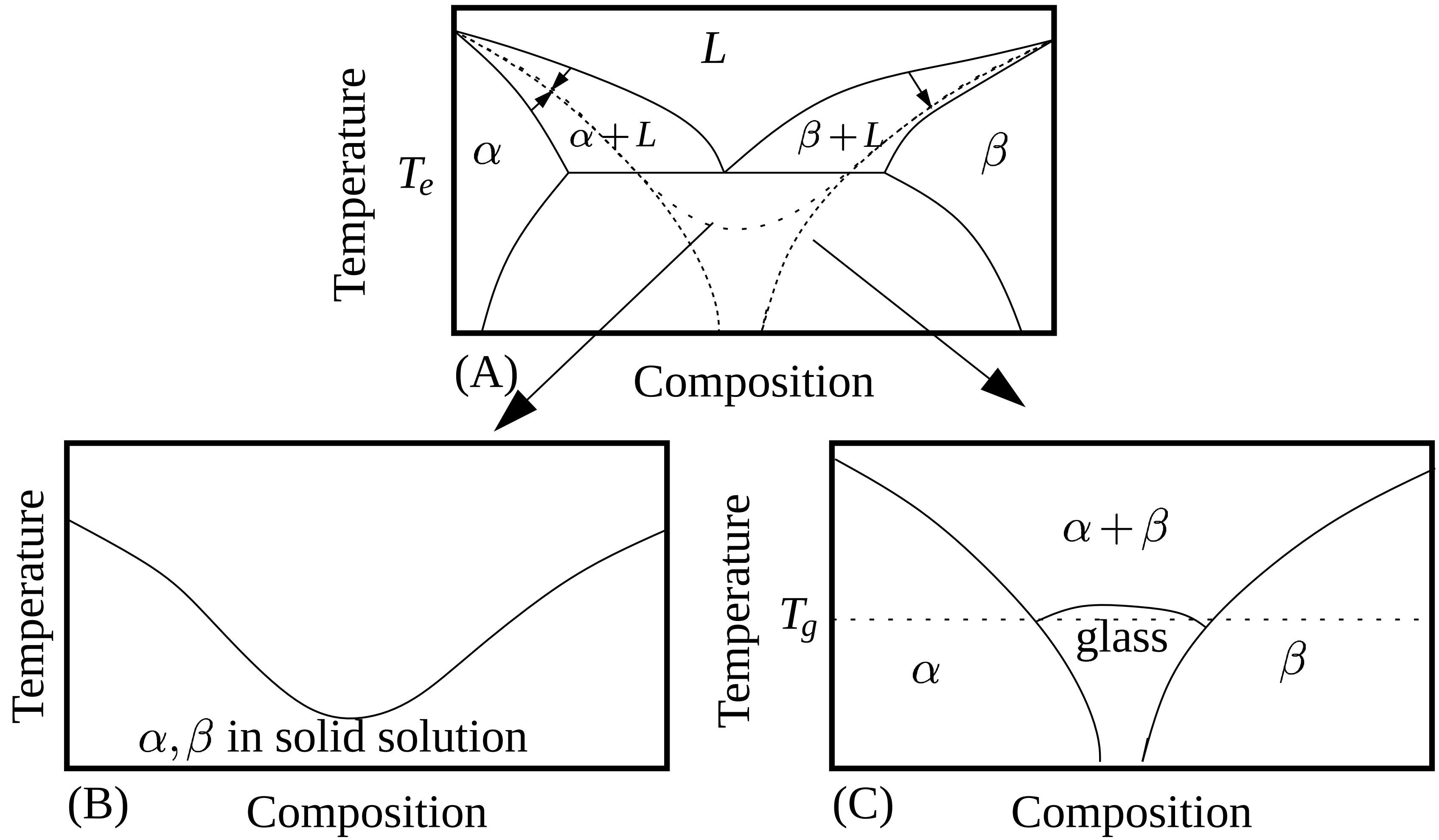
Dense Random Packing, Bernal model, Hard spheres



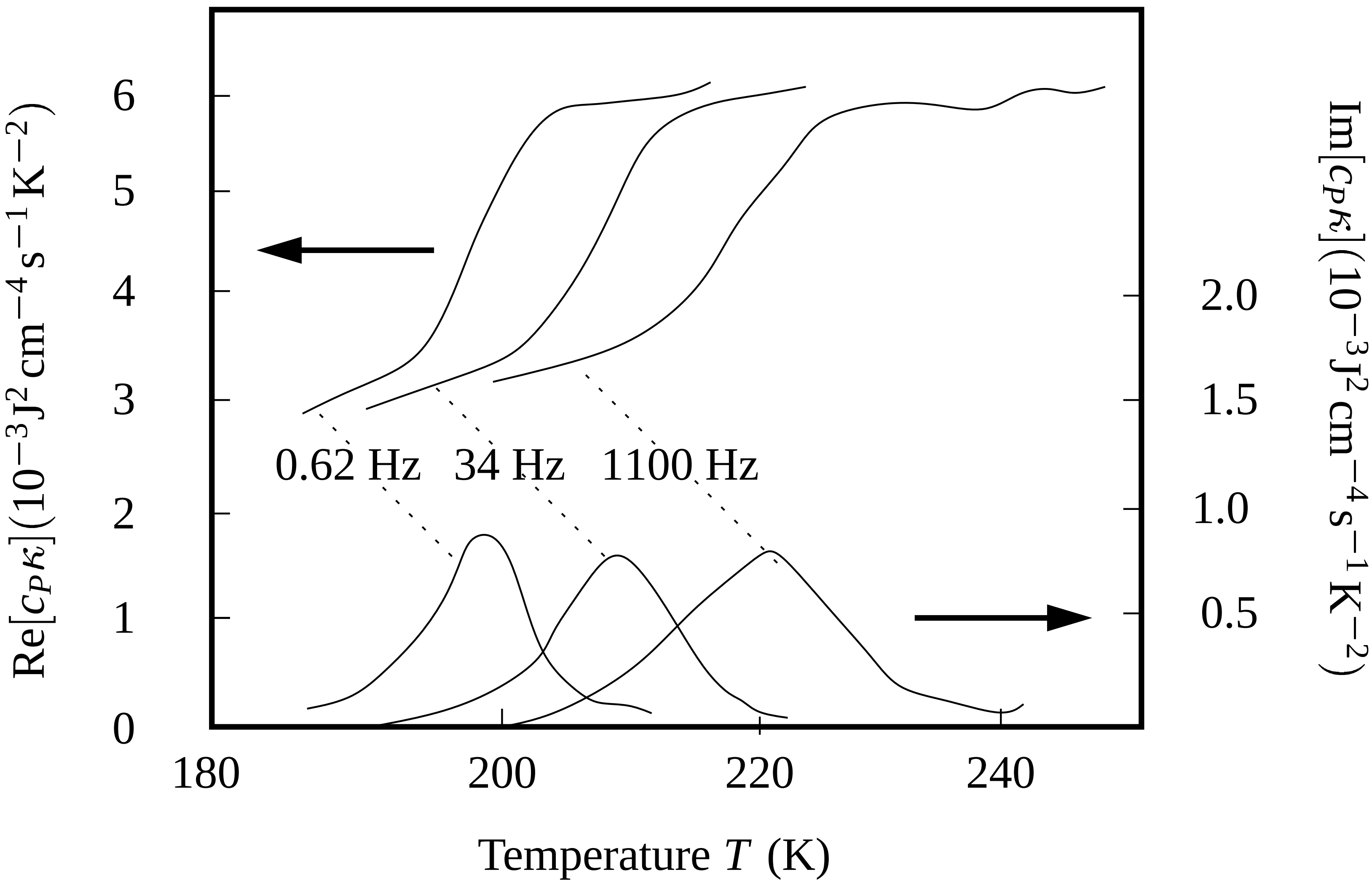
The radial distribution function $g(r)$ for hard spheres (disks) of radius d in two dimensions.

Glasses

$$\eta \propto \exp\left[C/(T - T_0)\right]. \quad \text{(L29)}$$

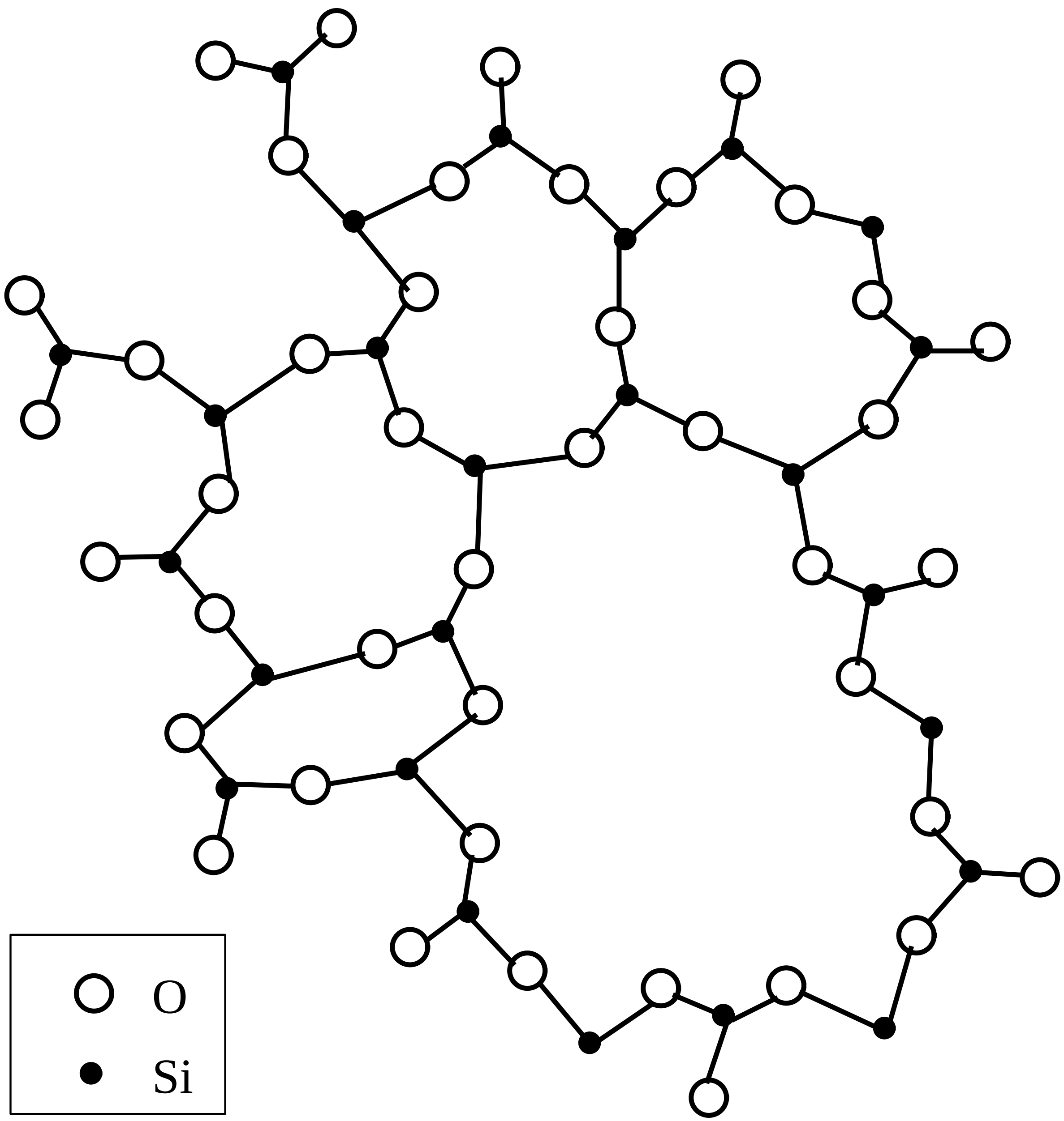


Properties depend upon time one waits.



Specific heat c_P times thermal conductivity κ for the glassy liquid glycerol as a function of temperature. Birge and Nagel (1985)

Continuous Random Network



Bond-counting and constraint argument of Phillips

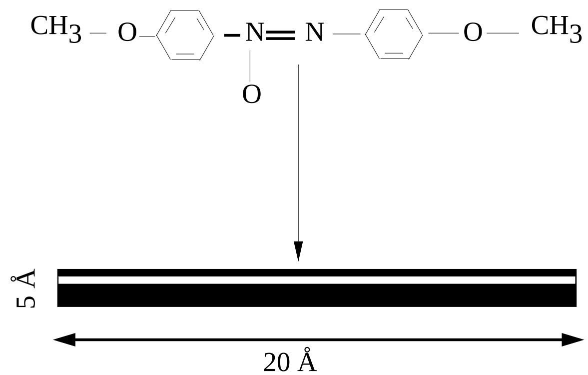
N number of atoms, b number of bonds per atom.

$Nb/2$ total bonds. If there is an optimal angle, $N(2b-3)$ extra constraints per atom.

$$3N = N(2b-3) + \frac{Nb}{2}, \tag{L30}$$

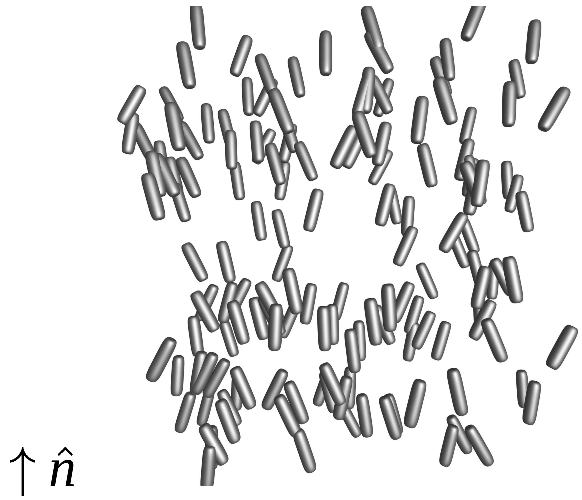
it follows that

$$b = 2.4, \tag{L31}$$



Picture of the organic molecule p-azoxyanisole (PAA), which forms a nematic liquid crystal between 116 °C and 135 °C. It can roughly be regarded as a rigid rod of length 20 Å and width 5 Å.

- Nematics
- Cholesterics
- Smectics



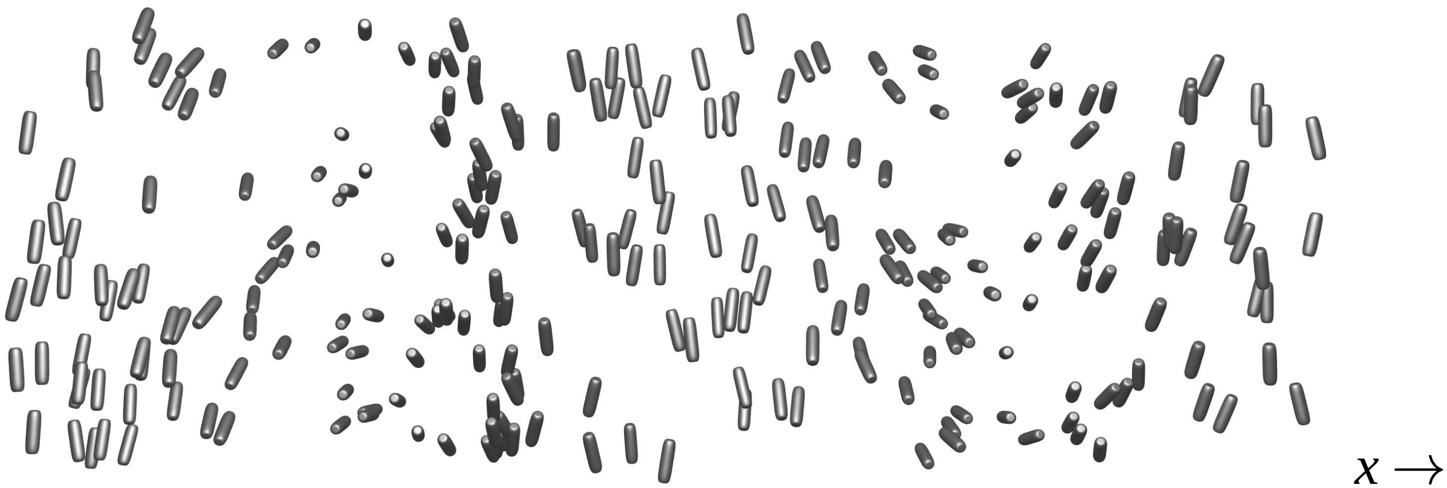
Nematic liquid crystal

Cholesterics

$$n_x = 0 \tag{L32a}$$

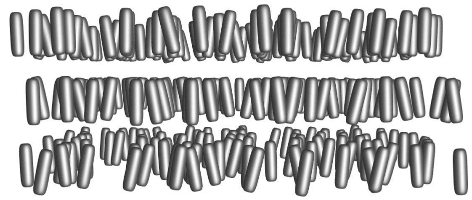
$$n_y = \cos q_0 x \tag{L32b}$$

$$n_z = \sin q_0 x. \tag{L32c}$$



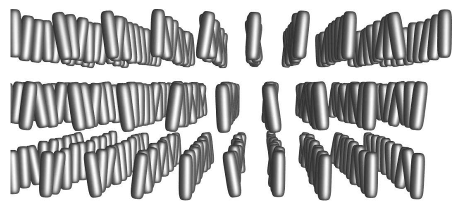
Smectics

Smectic A

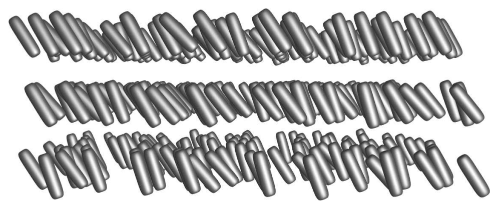


$\uparrow \hat{n}$

Smectic B



Smectic C



$$\mathcal{O} = \int d^3 r_1 d\theta_1 n_1(\vec{r}_1, \theta_1) \frac{1}{2}(3\cos^2\theta_1 - 1). \qquad \text{(L33)}$$

$$Q_{\alpha\beta} = \epsilon_{\alpha\beta} - \frac{1}{3}\delta_{\alpha\beta} \sum_{\gamma} \epsilon_{\gamma\gamma}, \qquad \text{(L34)}$$

Polymer as a random walk.

Ideal Radius of Gyration

$$\mathcal{P}_{N+1}(\vec{R}) = \int d\vec{R}' \mathcal{P}_N(\vec{R}')\mathcal{P}_1(\vec{R}-\vec{R}') \quad \text{(L35)}$$

$$\Rightarrow \quad \mathcal{P}_{N+1}(\vec{k}) = \mathcal{P}_N(\vec{k})\mathcal{P}_1(\vec{k}) \quad \text{(L36)}$$

$$\Rightarrow \quad \mathcal{P}_N(\vec{k}) = [\mathcal{P}_1(\vec{k})]^N. \quad \text{(L37)}$$

$$\int d\vec{R} \qquad \mathcal{P}_1(\vec{R}) = 1 \Rightarrow \mathcal{P}_1(\vec{k}=0) = 1. \quad \text{(L38)}$$

$$\mathcal{P}_1(\vec{k}) \approx 1 - \frac{c}{2}k^2 \approx e^{-ck^2/2} \tag{L39}$$

$$\Rightarrow \qquad \mathcal{P}_N(\vec{k}) \approx e^{-Nck^2/2} \tag{L40}$$

$$\Rightarrow \qquad \mathcal{P}_N(\vec{R}) = \frac{1}{\sqrt{2\pi Nc}^3} e^{-R^2/2Nc}. \tag{L41}$$

Central limit theorem

$$c = -\frac{\partial^2}{\partial k^2}|_{\vec{k}=0}\mathcal{P}_1(\vec{k}) = \int d\vec{R}\, R^2 \mathcal{P}_1(\vec{R}) \equiv a^2 \tag{L42}$$

$$\mathcal{R}_{\mathrm{I}}{}^2 \quad = \quad \int d\vec{R}\, R^2 \mathcal{P}_N(\vec{R}) = 3cN = 3a^2 N \tag{L43}$$

$$\Rightarrow \mathcal{R}_{\mathrm{I}} \quad = \quad a\sqrt{3N}. \tag{L44}$$

$$S = S_0 - \frac{3}{2}k_B \frac{R^2}{\mathcal{R}_{\mathrm{I}}{}^2} \tag{L45}$$

$$\mathcal{F} = \mathcal{F}_0 + \frac{3}{2} k_B T \frac{R^2}{\mathcal{R}_\mathrm{I}{}^2} = \mathcal{F}_0 + \frac{1}{2} k_B T \frac{R^2}{a^2 N}, \qquad \text{(L46)}$$

$$\vec{F} = 3 k_B T \frac{\vec{R}}{\mathcal{R}_\mathrm{I}{}^2} = \frac{k_B T}{a^2 N} \vec{R} \equiv \frac{\mathcal{K}}{N} \vec{R}. \qquad \text{(L47)}$$

Polymer behaves like an ideal spring

Spring constant that rises in proportion to temperature, falls in proportion to the molecular weight $\mathcal{R}_\mathrm{I}{}^2 \propto N$

$$M \sim \frac{\mathcal{R}^2}{a^2} \qquad \text{(L48)}$$

$$\mathcal{F} = \mathcal{F}_0 + k_B T (\frac{N}{M}) \frac{1}{2} \frac{\mathcal{R}^2}{a^2 M} = \mathcal{F}_0 + k_B T \frac{N}{2} \frac{a^2}{\mathcal{R}^2} = \mathcal{F}_0 + k_B T \frac{\mathcal{R}_\mathrm{I}^2}{6 \mathcal{R}^2}. \qquad \text{(L49)}$$

$$P = -\frac{\partial}{\partial \mathcal{R}^3} k_B T N \frac{a^2}{\mathcal{R}^2} \propto \frac{k_B T (N/M)}{\mathcal{R}^3}, \qquad \text{(L50)}$$

Pressure of an ideal gas of N/M particles in volume $\mathcal{R}^3$.

$$n = \frac{N}{\mathcal{R}^3} = \frac{\mathcal{R}_\mathrm{I}^2}{a^2\mathcal{R}^3}. \tag{L51}$$

$$\mathcal{F} \propto k_B T \mathcal{R}^3 [An + Bn^2 + Cn^3 + \ldots]. \tag{L52}$$

$$\mathcal{F} = \mathcal{F}_0 + k_B T \left[\frac{\mathcal{R}^2}{{\mathcal{R}_\mathrm{I}}^2} + \frac{\mathcal{R}_\mathrm{I}^2}{\mathcal{R}^2} + \mathcal{R}^3 \left[A\left(\frac{\mathcal{R}_\mathrm{I}^2}{a^2\mathcal{R}^3}\right) + B\left(\frac{\mathcal{R}_\mathrm{I}^2}{a^2\mathcal{R}^3}\right)^2 + C\left(\frac{\mathcal{R}_\mathrm{I}^2}{a^2\mathcal{R}^3}\right)^3 + \ldots\right]\right]. \tag{L53}$$

$$2\frac{\mathcal{R}}{\mathcal{R}_\mathrm{I}^2} - 2\frac{\mathcal{R}_\mathrm{I}^2}{\mathcal{R}^3} - 3B\frac{\mathcal{R}_\mathrm{I}^4}{a^4\mathcal{R}^4} - 6C\frac{\mathcal{R}_\mathrm{I}^6}{a^6\mathcal{R}^7} = 0. \tag{L54}$$

$$2\frac{\mathcal{R}}{\mathcal{R}_\mathrm{I}^2} - 3B\frac{\mathcal{R}_\mathrm{I}^4}{a^4\mathcal{R}^4} = 0 \tag{L55}$$

$$\Rightarrow \quad \mathcal{R}^5 \propto \frac{B\mathcal{R}_\mathrm{I}^6}{a^4} \Rightarrow \mathcal{R} \propto \mathcal{R}_\mathrm{I}^{6/5} \propto N^{3/5}. \tag{L56}$$

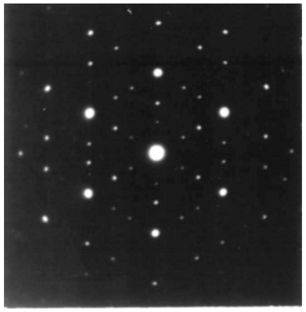
$$\frac{|B|\mathcal{R}_{\mathrm{I}}^4}{a^4\mathcal{R}^4} = 2C\frac{\mathcal{R}_{\mathrm{I}}^6}{a^6\mathcal{R}^7} \Rightarrow \mathcal{R}^3 \sim \frac{C\mathcal{R}_{\mathrm{I}}^2}{|B|a^2} \sim N \Rightarrow \mathcal{R} \sim N^{1/3}. \quad \text{(L57)}$$

Θ solvent

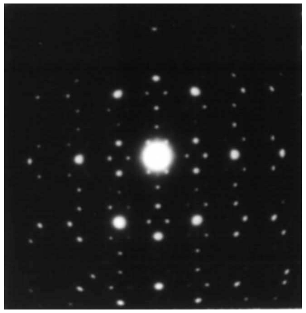
Quasicrystals

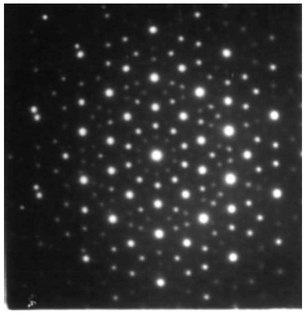
Five–fold symmetry is impossible... and yet

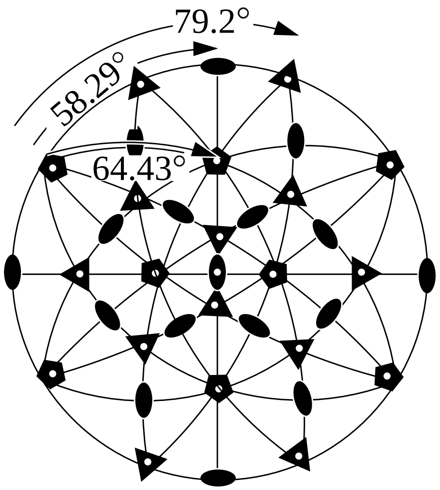
79.2°



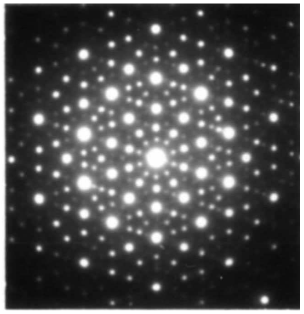
58.29°

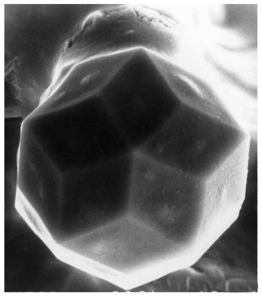






64.43°





Shechtman et al. (1984) Quasi-crystal site with several applets

$$x_n = n + (\tau - 1)\mathrm{int}(n/\tau). \quad \text{(L58)}$$

Golden Mean

$$\tau = 1 + \frac{1}{\tau} = \frac{\sqrt{5}+1}{2} = 1.618\ldots, \quad \text{(L59)}$$

Deflation rule:

Replace τ with sequence $\tau, 1,$

Replaces every 1 with a τ

$$\tau 1 \tau \tau 1 \ldots . \quad \text{(L60)}$$

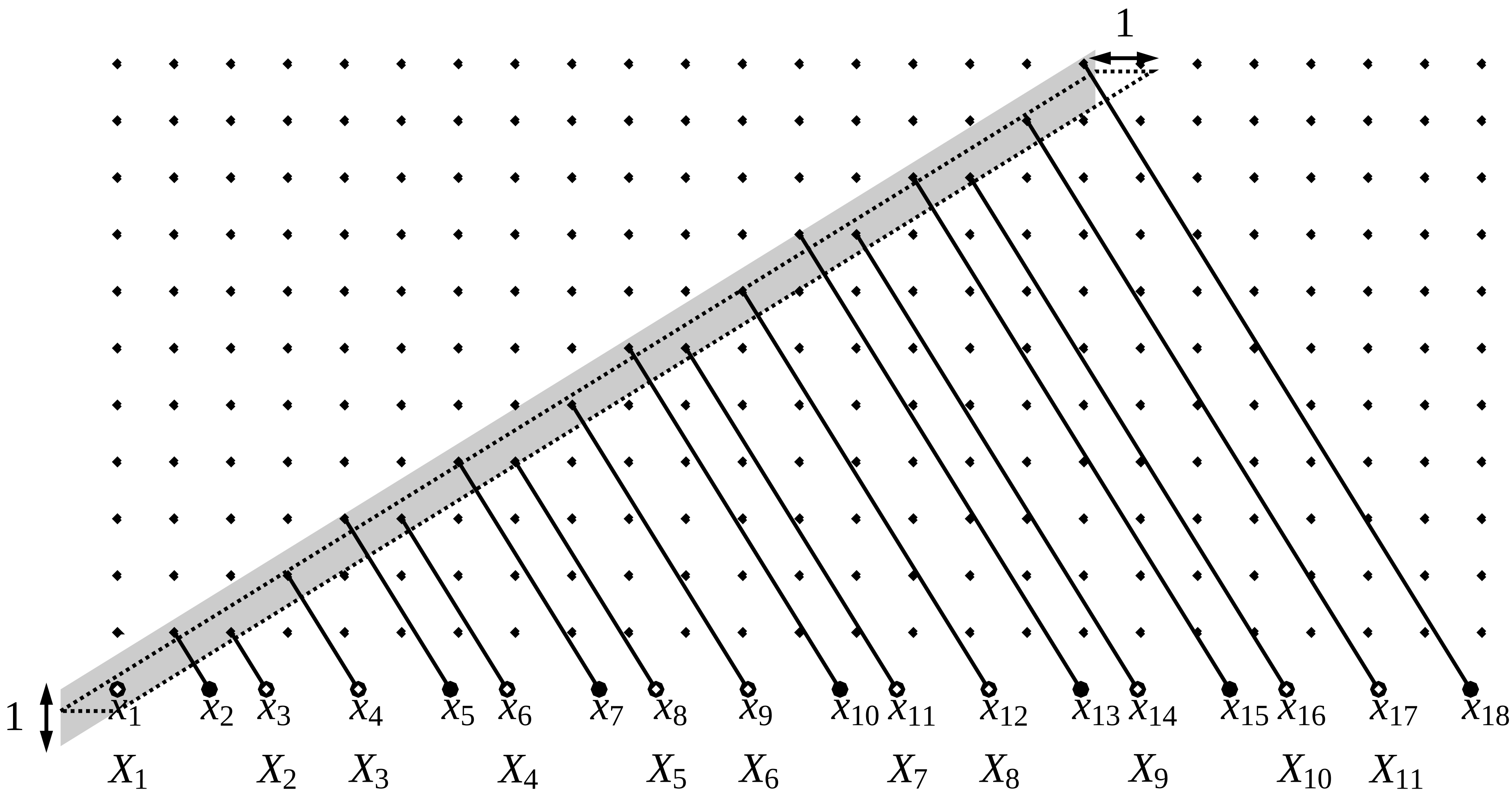
$$\tau 1 \tau \tau 1 \tau 1 \tau \ldots . \quad \text{(L61)}$$

$$X_{n+1} = X_n X_{n-1}, \quad \text{(L62)}$$

One-Dimensional Quasicrystal

$$X_{-1} = \tau; X_0 = \tau 1; X_1 = \tau 1 \tau; X_2 = \tau 1 \tau \tau 1 \ldots \tag{L63}$$

$$X_3 = X_2 X_1 = \tau 1 \tau \tau 1 \tau 1 \tau. \tag{L64}$$



One-Dimensional Quasicrystal

$$x_m = m + \sum_n n\theta(n - m/\tau + 1)\theta(m/\tau - n)/\tau \tag{L65}$$

$$x/\tau > y > x/\tau - 1. \tag{L66}$$

$$[m, \sum_n n\theta(m/\tau - n)\theta(n - [m/\tau - 1])]. \tag{L67}$$

$$(x+1)/\tau - 1 > y > x/\tau - 1. \tag{L68}$$

$$[\sum_m m\theta((m+1)/\tau - 1 - n)\theta(n - [m/\tau - 1]), n]. \tag{L69}$$

$$X_{n+1} = \sum_m m\theta((m+1)/\tau - n - 1)\theta(n - m/\tau + 1) + n/\tau. \tag{L70}$$

X_n hollow circles. , $X_m = -1/\tau + \tau x_m$.

Scattering from a One-Dimensional Quasicrystal

$$\Sigma_q = \sum_n e^{iqx_n} \tag{L71}$$

$$= \sum_{n,m} e^{iq(m+n/\tau)}\theta(n-m/\tau+1)\theta(m/\tau-n) \tag{L72}$$

$$= \int dxdy\, e^{i\vec{q}\cdot(x,y)}\left[\sum_{m,n}\delta(x-m)\delta(y-n)\right]\theta(y-x/\tau+1)\theta(x/\tau-y) \tag{L73}$$

$$\text{where } \vec{q} = (q, q/\tau). \tag{L74}$$

First piece

$$A(\vec{q}) = \int dxdy \sum_{m,n}\delta(x-m)\delta(y-n)e^{iq_x x}e^{iq_y y} \tag{L75}$$

$$= N\frac{(2\pi)^2}{\mathcal{V}}\sum_{n',m'}\delta(q_x-2\pi n')\delta(q_y-2\pi m'). \tag{L76}$$

Second piece

$$B(\vec{q}) = \int dx \int_{x/\tau-1}^{x/\tau} dy\, e^{iq_x x + iq_y y} = \int dx\, e^{iq_x x} \left[\frac{e^{iq_y(x/\tau)} - e^{iq_y(x/\tau-1)}}{iq_y} \right]. \tag{L77}$$

$$\Sigma_q \propto$$

$$\int dx dq'_x dq'_y \sum_{n',m'} \left\{ \begin{array}{c} \delta(q - q'_x - 2\pi n') \\ \times \delta(q/\tau - q'_y - 2\pi m') \end{array} \right\} \left[\frac{e^{iq'_y(x/\tau)} - e^{iq'_y(x/\tau-1)}}{iq'_y} \right] e^{iq'_x x} \tag{L78}$$

$$= \int dx \sum_{n',m'} \left[\frac{e^{i(q/\tau-2\pi m')(x/\tau)} - e^{i(q/\tau-2\pi m')(x/\tau-1)}}{iq/\tau - 2\pi i m'} \right] e^{i(q-2\pi n')x} \tag{L79}$$

$$= 2\pi \sum_{n',m'} \frac{1 - e^{-i(q/\tau-2\pi m')}}{iq/\tau - 2\pi i m'} \delta([2\pi m' - \frac{q}{\tau}]/\tau + 2\pi n' - q). \tag{L80}$$

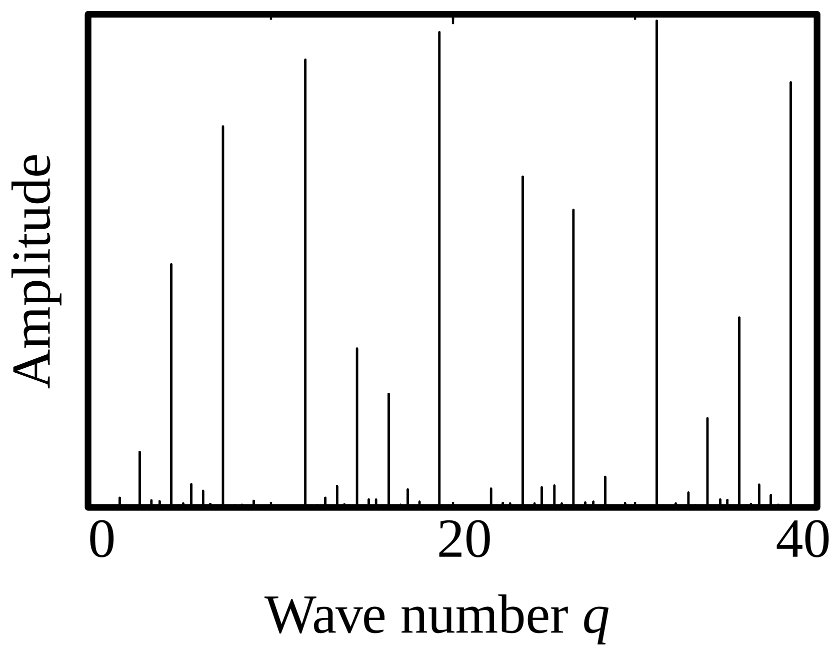
The peaks of (80) are at

$$\frac{2\pi(m'/\tau + n')}{\tau^{-2} + 1} = q \tag{L81}$$

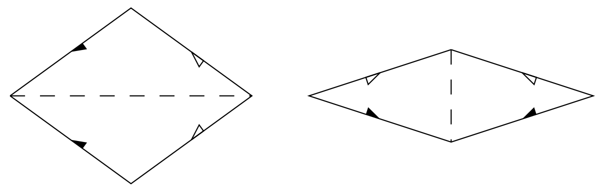
Scattering from a One-Dimensional Quasicrystal

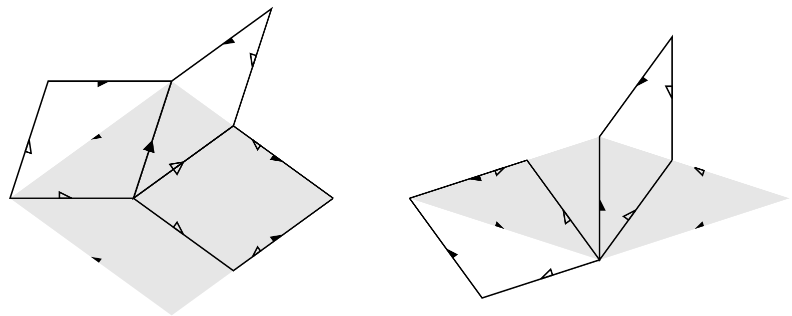
Square amplitude is proportional to

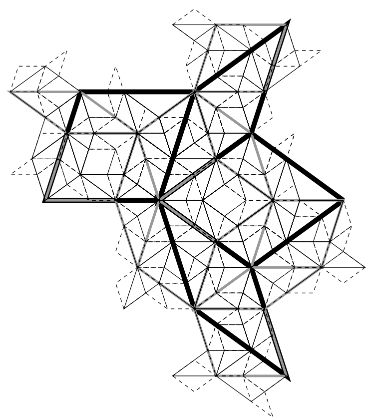
$$\sin^2\left(\pi\left[\frac{m'\tau - n'}{\tau+\tau^{-1}}\right]\right)/\left(q/\tau - 2\pi m'\right)^2. \tag{L82}$$

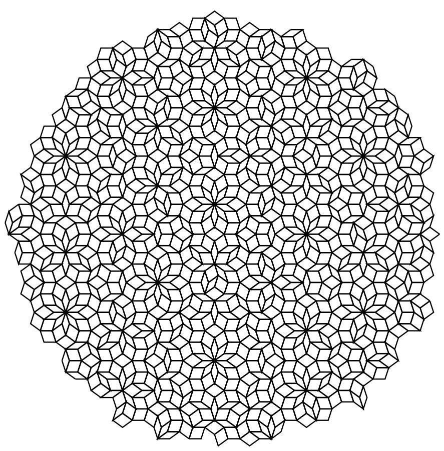


Penrose, Gardner



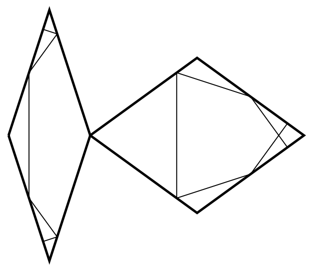




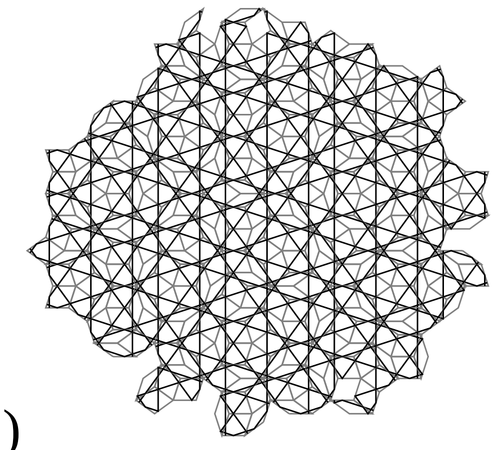


Amman lines

(A)

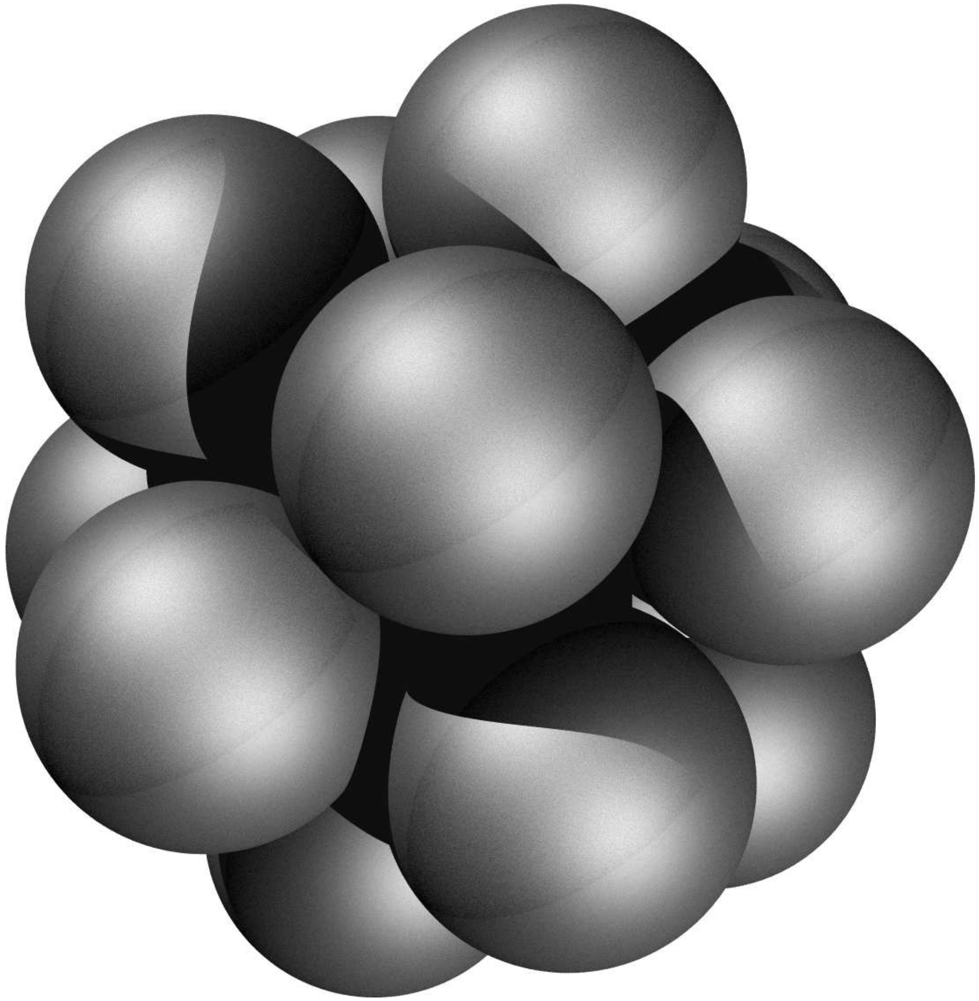


(B)



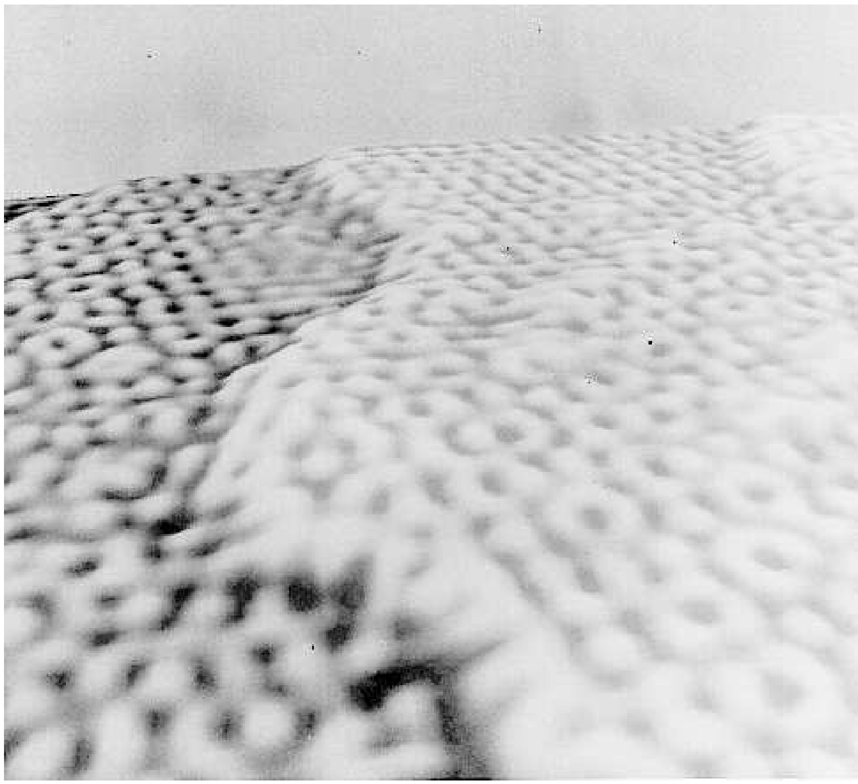
$$\vec{r} \cdot \hat{e}_\alpha = x_{n_\alpha}, \; \vec{r} \cdot \hat{e}_\beta = x_{n_\beta}, \tag{L83}$$

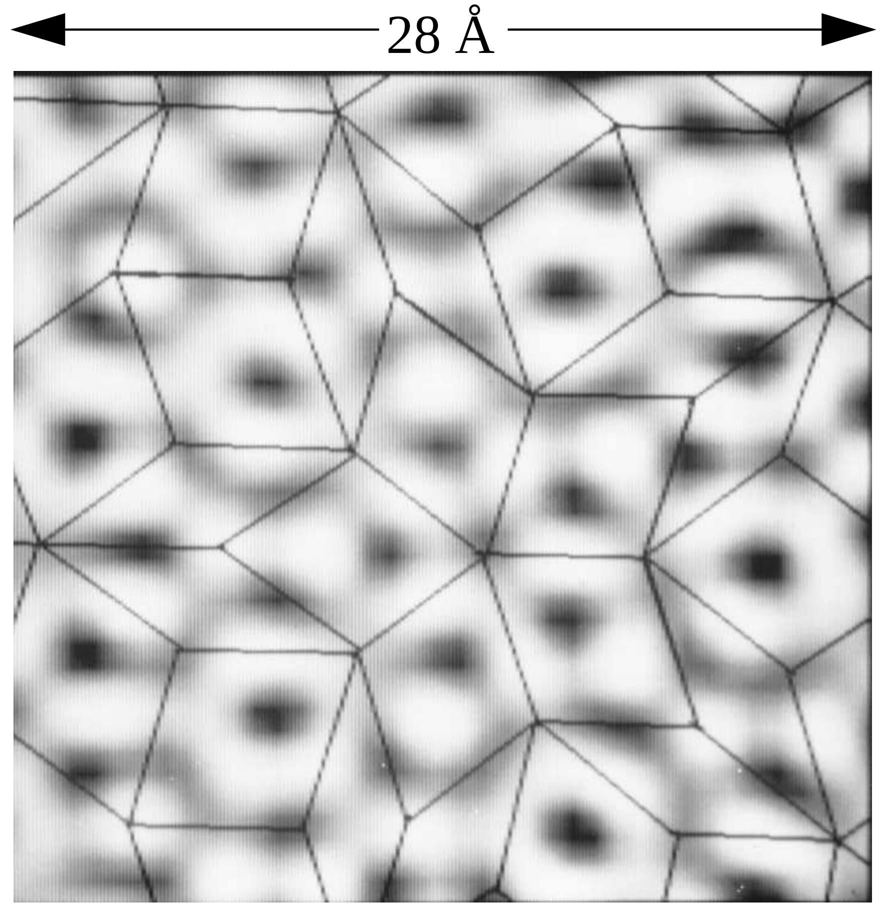
Physical reasons for quasicrystals



Al_6Li_3Cu is real equilibrium quasicrystal

Physical reasons for quasicrystals

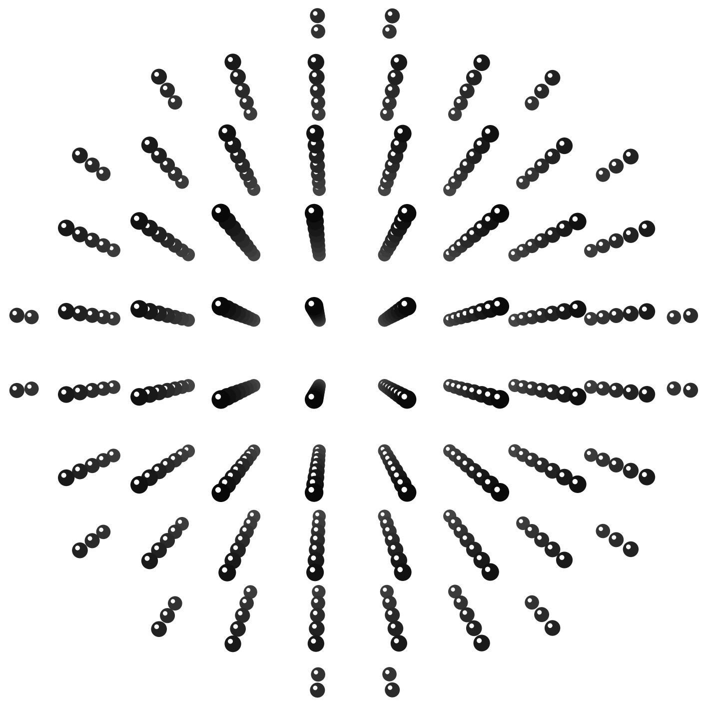
(A) 

(B) 

Kortan (1996)

David Tomanek's Nanotube Site

The Single-Electron Model



$$\hat{\mathcal{H}} = \sum_l \frac{\hat{P}_l^2}{2M_l} + \frac{1}{2} \sum_{l \neq l'} \frac{q_l q_{l'}}{|\hat{R}_l - \hat{R}_{l'}|}. \tag{L1}$$

Approximations

$$\hat{\mathcal{H}} = \sum_l \frac{\hat{P}_l^2}{2M_l} + \frac{1}{2}\sum_{l \neq l'} \frac{q_l q_{l'}}{|\hat{R}_l - \hat{R}_{l'}|}$$

Nuclei treated as classical potentials. Many electrons combined with nuclei in closed shells to form ions.

All electronic degrees of freedom eliminated, turned to effective potential for ions. Phonon dynamics.

Ions treated as static potential. **Born-Oppenheimer approximation**.

Ions treated classically. Studies of cohesive energy, molecular dynamics.

Coulomb interaction incorporated self-consistently into lattice potential. **Single electron approximation**, partially justified by Fermi liquid theory

Ionic potential eliminated, interacting electrons move in uniform positive potential. **Jellium,** starting point for field theoretic work.

Ions arranged in a lattice, forming periodic potential for single electrons. Starting point for first-principles' calculations. Weak ionic potentials justified by **pseudopotentials.**

Ionic potential eliminated. **Free Fermi gas**, surprisingly effective with alkali metals.

Approximations

Main physical idea is the Pauli principle, which has two consequences:

1. It populates solids with electrons whose energies would classically signify temperatures on the order of 10,000 K.

2. It prevents all electrons but those whose energy differs slightly from the highest occupied state from participating in transport processes

Important terms:

- ☞ Occupation number
- ☞ Fermi energy
- ☞ Fermi surface
- ☞ Density of states
- ☞ Sommerfeld expansion
- ☞ Effective mass

The Basic Hamiltonian

$$\hat{\mathcal{H}}\Psi = \sum_{l=1}^{N}(\frac{-\hbar^2\nabla_l^2}{2m} + U(\vec{r}_l))\Psi(\vec{r}_1 \ldots \vec{r}_N) = \mathcal{E}\Psi(\vec{r}_r \ldots \vec{r}_N). \tag{L2}$$

Single electron problem:

$$\left(\frac{-\hbar^2\nabla^2}{2m} + U(\vec{r})\right)\psi_l(\vec{r}) = \mathcal{E}_l\psi_l(\vec{r}), \tag{L3}$$

Free electron gas

$$\frac{-\hbar^2}{2m}\sum_{l=1}^{N}\nabla_l^2\Psi(\vec{r}_1 \ldots \vec{r}_N) = \mathcal{E}\Psi(\vec{r}_1 \ldots \vec{r}_N), \tag{L4}$$

Periodic Boundary Conditions

$$\begin{aligned} \Psi(x_1+L, y_1, z_1 \ldots, z_N) &= \Psi(x_1, y_1, z_1 \ldots z_N) \\ \Psi(x_1, y_1+L, z_1 \ldots, z_N) &= \Psi(x_1, y_1, z_1 \ldots z_N). \\ &. \\ &. \\ &. \end{aligned} \tag{L5}$$

$$\psi_{\vec{k}} = \frac{1}{\sqrt{\mathcal{V}}} e^{i\vec{k}\cdot\vec{r}} \tag{L6}$$

with $\vec{k}$ of the form

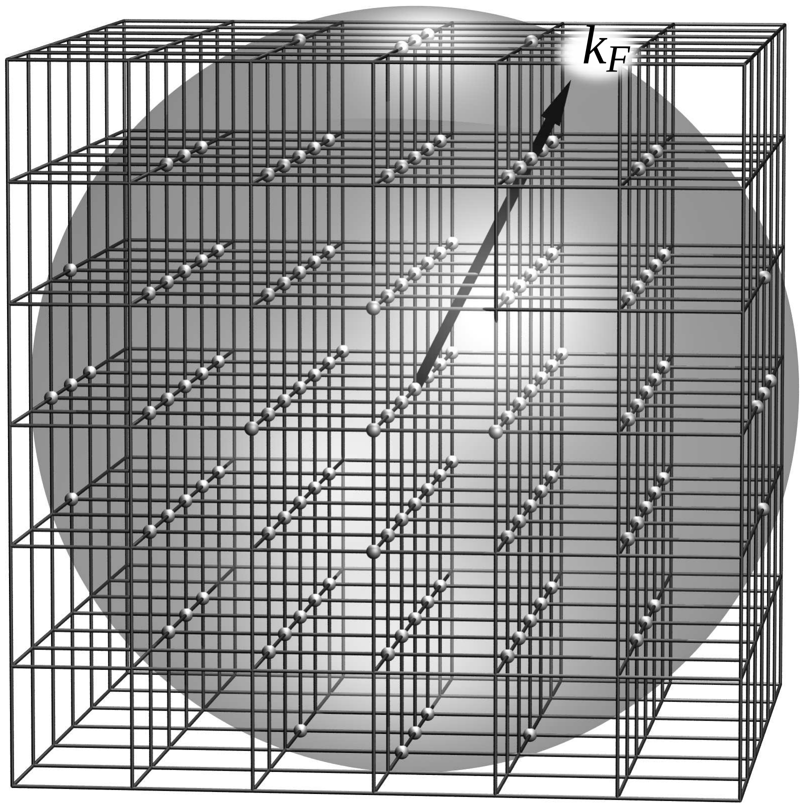
$$\vec{k} = \frac{2\pi}{L}(l_x, l_y, l_z)\,. \tag{L7}$$

The eigenvalue corresponding to the eigenfunction (6) is

$$\mathcal{E}^0_{\vec{k}} = \frac{\hbar^2 k^2}{2m} \tag{L8}$$

Occupation number $f_{\vec{k}}$ of a state indexed by $\vec{k}$ is 1 if this one-electron state is part of the ground state, and 0 otherwise.

Densities of States



$\vec{k}$ states described by Eq. (L7) occupy a cubic lattice in $\vec{k}$ or reciprocal space, with neighboring points separated by distances of $2\pi/L$,

k space volume per state is $(2\pi/L)^3$.

$$\sum_{\vec{k}} F_{\vec{k}}, \tag{L9}$$

$$\int d\vec{k} F_{\vec{k}} = \sum_{\vec{k}} (\frac{2\pi}{L})^3 F_{\vec{k}} \tag{L10}$$

$$\Rightarrow \sum_{\vec{k}} F_{\vec{k}} = \frac{\mathcal{V}}{(2\pi)^3} \int d\vec{k} F_{\vec{k}}. \tag{L11}$$

corresponds to

$$\delta_{\vec{k}\vec{q}} \rightarrow \frac{(2\pi)^3}{\mathcal{V}} \delta(\vec{k} - \vec{q}). \tag{L12}$$

Definition of Density of States D

Density of electronic states or density of levels

$$D_{\vec{k}} = 2\frac{1}{(2\pi)^3}, \tag{L13}$$

defined so that

$$\sum_{\vec{k}\sigma} F_{\vec{k}} = \mathcal{V}\int d\vec{k}\, D_{\vec{k}} F_{\vec{k}}. \tag{L14}$$

To avoid perpetually writing $D_{\vec{k}}$, adopt the notation

$$\int [d\vec{k}] \equiv \frac{2}{\mathcal{V}}\sum_{\vec{k}} = \int d\vec{k}\, D_{\vec{k}} = \frac{2}{(2\pi)^3}\int d\vec{k} \tag{L15}$$

Energy Density of States

From here onwards, red question marks bracket areas deliberately left blank so that students can fill them in!

$$\sum_{\vec{k}\sigma} F(\mathcal{E}_{\vec{k}}) = \mathcal{V} \int d\mathcal{E}\, D(\mathcal{E}) F(\mathcal{E}) \qquad . \qquad \text{(L16)}$$

To find $D(\mathcal{E})$, note that

$$\sum_{\vec{k}\sigma} F(\mathcal{E}_{\vec{k}}) \quad = \quad ?$$

$$? \Rightarrow D(\mathcal{E}) = \int [d\vec{k}]\, \delta(\mathcal{E} - \mathcal{E}_{\vec{k}}) \qquad . \qquad \text{(L19)}$$

Results for Free Electrons

$$D(\mathcal{E}) = \int [d\vec{k}]\,\delta(\mathcal{E} - \mathcal{E}^0_{\vec{k}}) \quad \text{(L20)}$$

$$= \;?$$

$$? = \frac{m}{\hbar^3\pi^2}\sqrt{2m\mathcal{E}} \quad \text{(L23)}$$

$$= 6.812 \cdot 10^{21}\,\sqrt{\mathcal{E}/\text{eV}}\ \text{eV}^{-1}\ \text{cm}^{-3}. \quad \text{(L24)}$$

Electrons in sphere of radius k_F is

$$N = \sum_{\vec{k}\sigma} f_{\vec{k}} \tag{L25}$$

$$= ?$$

$$? \frac{\mathcal{V} k_F^3}{3\pi^2}, \tag{L28}$$

$$k_F = (3\pi^2 n)^{1/3} = 3.09\,[n \cdot \mathring{A}^3]^{1/3} \mathring{A}^{-1}. \tag{L29}$$

Results for Free Electrons

radius parameter r_s

$$\frac{4\pi}{3} r_s^3 \equiv \frac{\mathcal{V}}{N} \Rightarrow r_s = \left[\frac{3}{4\pi}\frac{\mathcal{V}}{N}\right]^{1/3}. \tag{L30}$$

Fermi energy, $\mathcal{E}_F$, or Fermi level

$$\mathcal{E}_F = \frac{\hbar^2 k_F^2}{2m} = 36.46\,[n \cdot \text{Å}^3]^{2/3}\text{eV}. \tag{L31}$$

Fermi surface, electrons with energy $\mathcal{E}_F$.

$$v_F = \hbar k_F/m = 3.58\,[n \cdot \text{Å}^3]^{1/3} \cdot 10^8\,\text{cm s}^{-1}. \tag{L32}$$

$$D(\mathcal{E}_F) \quad = \quad \frac{3}{2}\frac{n}{\mathcal{E}_F} = 4.11 \cdot 10^{-2}\,[n \cdot \text{Å}^3]\ \text{eV}^{-1}\ \text{Å}^{-3}. \tag{L33}$$

One dimension:

$$D_{\vec{k}} = 2(\frac{1}{2\pi})^d. \quad \text{(L34)}$$

$$D(\mathcal{E}) = ? \qquad ? \quad \text{(L35)}$$

Two dimensions:

$$D(\mathcal{E}) = ? \qquad ? \quad \text{(L36)}$$

$$Z_{\rm gr} = \sum_{\rm states} e^{\beta(\mu N - \mathcal{E})} \tag{L37}$$

$$= \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \sum_{n_3=0}^{1} \ldots ? \qquad ? \tag{L38}$$

Using the mathematical fact that

$$\sum_{n_1=0}^{N} \qquad \sum_{n_2=0}^{N} \cdots \sum_{n_M=0}^{N} \prod_{l=1}^{M} A_{n_l} = ? \qquad ? \tag{L39}$$

one has that

$$Z_{\rm gr} = ?$$

$$? \tag{L41}$$

Therefore the grand potential is given by

$$\Pi \equiv -k_B T \ln Z_{\text{gr}} \tag{L42}$$

$$= -k_B T \sum_l \ln\left[1 + e^{\beta[\mu - \mathcal{E}_l]}\right]. \tag{L43}$$

$$= -k_B T \mathcal{V} \int d\mathcal{E}\, ? \qquad ? \tag{L44}$$

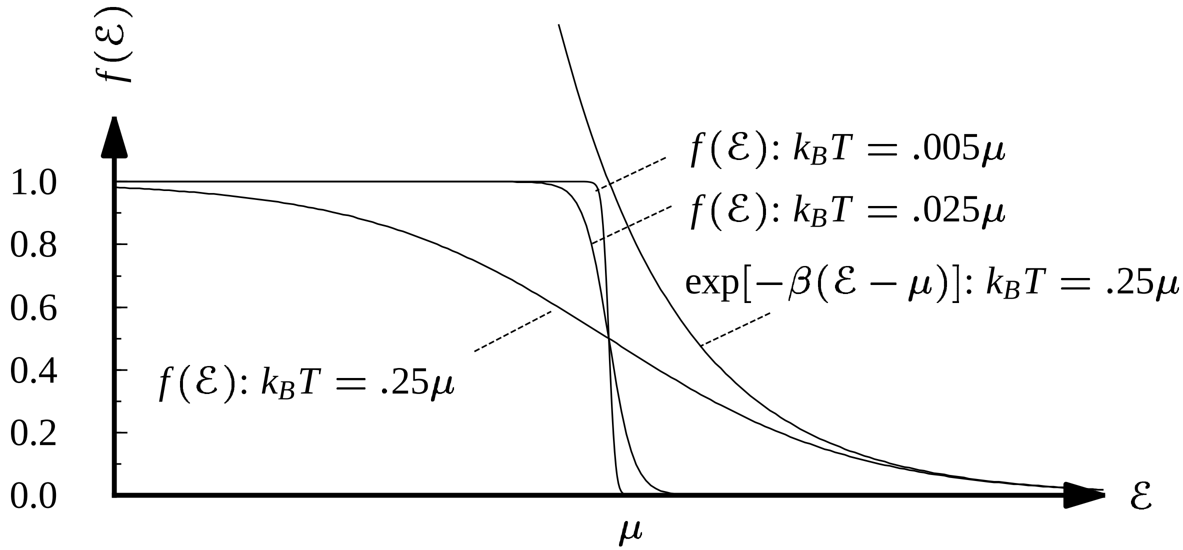
Fermi Function

$$N = ?$$

$$? \Rightarrow n = ? \qquad ? \qquad \text{(L47)}$$

where...

Fermi Function



$$f(\mathcal{E}) = ? \qquad ? \tag{L48}$$

$$f_{\vec{k}} = ? \qquad ? \tag{L49}$$

$$\frac{\partial \beta \Pi}{\partial \beta}\Big|_{\mu} = \mathcal{E} - \mu N = \mathcal{V} \int d\mathcal{E}' \, D(\mathcal{E}') \, (\mathcal{E}' - \mu) \, f(\mathcal{E}') \tag{L50}$$

$$\Rightarrow \frac{\mathcal{E}}{\mathcal{V}} = \int d\mathcal{E}' \, D(\mathcal{E}') \, \mathcal{E}' \, f(\mathcal{E}'). \tag{L51}$$

Classical Limit

Boltzmann statistics

$$f(\mathcal{E}) = Ce^{-\beta\mathcal{E}}. \tag{L52}$$

when

$$f(\mathcal{E}) \ll 1 \Rightarrow e^{\beta(\mathcal{E}-\mu)} \gg 1. \tag{L53}$$

At low temperatures

$$f(\mathcal{E}) \rightarrow ? \qquad\qquad ? \tag{L54}$$

Fermi temperature:

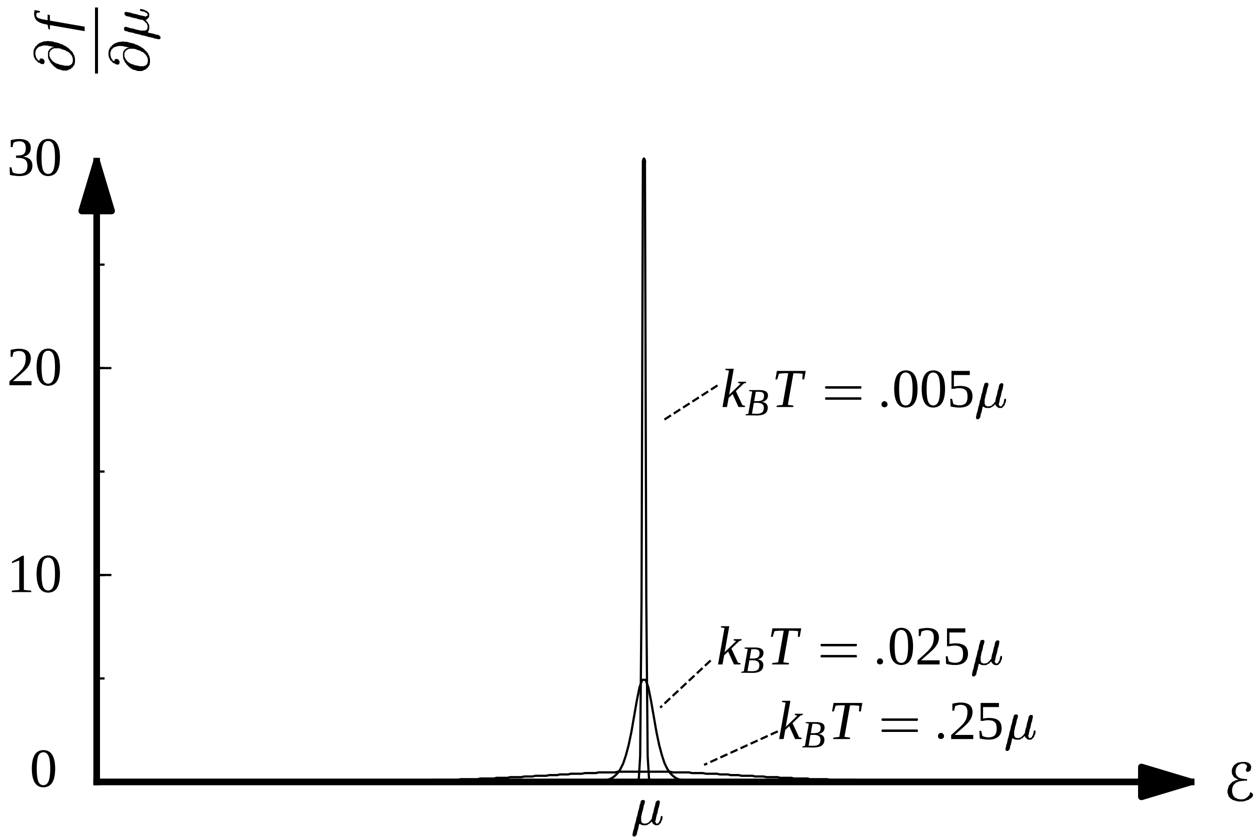
$$T_F = \mathcal{E}_F / k_B, \tag{L55}$$

Elements as free electron gases

Element	Z	n $(10^{22}\,\text{cm}^{-3})$	k_F $(10^{8}\,\text{cm}^{-1})$	$\mathcal{E}_F$ (eV)	T_F $(10^{4}\,\text{K})$	v_F $(10^{8}\,\text{cm}\,\text{s}^{-1})$	r_s/a_0
Li	1	4.60	1.11	4.68	5.43	1.28	3.27
Ag	1	5.86	1.20	5.50	6.38	1.39	3.02
Be	2	24.72	1.94	14.36	16.67	2.25	1.87
Al	3	18.07	1.75	11.66	13.53	2.02	2.07
Sn	4	14.83	1.64	10.22	11.86	1.89	2.22
Sb	5	16.54	1.70	10.99	12.75	1.97	2.14
Mn	4	32.61	2.13	17.28	20.05	2.46	1.70
Fe	2	16.90	1.71	11.15	12.94	1.98	2.12
Co	2	18.18	1.75	11.70	13.58	2.03	2.07
Ni	2	18.26	1.76	11.74	13.62	2.03	2.07

Paradox that density of states too small solved by

$$c_V \propto T D(\mathcal{E}_F), \tag{L56}$$



Sommerfeld Expansion

$$\langle H \rangle = \int_{-\infty}^{\infty} d\mathcal{E}\, H(\mathcal{E}) f(\mathcal{E}). \tag{L57}$$

$$\langle H \rangle = \int_{-\infty}^{\mu} d\mathcal{E}\, H(\mathcal{E}) + \sum_{n=1}^{\infty} ?$$

$$? \Rightarrow \langle H \rangle = \int_{-\infty}^{\mu} d\mathcal{E}\, H(\mathcal{E}) + \frac{\pi^2}{6}[k_B T]^2 H'(\mu) + \frac{7\pi^4}{360}[k_B T]^4 H'''(\mu) + \ldots. \tag{L62}$$

$$c_{\mathcal{V}} = \frac{1}{\mathcal{V}} \frac{\partial \mathcal{E}}{\partial T} |_{N\mathcal{V}} . \tag{L63}$$

$$\frac{\mathcal{E}}{\mathcal{V}} \quad = \quad ?$$

$$? \tag{L65}$$

$$\frac{\partial \mu}{\partial T} |_{N\mathcal{V}} = -\frac{\frac{\partial N}{\partial T} |_{\mu\mathcal{V}}}{\frac{\partial N}{\partial \mu} |_{T\mathcal{V}}} . \tag{L66}$$

$$N = \mathcal{V} \int d\mathcal{E}' ? \qquad ? \tag{L67}$$

$$\frac{\partial \mu}{\partial T} |_{N\mathcal{V}} = ? \qquad ? \tag{L68}$$

Specialize to Free Fermi Gas

$$\mu = ? \qquad\qquad ? \tag{L69}$$

To order T^2

$$\begin{aligned}\frac{\mathcal{E}}{\mathcal{V}} &= \int_0^{\mathcal{E}_F} d\mathcal{E}'\, \mathcal{E}' D(\mathcal{E}') + \frac{\pi^2}{6}(k_B T)^2 D(\mathcal{E}_F) \\ &\quad + \mathcal{E}_F \left\{ (\mu - \mathcal{E}_F) D(\mathcal{E}_F) + \frac{\pi^2}{6}(k_B T)^2 D'(\mathcal{E}_F) \right\}\end{aligned} \tag{L70}$$

$$\Rightarrow \frac{\mathcal{E}}{\mathcal{V}} = \int_0^{\mathcal{E}_F} d\mathcal{E}\, \mathcal{E} D(\mathcal{E}) + \frac{\pi^2}{6}(k_B T)^2 D(\mathcal{E}_F) \tag{L71}$$

$$\Rightarrow c_{\mathcal{V}} = \frac{\pi^2}{3} k_B^2 T D(\mathcal{E}_F). \tag{L72}$$

As predicted, $c_{\mathcal{V}} \propto D(\mathcal{E}_F) T$.

Linear coeffi cient, Sommerfeld parameter

$\gamma \equiv c_{\mathcal{V}} / T$

Specialize to Free Fermi Gas

$$\gamma \equiv \frac{c_{\mathcal{V}}}{T} = ? \qquad\qquad ? \tag{L73}$$

Specifi c heat effective mass of the electron.

Specialize to Free Fermi Gas

Metal	Z	γ (mJ mole^{-1} K^{-2}) Expt.	Eq. (L73)	Metal	Z	γ (mJ mole^{-1} K^{-2}) Expt.	Eq. (L73)
Li	1	1.65	0.74	Al	3	1.35	0.91
Na	1	1.38	1.09	Ga	3	0.60	1.02
K	1	2.08	1.67	In	3	1.66	1.23
Rb	1	2.63	1.90	Sn	4	1.78	1.41
Cs	1	3.97	2.22	Pb	4	2.99	1.50
Cu	1	0.69	0.50	Sb	5	0.12	1.61
Ag	1	0.64	0.64	Bi	5	0.008	1.79
Au	1	0.69	0.64	Mn	2	12.8	1.10
Be	2	0.17	0.5	Fe	2	4.90	1.06
Mg	2	1.6	0.99	UPt_3		450	
Ca	2	2.73	1.51	UBe_{13}		1100	
Sr	2	3.64	1.79				
Ba	2	2.7	1.92				
Zn	2	0.64	0.75				
Cd	2	0.69	0.95				

Stewart (1983), and Stewart (1984).

Heavy Fermions

$$m\dot{\vec{v}} = -e\vec{E} - m\frac{\vec{v}}{\tau}, \tag{L1}$$

τ is the relaxation time.

$$\vec{v}(t) = \vec{v}_0 e^{-t/\tau}. \tag{L2}$$

Steady state, times much longer than τ:

$$\vec{v} = ? \qquad ? \tag{L3}$$

Current therefore is

$$\vec{j} = ? \qquad ? \tag{L4}$$

$$\Rightarrow \sigma = ? \qquad ?, \tag{L5}$$

σ is the electrical conductivity

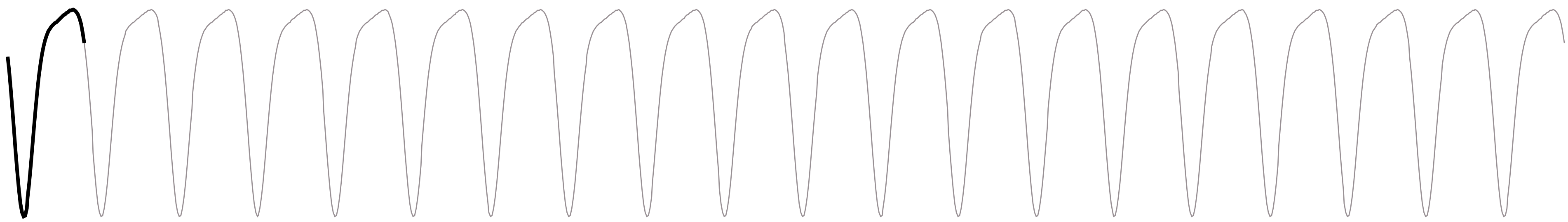
Problem of conductivity: Drude model

$$\tau = ? \qquad ? = \frac{3.55 \cdot 10^{-13}\,\mathrm{s}}{n/[10^{22}\,\mathrm{cm}^{-3}]\ \rho/[\mu\Omega\,\mathrm{cm}]} \tag{L6}$$

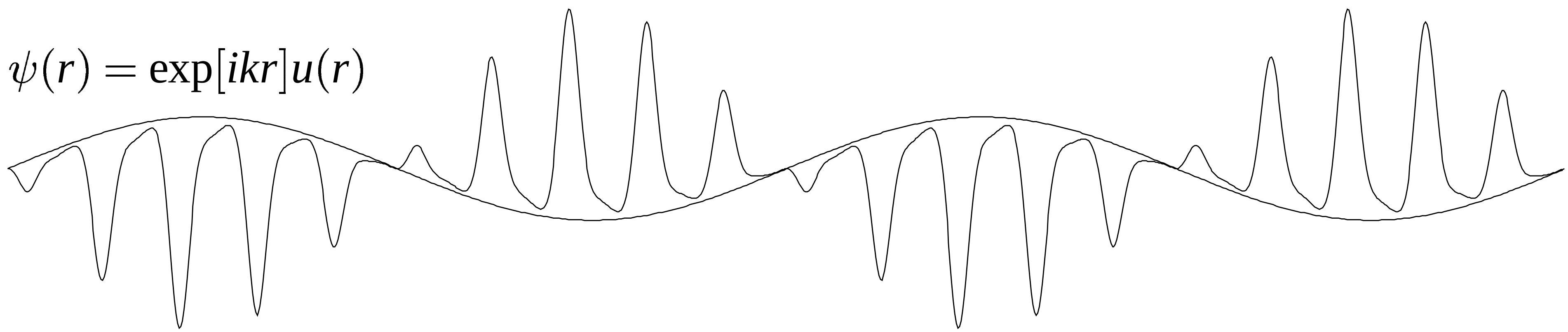
Exercise:

1. Estimate typical value of τ.
2. How does this compare with rate at which classical thermal electrons scatter off nuclei?
3. How does this compare with rate at which electrons at Fermi velocity scatter off nuclei?
4. What happens if one starts over and takes the relaxation time proportional to the electron velocity?

Periodic function $u(r)$



$\psi(r) = \exp[ikr]u(r)$



Single particle in periodic potential U:

$$U(\vec{r}+\vec{R}) = U(\vec{r}). \tag{L7}$$

Solve

Bloch's solution

$$\hat{\mathcal{H}} = \frac{\hat{P}^2}{2m} + U(\hat{R}). \tag{L8}$$

WRONG:

$$\psi(\vec{r} + \vec{R}) = \psi(\vec{r}). \tag{L9}$$

Can see this is wrong from case $U = 0$

$$\psi_{\vec{k}}(\vec{r}) \propto e^{i\vec{k}\cdot\vec{r}}. \tag{L10}$$

Translation operators

Let $\hat{T}_{\vec{R}}$ translate wave function by $\vec{R}$

$$\hat{T}_{\vec{R}} = e^{-i\hat{P}\cdot\vec{R}/\hbar}, \tag{L11}$$

Theorem: if one has a collection of Hermitian operators that commute with one another, they can be diagonalized simultaneously

Suppose $\mathcal{O}_2$ has unique eigenvector $|a\rangle$ with eigenvalue a.

$$\mathcal{O}_1\mathcal{O}_2|a\rangle = a\mathcal{O}_1|a\rangle = \mathcal{O}_2\mathcal{O}_1|a\rangle \tag{L12}$$

so $\mathcal{O}_1|a\rangle$ is eigenvector of $\mathcal{O}_2$; by uniqueness, must be some constant times $|a\rangle$.

In case of degenerate eigenvalues, one operator may categorize further states of other; parity.

Use theorem:

$$\hat{T}^{\dagger}_{\vec{R}}|\psi\rangle = e^{i\hat{P}\cdot\vec{R}/\hbar}|\psi\rangle = C_{\vec{R}}|\psi\rangle. \tag{L13}$$

$$\psi(\vec{r}+\vec{R}) = C_{\vec{R}}\psi(\vec{r}). \tag{L14}$$

Translation operators

$$e^{i\vec{k}\cdot\vec{R}}\langle\vec{k}|\psi\rangle = C_{\vec{R}}\langle\vec{k}|\psi\rangle \tag{L15}$$

$$\Rightarrow \text{ either } C_{\vec{R}} = e^{i\vec{k}\cdot\vec{R}} \text{ or } \langle\vec{k}|\psi\rangle = 0. \tag{L16}$$

☞ $\vec{k}$: Bloch wave vector

☞ $\hbar\vec{k}$: Crystal momentum

$$\hat{\mathcal{H}}|\psi_{n\vec{k}}\rangle = \mathcal{E}_{n\vec{k}}|\psi_{n\vec{k}}\rangle \quad \text{(L17a)}$$

$$\hat{T}^{\dagger}_{\vec{R}}|\psi_{n\vec{k}}\rangle = e^{i\vec{k}\cdot\vec{R}}|\psi_{n\vec{k}}\rangle. \quad \text{(L17b)}$$

Restate as

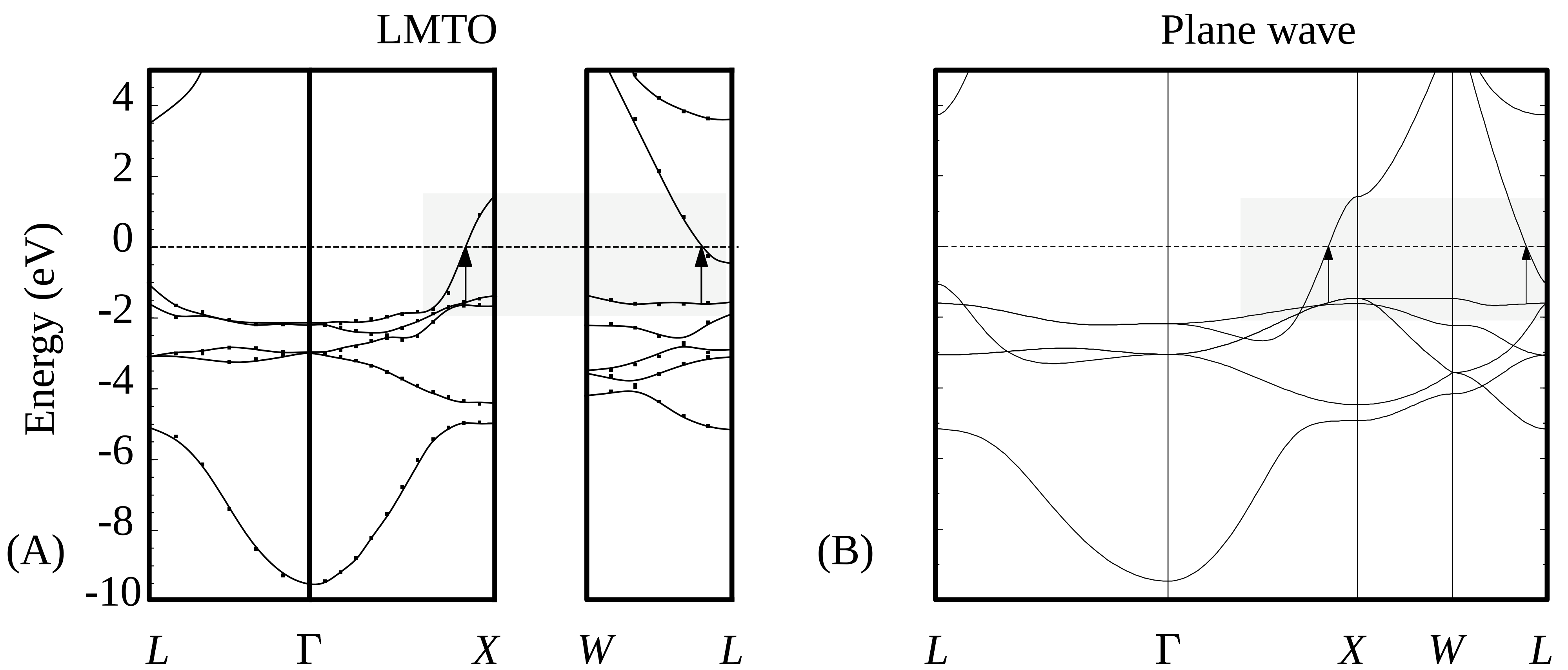
$$\psi_{n\vec{k}}(\vec{r}+\vec{R}) = e^{i\vec{k}\cdot\vec{R}}\psi_{n\vec{k}}(\vec{r}). \quad \text{(L18)}$$

or

$$u_{n\vec{k}}(\vec{r}) = e^{-i\vec{k}\cdot\vec{r}}\psi_{n\vec{k}}(\vec{r}). \quad \text{(L19)}$$

$$u(\vec{r}+\vec{R}) = ? \qquad ? \text{ and } \psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n\vec{k}}(\vec{r}). \quad \text{(L20)}$$

Energy Bands



$$\hat{\mathcal{H}}_{\vec{k}} u(\vec{r}) = \frac{\hbar^2}{2m}[-\nabla^2 - 2i\vec{k}\cdot\vec{\nabla} + k^2]u(\vec{r}) + U(\vec{r})u(\vec{r}) = \mathcal{E}u(\vec{r}). \quad \text{(L21)}$$

Allowed values of $\vec{k}$

If crystal is periodic with (macroscopic) dimensions $M_1\vec{a}_1, M_2\vec{a}_2, M_3\vec{a}_3$

then requiring $\exp[i\vec{k}\cdot\vec{r}]$ to be periodic constrains $\vec{k}$ to

$$\vec{k} = \sum_{l=1}^{3} \frac{m_l}{M_l}\vec{b}_l,\ 0 \le m_l < M_l, \qquad \text{(L22)}$$

$\vec{b}_1 \dots \vec{b}_3$

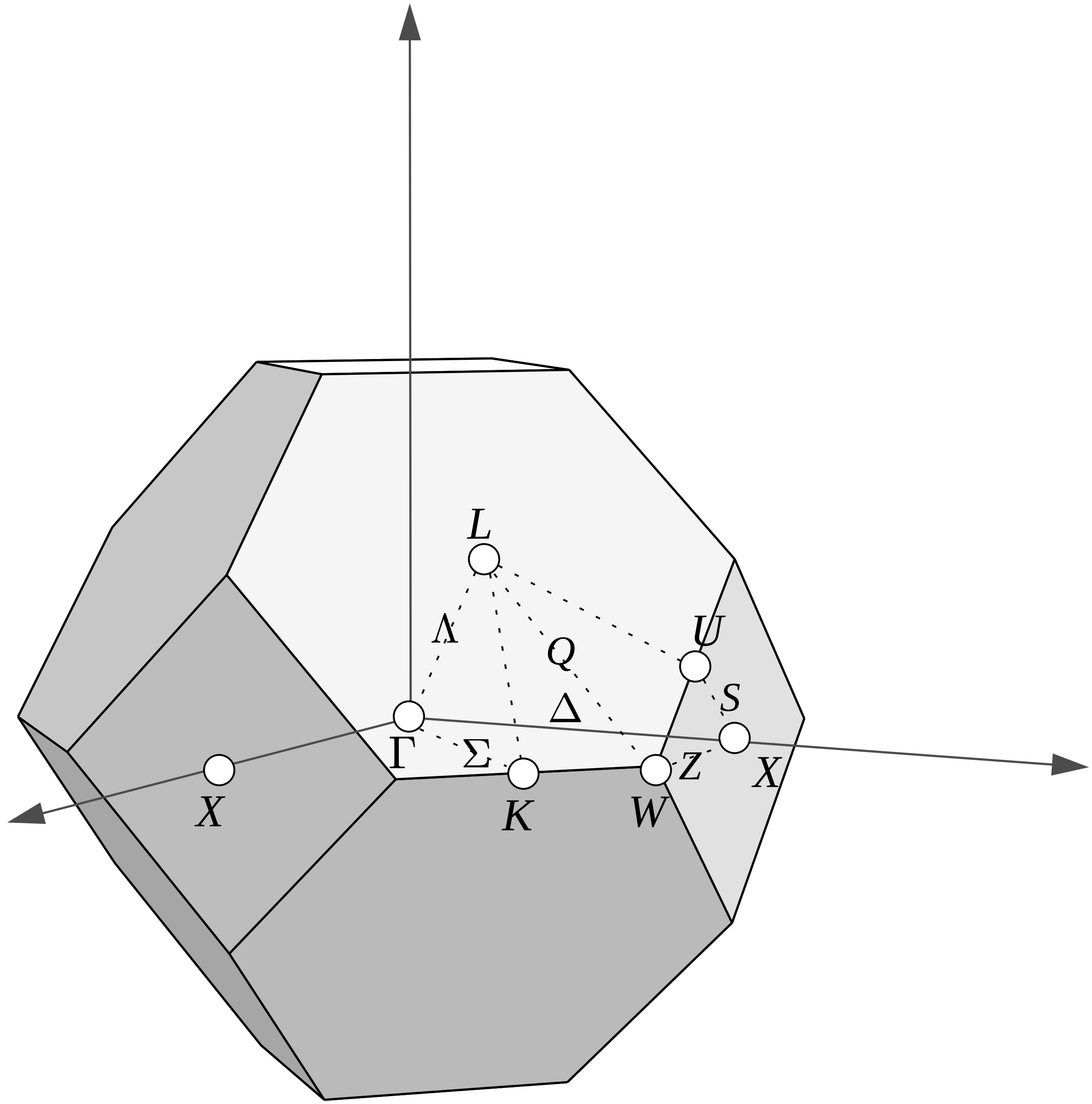
$$\vec{b}_l \cdot \vec{a}_{l'} = 2\pi\delta_{ll'}. \qquad \text{(L23)}$$

Periodic boundary conditions place a condition on how small k can be.

Demanding that $C_{\vec{R}} = \exp[i\vec{k}\cdot\vec{R}]$ be unique places conditions on how big k can be.

Number of points in crystal equals number of unique Bloch wave vectors.

Brillouin Zone



$$\frac{\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)}{M_1 M_2 M_3} \tag{L24}$$

$$= \frac{2\pi}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)} \frac{\vec{b}_1 \cdot (\vec{b}_2 \times (\vec{a}_1 \times \vec{a}_2))}{M_1 M_2 M_3} \tag{L25}$$

$$= \frac{(2\pi)^3}{M_1 M_2 M_3 \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \tag{L26}$$

$$= \frac{(2\pi)^3}{\mathcal{V}} \tag{L27}$$

$$\sum_{\vec{k}\sigma} F_{\vec{k}} = \mathcal{V} \int [d\vec{k}]\, F_{\vec{k}}, \tag{L28}$$

Define $D_{\vec{k}}$ as before:

$$D_n(\mathcal{E}) = \int [d\vec{k}]\, \delta(\mathcal{E} - \mathcal{E}_{n\vec{k}}). \tag{L29}$$

Dynamical importance of energy bands

$$\vec{v}_{n\vec{k}} = \frac{1}{\hbar}\vec{\nabla}_{\vec{k}}\mathcal{E}_{n\vec{k}}. \tag{L30}$$

$v = \partial\omega/\partial k$

Wave packet:

$$W(\vec{r},\vec{k},t) = \int [d\vec{k}'] \, w(\vec{k}'-\vec{k}) \, e^{i\vec{k}'\cdot\vec{r}-i\mathcal{E}_{\vec{k}'}t/\hbar}\psi_{\vec{k}'}e^{-i\vec{k}'\cdot\vec{r}}, \tag{L31}$$

$$\approx e^{i\vec{k}\cdot\vec{r}-i\mathcal{E}_{\vec{k}}t/\hbar}\int [d\vec{k}''] \, w(\vec{k}'')? \qquad ? \tag{L32}$$

$$\approx ? \qquad ? \tag{L33}$$

$$D(\mathcal{E}) = \int dk\,(2/2\pi)\delta\left(\mathcal{E}-\mathcal{E}_k\right) \quad \text{(L34)}$$

$$= \frac{2}{\pi}\int \frac{d\mathcal{E}_k}{|d\mathcal{E}_k/dk|}\delta\left(\mathcal{E}-\mathcal{E}_k\right) \quad \text{(L35)}$$

$$= \frac{2}{\pi}\frac{1}{|d\mathcal{E}_k/dk|}. \quad \text{(L36)}$$

$$D(\mathcal{E}) \sim \frac{1}{k-\pi/a} \sim \frac{1}{\sqrt{\mathcal{E}_{\max}-\mathcal{E}}} \quad \text{(L37)}$$

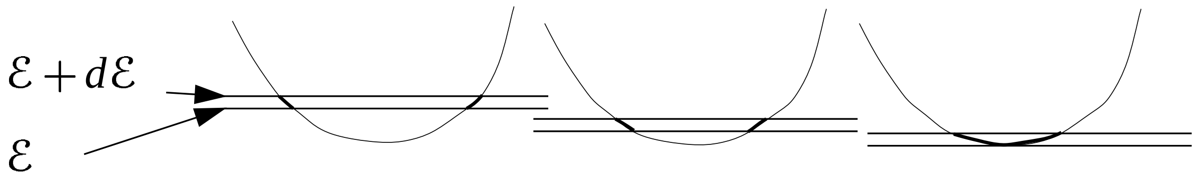
$d\mathcal{E}/dk$

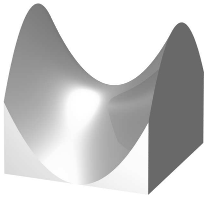
$$D(\mathcal{E}) = \int d\vec{k}\,2\frac{L^d}{(2\pi)^d}\delta(\mathcal{E}-\mathcal{E}_{\vec{k}}). \quad \text{(L38)}$$

$$D(\mathcal{E}) \sim \ln|\mathcal{E}/\mathcal{E}_0-1| \quad \text{or} \quad \theta(\pm\mathcal{E}) \quad \text{(L39)}$$

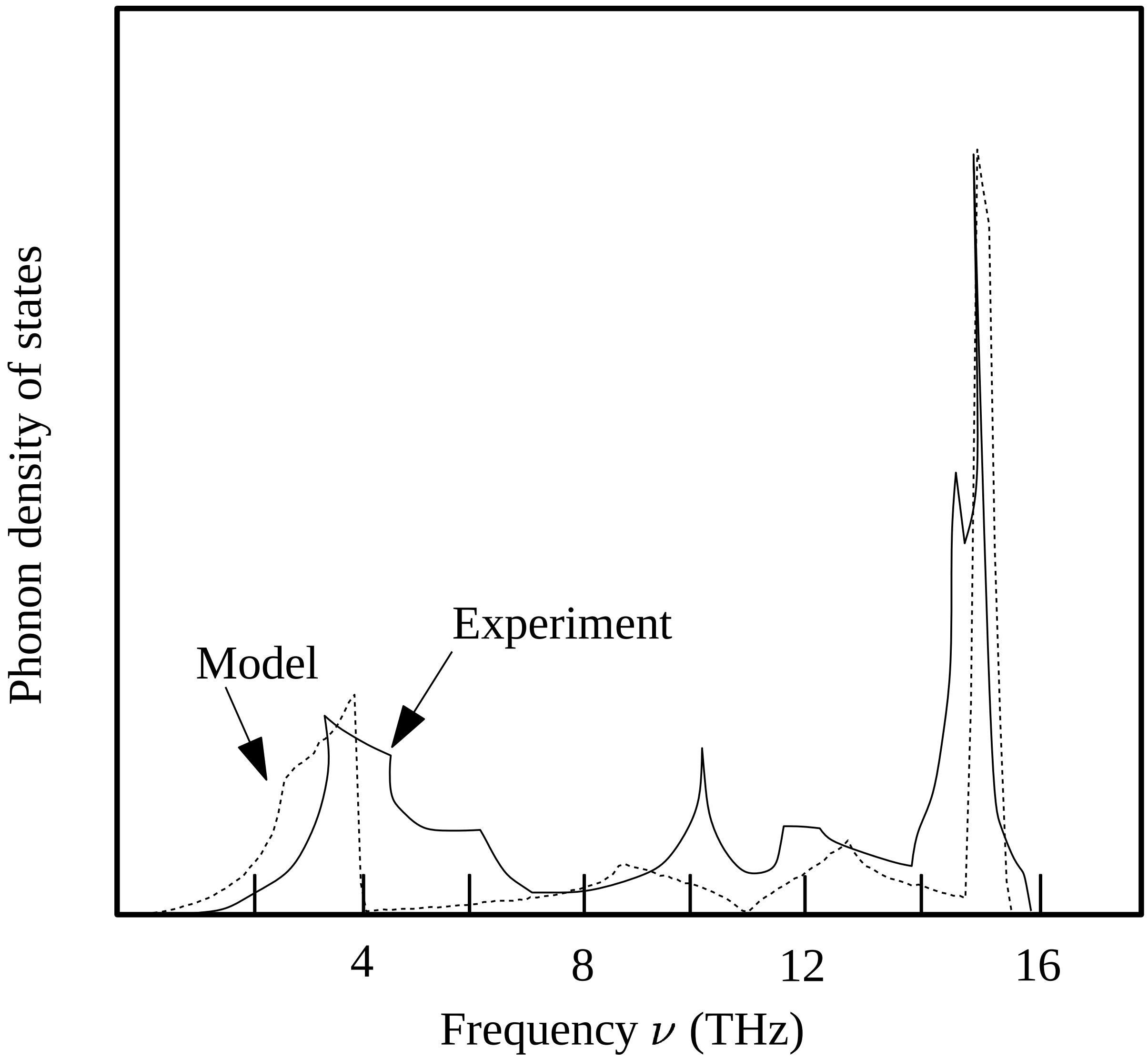
Van Hove Singularities

$$D(\mathcal{E}) \sim \begin{cases} \sqrt{\mathcal{E}} & \text{for} \quad \mathcal{E} > 0,\ 0 \text{ else,} \\ & \text{or} \\ \sqrt{-\mathcal{E}} & \text{for} \quad \mathcal{E} < 0,\ 0 \text{ else,} \end{cases} \qquad \text{(L40)}$$





Van Hove Singularities



Uniqueness of Bloch vectors

$$e^{i(\vec{k}+\vec{K})\cdot\vec{R}} = e^{i\vec{k}\cdot\vec{R}}, \tag{L41}$$

it follows that

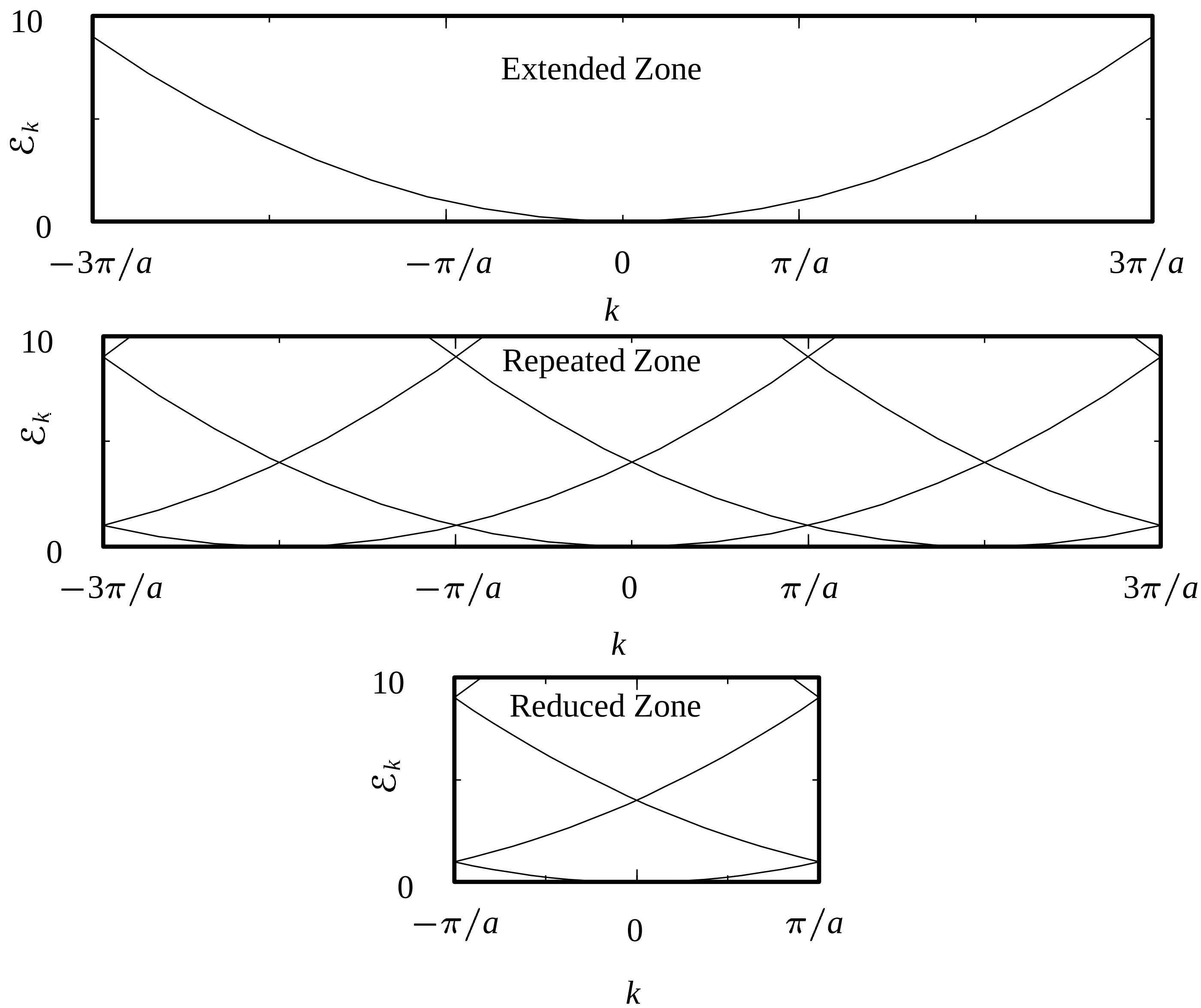
$$\psi_{n,\vec{k}+\vec{K}} = \psi_{n',\vec{k}}. \tag{L42}$$

$$\psi_{nk} = e^{ikr} e^{inKr}, \tag{L43}$$

☞ Reduced zone scheme

☞ Extended zone scheme

Uniqueness of Bloch vectors



$$e^{i\vec{k}\cdot(\vec{r}+\vec{R})} = e^{i\vec{k}\cdot\vec{r}}. \tag{L44}$$

$$\int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} U(\vec{r}) = \sum_{\vec{R}} \int_{\substack{\text{unit}\\ \text{cell}}} d\vec{r}\, e^{-i\vec{q}\cdot\vec{R}} U(\vec{r}+\vec{R}) e^{-i\vec{q}\cdot\vec{r}} \tag{L45}$$

$$= \Omega \sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} U_{\vec{q}}, \tag{L46}$$

where Ω is the volume of the unit cell, and

$$U_{\vec{q}} \equiv ? \qquad\qquad ?. \tag{L47}$$

Ω is volume of unit cell

$$\sum_{\vec{R}} e^{-i\vec{q}\cdot\vec{R}} = N \sum_{\vec{K}} \delta_{\vec{q}\vec{K}} \tag{L48}$$

Explicit construction of Bloch functions

$$\Rightarrow \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} U(\vec{r}) \quad = \quad \mathcal{V} \sum_{\vec{K}} \delta_{\vec{q}\vec{K}} U_{\vec{K}}. \tag{L49}$$

$$U(\vec{r}) = ? \qquad ? \sum_{\vec{K}} e^{i\vec{K}\cdot\vec{r}} U_{\vec{K}}. \tag{L50}$$

Periodic boundary conditions imply

$$\psi(\vec{r}) = \frac{1}{\mathcal{V}} \sum_{\vec{q}} \psi(\vec{q}) e^{i\vec{q}\cdot\vec{r}}. \tag{L51}$$

$$\int d\vec{r} e^{i\vec{q}\cdot\vec{r}} = \mathcal{V} \delta_{\vec{q}\vec{0}}. \tag{L52}$$

$$0 \quad = \quad \frac{1}{\mathcal{V}} \sum_{\vec{q}'} \left[\mathcal{E}^0_{\vec{q}'} - \mathcal{E} + U(\vec{r}) \right] \psi(\vec{q}') e^{i\vec{q}'\cdot\vec{r}} \tag{L53}$$

$$= \quad ?$$

Explicit construction of Bloch functions

$$? \Rightarrow 0 \quad = \quad ?$$

$$? \quad = \quad ?$$

$$? \Rightarrow 0 \quad = \quad (\mathcal{E}^0_{\vec{q}} - \mathcal{E})\psi(\vec{q}) + \sum_{\vec{K}} U_{\vec{K}}\psi(\vec{q}-\vec{K}). \tag{L57}$$

$$\psi(\vec{r}) = \frac{1}{\mathcal{V}}\sum_{\vec{K}} \psi(\vec{k}-\vec{K})e^{i(\vec{k}-\vec{K})\cdot\vec{r}}. \tag{L58}$$

$$\hat{\mathcal{H}} = \sum_{\vec{q}\,'} |\vec{q}\,'\rangle \mathcal{E}^0_{\vec{q}\,'} \langle \vec{q}\,'| + \sum_{\vec{q}\,'\vec{K}'} |\vec{q}\,'\rangle U_{\vec{K}'} \langle \vec{q}\,' - \vec{K}'|. \tag{L59}$$

Structure of equations

$$
\begin{pmatrix}
\begin{pmatrix}
\mathcal{O}^{(1)}_{11} & \mathcal{O}^{(1)}_{12} & \mathcal{O}^{(1)}_{13}\cdots & \mathcal{O}^{(1)}_{1M} \\
\mathcal{O}^{(1)}_{21} & \mathcal{O}^{(1)}_{22} & \mathcal{O}^{(1)}_{23}\cdots & \mathcal{O}^{(1)}_{2M} \\
\mathcal{O}^{(1)}_{31} & \mathcal{O}^{(1)}_{32} & \mathcal{O}^{(1)}_{33}\cdots & \mathcal{O}^{(1)}_{3M} \\
 & . & & \\
 & . & & \\
 & . & & \\
 & & & \mathcal{O}^{(1)}_{MM}
\end{pmatrix} & 0 \\
0 & \begin{pmatrix}
\mathcal{O}^{(2)}_{11} & \mathcal{O}^{(2)}_{12} & \mathcal{O}^{(2)}_{13}\cdots & \mathcal{O}^{(2)}_{1M} \\
\mathcal{O}^{(2)}_{21} & \mathcal{O}^{(2)}_{22} & \mathcal{O}^{(2)}_{23}\cdots & \mathcal{O}^{(2)}_{2M} \\
\mathcal{O}^{(2)}_{31} & \mathcal{O}^{(2)}_{32} & \mathcal{O}^{(2)}_{33}\cdots & \mathcal{O}^{(2)}_{3M} \\
 & . & & \\
 & . & & \\
 & . & & \\
 & & & \mathcal{O}^{(2)}_{MM}
\end{pmatrix}
\end{pmatrix}
\begin{pmatrix}
\psi(\vec{q}_1 - \vec{K}_1) \\
\psi(\vec{q}_1 - \vec{K}_2) \\
\psi(\vec{q}_1 - \vec{K}_3) \\
. \\
. \\
. \\
\underline{\psi(\vec{q}_1 - \vec{K}_M)} \\
\psi(\vec{q}_2 - \vec{K}_1) \\
\psi(\vec{q}_2 - \vec{K}_2) \\
\psi(\vec{q}_2 - \vec{K}_3) \\
. \\
. \\
\underline{\psi(\vec{q}_2 - \vec{K}_M)} \\
.
\end{pmatrix}
$$

$$U_0 a\delta(x), \tag{L60}$$

$$U_K = U_0, \tag{L61}$$

$$0 = (\mathcal{E}^0_q - \mathcal{E})\psi(q) + \sum_K U_0\psi(q-K). \tag{L62}$$

$$Q_q = \sum_K \psi(q-K). \tag{L63}$$

Then Eq. (L62) becomes

$$\psi(q) + \frac{U_0}{\mathcal{E}^0_q - \mathcal{E}} Q_q = 0. \tag{L64}$$

Note from its definition (63) that

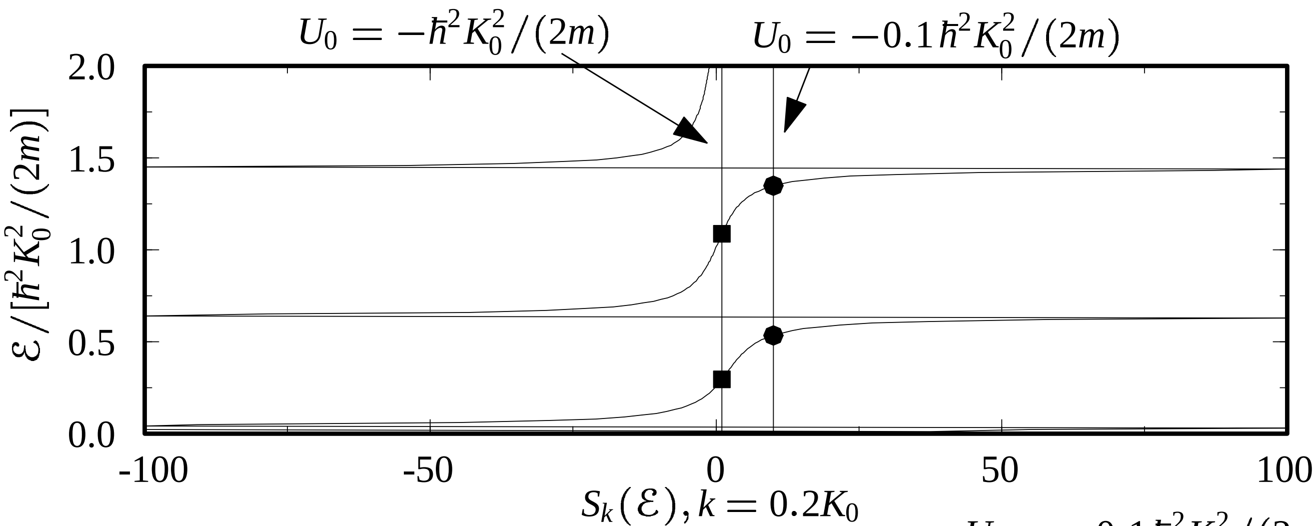
$$Q_q = Q_{q-K} \tag{L65}$$

$$? \qquad ? = 0 \tag{L66}$$

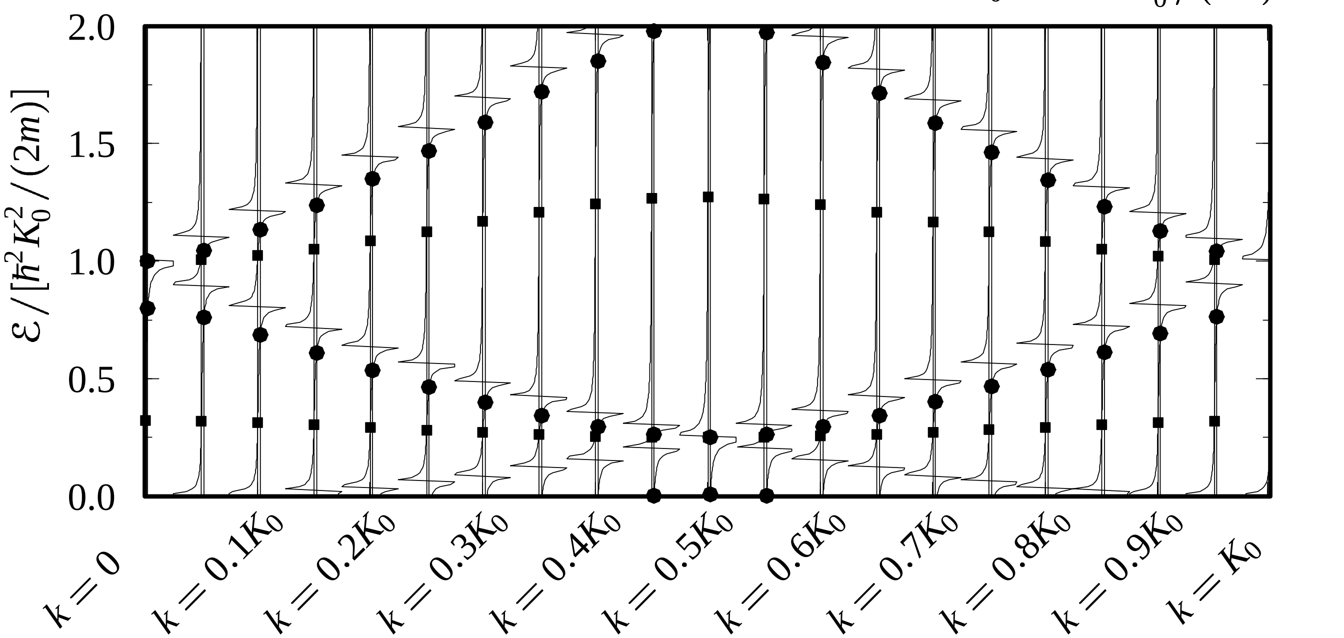
$$? \qquad ? = 0 \tag{L67}$$

$$\Rightarrow \qquad Q_k + ? \qquad ?0. \tag{L68}$$

$$-\frac{1}{U_0} = \sum_K \frac{1}{\mathcal{E}^0_{k-K} - \mathcal{E}} \equiv S_k(\mathcal{E}). \tag{L69}$$

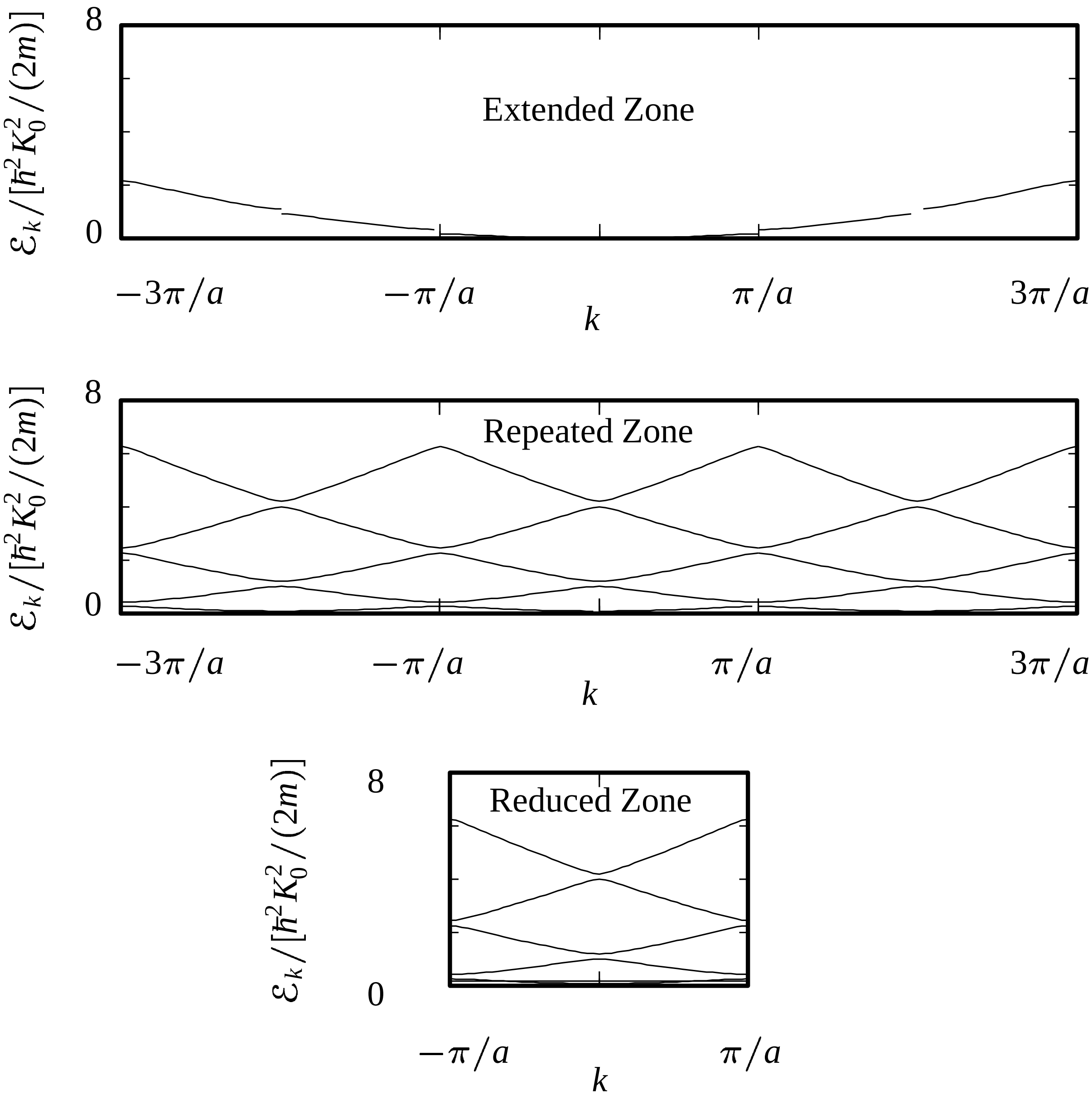


$U_0 = -\hbar^2 K_0^2/(2m)$
$U_0 = -0.1\hbar^2 K_0^2/(2m)$
2.0
1.5
1.0
0.5
0.0
$\mathcal{E}/[\hbar^2 K_0^2/(2m)]$
-100
-50
0
50
100
$S_k(\mathcal{E}), k = 0.2K_0$

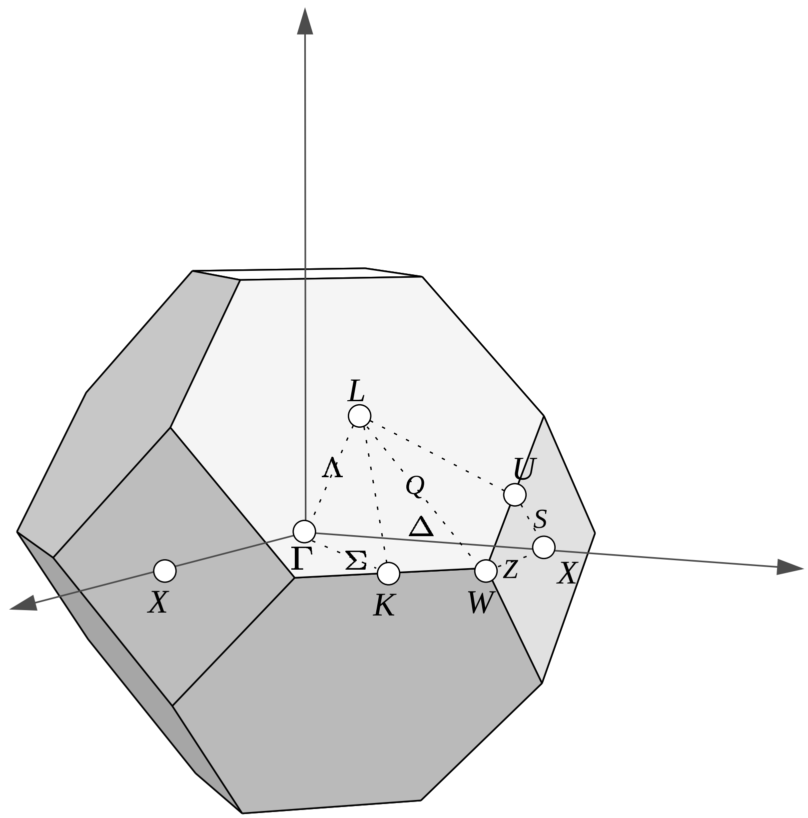


● $U_0 = -0.1\hbar^2 K_0^2/(2m)$
■ $U_0 = -\hbar^2 K_0^2/(2m)$
2.0
1.5
1.0
0.5
0.0
$\mathcal{E}/[\hbar^2 K_0^2/(2m)]$
$k = 0$
$k = 0.1K_0$
$k = 0.2K_0$
$k = 0.3K_0$
$k = 0.4K_0$
$k = 0.5K_0$
$k = 0.6K_0$
$k = 0.7K_0$
$k = 0.8K_0$
$k = 0.9K_0$
$k = K_0$

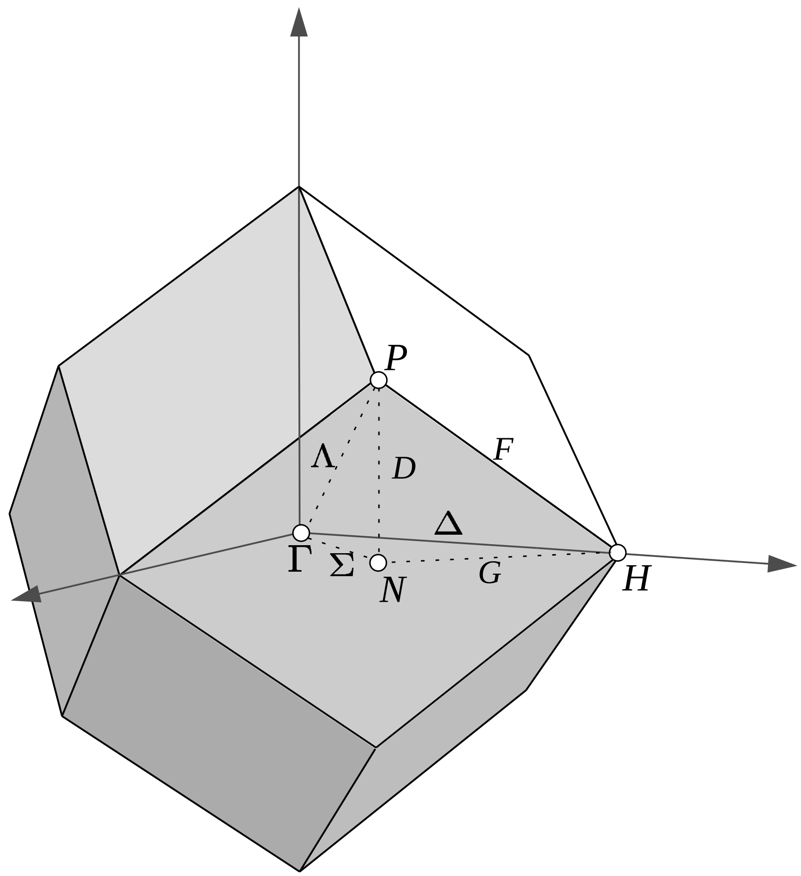
Kronig–Penney model



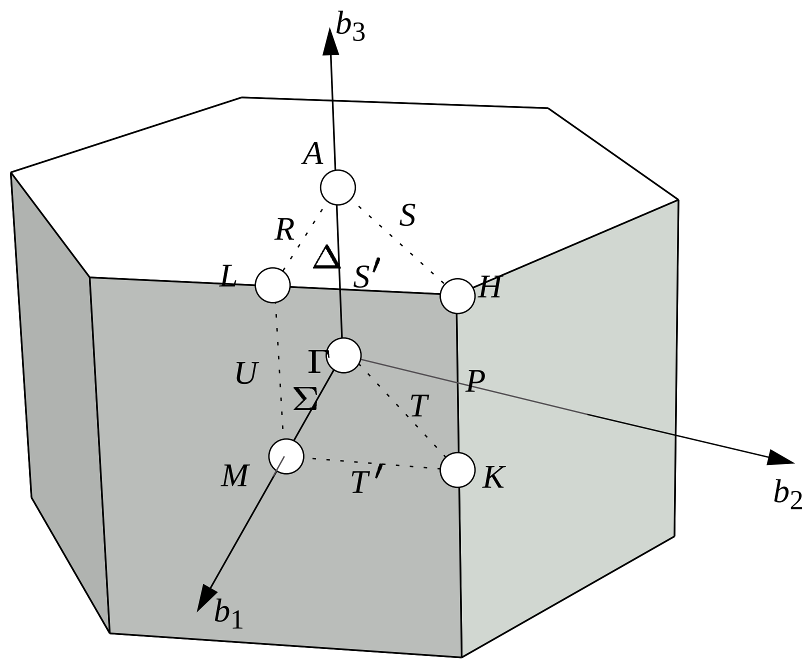
Brillouin zones and rotational symmetry



In units of $2\pi/a$, $\Gamma = (0\ 0\ 0)$, $X = (0\ 1\ 0)$, $L = (1/2\ 1/2\ 1/2)$, $W = (1/2\ 1\ 0)$, $K = (3/4\ 3/4\ 0)$, and $U = (1/4\ 1\ 1/4)$.



In units of $2\pi/a$, $\Gamma = (0\ 0\ 0)$, $H = (0\ 1\ 0)$, $N = (1/2\ 1/2\ 0)$, and $P = (1/2\ 1/2\ 1/2)$.



In units of $4\pi/a\sqrt{3}$, $4\pi/a\sqrt{3}$, and $2\pi/c$, along the three primitive vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$; $\Gamma = (0\ 0\ 0)$, $A = (0\ 0\ 1/2)$, $M = (1/2\ 0\ 0)$, $K = (1/3\ 1/3\ 0)$, $H = (1/3\ 1/3\ 1/2)$, and $L = (1/2\ 0\ 1/2)$.

Summary

- Energy states indexed by $\vec{k}$ and n. The first index describes symmetry properties during translation, while the second distinguishes energy states with same symmetry.
- The eigenvalue corresponding to translation symmetry is

$$e^{i\vec{k}\cdot\vec{R}}, \tag{L1}$$

not $\vec{k}$. The eigenvalue and eigenstates are periodic functions of $\vec{k}$, unchanged when $\vec{k} \to \vec{k} + \vec{K}$.

- Essential result:

$$(\mathcal{E}^0_{\vec{q}} - \mathcal{E})\psi(\vec{q}) + \sum_{\vec{K}} U_{\vec{K}}\psi(\vec{q} - \vec{K}) = 0. \tag{L2}$$

$$k = \frac{K}{2\hat{k}\cdot\hat{K}} \Rightarrow \vec{k}\cdot\vec{K} = \frac{1}{2}K^2. \tag{L3}$$

➾ Energy degeneracy:

$$\frac{1}{2}k^2 = \frac{1}{2}k^2 - \vec{k}\cdot\vec{K} + \frac{1}{2}K^2 \tag{L4}$$

$$\Rightarrow \mathcal{E}^0_{\vec{k}} = \mathcal{E}^0_{\vec{k}-\vec{K}} \tag{L5}$$

➾ Geometry: Plane that bisects line between origin and $\vec{K}$ is given by

$$\vec{k}\cdot\hat{K} = \frac{K}{2} \Rightarrow \vec{k}\cdot\vec{K} = \frac{K^2}{2} \tag{L6}$$

$$U_{\vec{K}} = \Delta w_{\vec{K}} \tag{L7}$$

Exercise:

Starting with

$$(\mathcal{E}^0_{\vec{q}} - \mathcal{E})\psi(\vec{q}) + \sum_{\vec{K}} U_{\vec{K}}\psi(\vec{q} - \vec{K}) = 0. \tag{L8}$$

and

$$\psi(\vec{q}) = \psi^{(0)}(\vec{q}) + \psi^{(1)}(\vec{q})\Delta + \ldots; \quad \mathcal{E} = \mathcal{E}^{(0)} + \Delta\mathcal{E}^{(1)} + \ldots. \tag{L9}$$

find the zero'th order solution $\psi^{(0)}$:

$$\psi^{(0)}? \qquad\qquad ? = 0. \tag{L10}$$

$$\psi^{(0)}_{\vec{k}}(\vec{q}) = ? \quad ? \Rightarrow \psi^{(0)}_{\vec{k}}(\vec{r}) = ? \quad ? \tag{L11}$$

$$\Rightarrow \mathcal{E}^{(0)} = ? \quad ? \tag{L12}$$

Perturbation Theory: First Order

Exercise:

Next, expand Bloch's equation out to first order in Δ and find both the energy and wave function to this order:

$$[\mathcal{E}^0_{\vec{q}} - \mathcal{E}^0_{\vec{k}}]\psi^{(1)}_{\vec{k}}(\vec{q}) + \sum_{\vec{K}} w_{\vec{K}} \psi^{(0)}_{\vec{k}}(\vec{q}-\vec{K}) - \mathcal{E}^{(1)}\psi^{(0)}_{\vec{k}}(\vec{q}) = 0. \tag{L13}$$

$$\mathcal{E}^{(1)} = ? \quad ? \tag{L14}$$

$$\left.\psi^{(1)}_{\vec{k}}(\vec{q}) \quad = \quad ? \qquad\qquad ?\right\} \tag{L15}$$

$$\Rightarrow \psi_{\vec{k}}(\vec{q}) \quad \approx \quad ? \qquad\qquad ? \tag{L16}$$

Perturbation theory breaks down

The condition for breakdown is

$$\mathcal{E}^0_{\vec{k}} = \mathcal{E}^0_{\vec{K}+\vec{k}} \tag{L17}$$

$$\hat{\mathcal{H}}^{\text{eff}}_{ij} = \langle \psi_i | (\hat{\mathcal{H}} - \mathcal{E}) | \psi_j \rangle \tag{L18}$$

$|\psi_1\rangle = |\vec{k}\rangle$

$|\psi_2\rangle = |\vec{k} + \vec{K}\rangle$

$$\hat{\mathcal{H}} = \sum_{\vec{q}\,'} |\vec{q}\,'\rangle \mathcal{E}^0_{\vec{q}\,'} \langle \vec{q}\,'| + \sum_{\vec{q}\,'\vec{K}'} |\vec{q}\,'\rangle U_{\vec{K}'} \langle \vec{q}\,' - \vec{K}'|. \tag{L19}$$

Exercise: Find off-diagonal components of matrix.

$$\begin{vmatrix} \mathcal{E}^0_{\vec{k}} - \mathcal{E} & ? & ? \\ ? & ? & \mathcal{E}^0_{\vec{k}+\vec{K}} - \mathcal{E} \end{vmatrix}. \tag{L20}$$

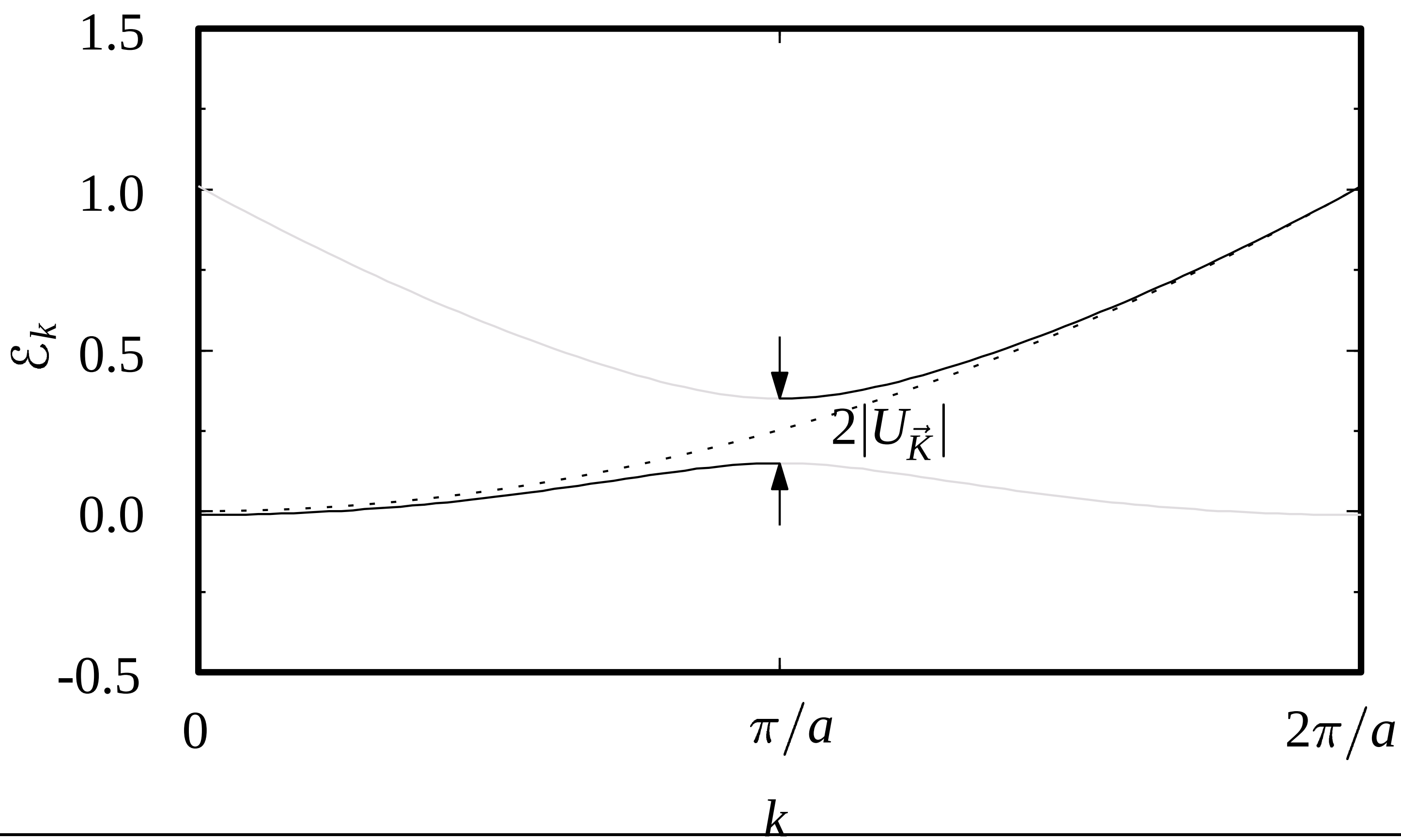
Exercise: find eigenvalues of matrix

$$\mathcal{E} = ? \qquad ? \tag{L21}$$

Right at $\vec{k} = \vec{K}$ have

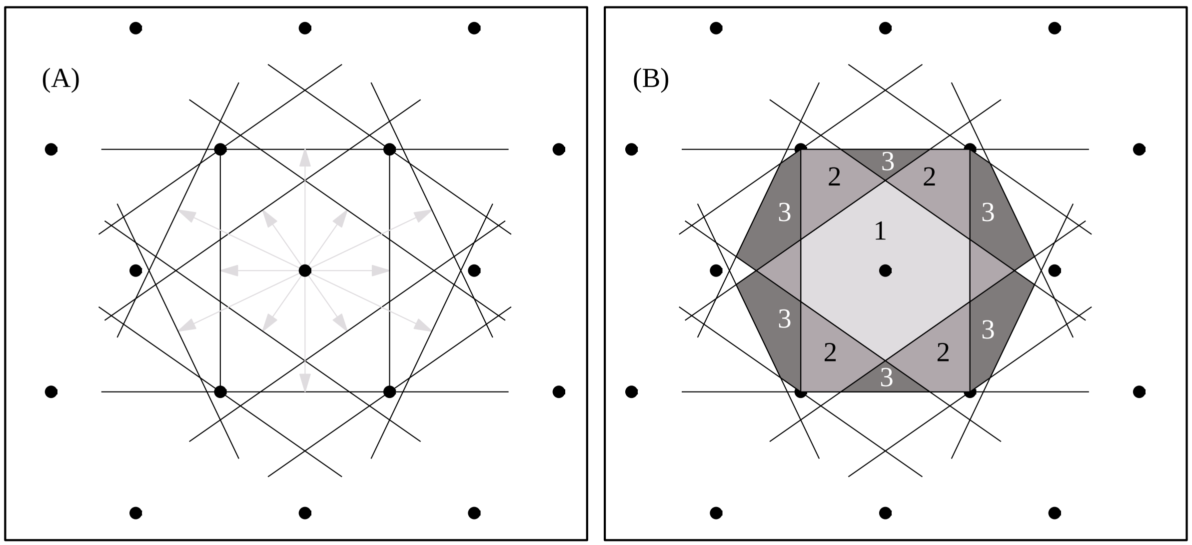
$$\mathcal{E} = \mathcal{E}^0_{\vec{k}} \pm \| U_{\vec{K}} |. \tag{L22}$$

$$\mathcal{E}_g = 2|U_{\vec{K}}|. \tag{L23}$$

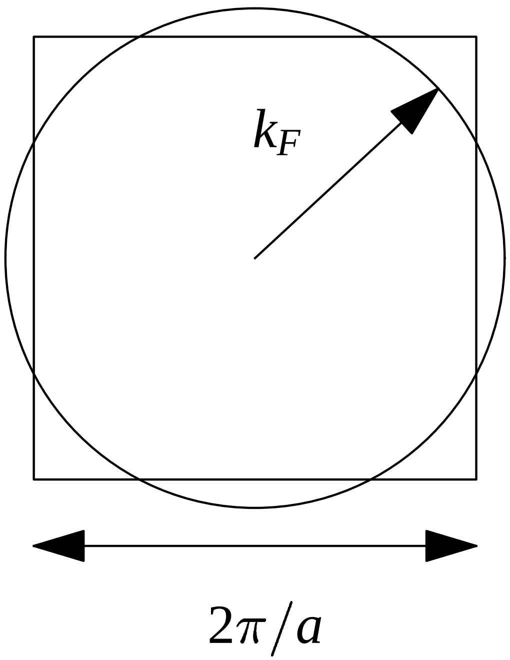


Geometrical view

$$\vec{k} \cdot \frac{\vec{K}}{K} = \frac{1}{2} K. \qquad \text{(L24)}$$



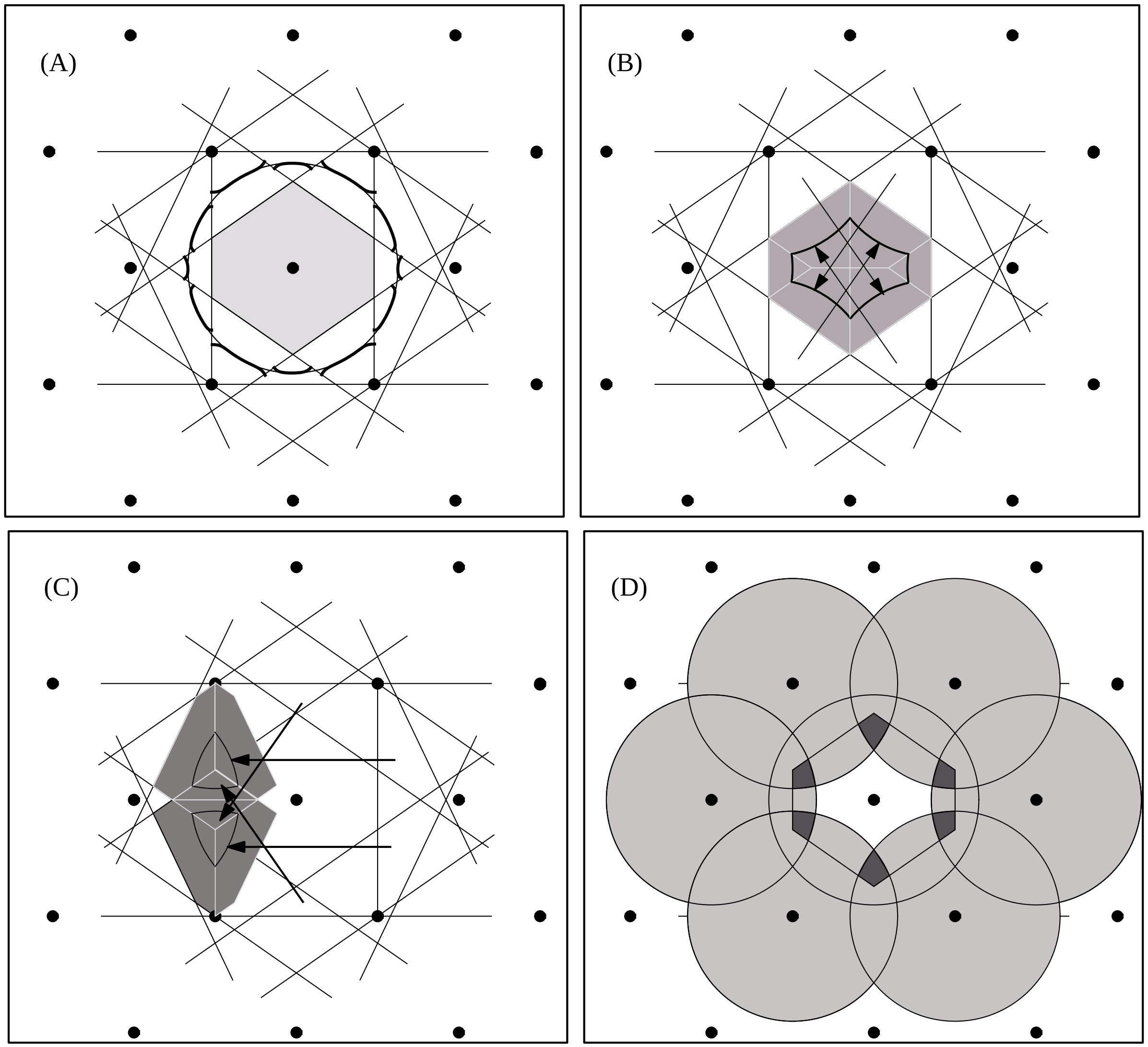
Example in two dimensions



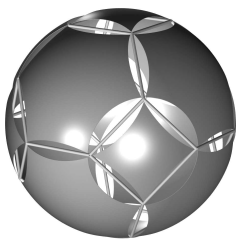
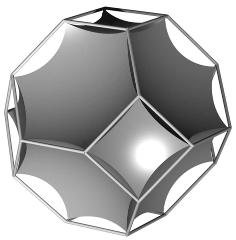
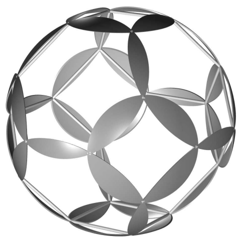
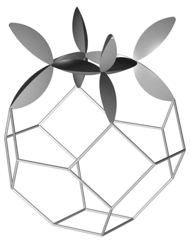
$$\pi k_F^2 = 4\pi^2/a^2$$

$$\Rightarrow k_F = 2\pi/\sqrt{\pi}a = 1.128\pi/a$$

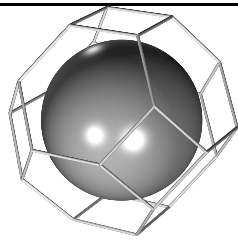
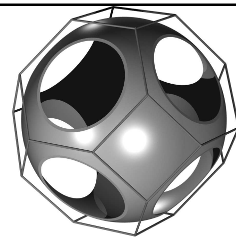
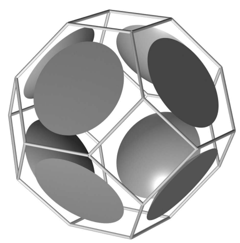
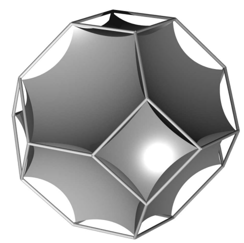
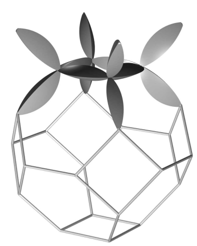
Example in two dimensions



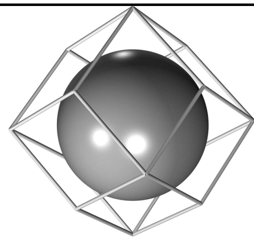
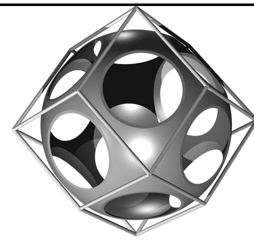
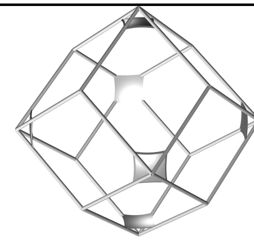
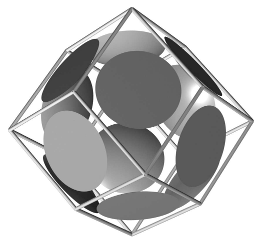
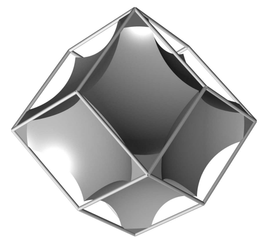
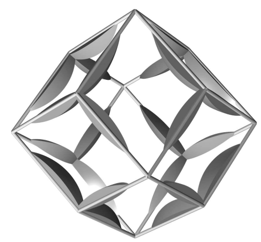
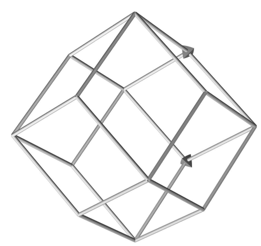
Nearly Free Electron Fermi Surface Gallery

Brillouin zone	Extended zone scheme	Reduced zone scheme
First	Empty	Empty
Second		
Third		

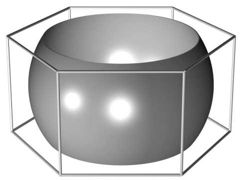
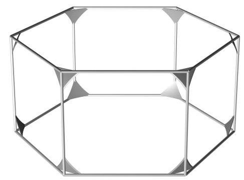
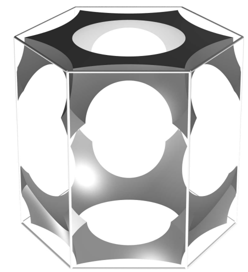
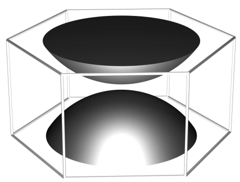
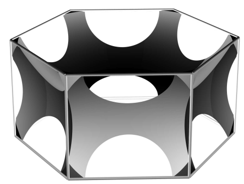
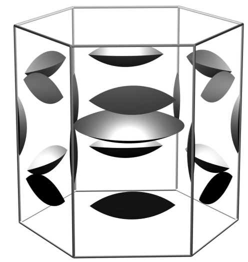
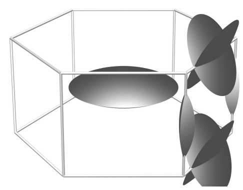
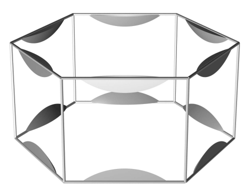
Nearly Free Electron Fermi Surface Gallery

Brillouin zone	1 electron/cell	2 electrons/cell	3 electrons/cell
First			
Second			
Third			

Nearly Free Electron Fermi Surface Gallery

Brillouin zone	1 electron/cell	2 electrons/cell	3 electrons/cell
First			
Second			
Third			
Fourth			

Nearly Free Electron Fermi Surface Gallery

Brillouin zone	2 electrons/cell	4 electrons/cell	4 electrons/cell with hcp extinction
First			
Second			
Third			
Fourth			

Periodic Table of Fermi Surfaces, University of Florida

Wannier Functions

$$\langle \vec{r}|\vec{R}\rangle \equiv w_n(\vec{R},\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}}\psi_{n\vec{k}}(\vec{r}). \tag{L25}$$

$$\int d\vec{r}\, w_n(\vec{R},\vec{r})w_m^*(\vec{R}',\vec{r}) = ?$$

$$? \tag{L27}$$

$$= \quad \delta_{\vec{R},\vec{R}'}\delta_{n,m}. \tag{L28}$$

$$\frac{1}{\sqrt{N}}\sum_{\vec{R}} w_n(\vec{R},\vec{r})e^{i\vec{k}\cdot\vec{R}} = \psi_{n\vec{k}}(\vec{r}). \tag{L29}$$

$$w_n(\vec{R},\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}+i\phi(\vec{k})}\psi_{n\vec{k}}(\vec{r}), \tag{L30}$$

$$\hat{\mathcal{H}} = \sum_{\vec{R}\vec{R}'} |\vec{R}'\rangle\langle\vec{R}'|\hat{\mathcal{H}}|\vec{R}\rangle\langle\vec{R}|. \tag{L31}$$

$$\mathcal{H}_{\vec{R}\vec{R}'} \equiv \langle\vec{R}'|\hat{\mathcal{H}}|\vec{R}\rangle = \int d\vec{r}\, w_n^*\left(\vec{R}',\vec{r}\right)[-\frac{\hbar^2\nabla^2}{2m} + U(\vec{r})]w_n(\vec{R},\vec{r}) \tag{L32}$$

$$\mathcal{H}_{\vec{R}\vec{R}'} = \sum_{\vec{k}} \frac{1}{N}\mathcal{E}_{n\vec{k}} e^{-i\vec{k}\cdot(\vec{R}-\vec{R}')}. \tag{L33}$$

$$\hat{\mathcal{H}}_{\mathrm{TB}} = \sum_{\vec{R}\vec{\delta}} |\vec{R}\rangle\,\mathfrak{t}\,\langle\vec{R}+\vec{\delta}| + \sum_{\vec{R}} |\vec{R}\rangle U \langle\vec{R}|. \tag{L34}$$

Tight Binding Hamiltonian

$$|\vec{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} |\vec{R}\rangle, \tag{L35}$$

$$|\vec{R}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}} |\vec{k}\rangle, \tag{L36}$$

$$\hat{\mathcal{H}}_{\mathrm{TB}} = ? \qquad ? \tag{L37}$$

$$= \sum_{\vec{k}} \mathcal{E}_{\vec{k}} |\vec{k}\rangle \langle \vec{k}| \tag{L38}$$

$$\mathcal{E}_{\vec{k}} = ? \qquad ? \tag{L39}$$

$$2\mathcal{W} = 2zt. \tag{L40}$$

$$\hat{P}_n = \sum_k |\psi_{nk}\rangle\langle\psi_{nk}|. \tag{L41}$$

$$R|R\rangle = \hat{P}\hat{R}\hat{P}|R\rangle. \tag{L42}$$

$$w(R,k) = \langle\psi_k|R\rangle. \tag{L43}$$

$$Rw(R,k) = \sum_{k'} \langle\psi_k|\hat{R}|\psi_{k'}\rangle w(R,k'). \tag{L44}$$

$$\psi_k(x) = e^{ikx}u_k(x), \tag{L45}$$

$$\begin{aligned}\langle\psi_k|\hat{R}|\psi_{k'}\rangle = \quad & 2\pi i\left[\frac{\partial}{\partial k}\delta(k-k')\right]\int_0^a \frac{dx}{a}u_k^*(x)u_k(x) \\ & +2\pi\delta(k-k')\int_0^a \frac{dx}{a}u_k^*(x)i\frac{\partial}{\partial k}u_k(x).\end{aligned} \tag{L46}$$

$$\tilde{u}_k(x) = e^{-i\phi(k)} u_k(x) \tag{L47}$$

$$\int_0^a \frac{dx}{a} \tilde{u}_k^*(x) i \frac{\partial}{\partial k} \tilde{u}_k(x) = 0, \tag{L48}$$

$$w(R,x) = \langle x|R\rangle \tag{L49}$$

$\psi_{k+2\pi/a}(x) = \exp[i\chi]\psi_k(x)$

$\exp[-i\gamma(k)]$

$\gamma(2\pi/a) = \chi$

$$\tilde{\psi}_{k+2\pi/a}(x) = e^{i\Gamma}\tilde{\psi}_k(x). \tag{L50}$$

$$R = \frac{\Gamma a}{2\pi} + la. \tag{L51}$$

Born-Oppenheimer approximation

$$\hat{\mathcal{H}}\Psi = \frac{-\hbar^2}{2m}\sum_{l=1}^{N}\nabla_l^2\Psi + \sum_{l=1}^{N}U_{\text{ion}}(\vec{r}_l)\Psi + \sum_{l<l'}\frac{e^2}{|\vec{r}_l - \vec{r}_{l'}|}\Psi = \mathcal{E}\Psi, \quad \text{(L1)}$$

“the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble” Dirac, 1929.

Hartree Equations

$$U_{\text{ee}}(\vec{r}) = \int d\vec{r}\,' \frac{e^2 n(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|}, \tag{L2}$$

$$n(\vec{r}) = \sum_j |\psi_j(\vec{r})|^2. \tag{L3}$$

$$\frac{-\hbar^2}{2m}\nabla^2\psi_l + [U_{\text{ion}}(\vec{r}) + U_{\text{ee}}(\vec{r})]\psi_l = \mathcal{E}_l\psi_l. \tag{L4}$$

Variational Principle

$$F_{\mathcal{H}}\{\Psi\} = \langle\Psi|\hat{\mathcal{H}}|\Psi\rangle, \tag{L5}$$

$$\Psi = \prod_{l=1}^{N} \psi_l(\vec{r}_l), \tag{L6}$$

$$\frac{\delta F_{\mathcal{H}}}{\delta\psi_l^*(\vec{r})} - \frac{\delta}{\delta\psi_l^*(\vec{r})} \sum_j \mathcal{E}_j \int d\vec{r}'\, \psi_j^*(\vec{r}')\psi_j(\vec{r}') = 0 \tag{L7}$$

Slater determinants

$$\Psi(\vec{r}_1\sigma_1 \ldots \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \sum_s (-1)^s \psi_{s_1}(\vec{r}_1\sigma_1) \ldots \psi_{s_N}(\vec{r}_N\sigma_N) \tag{L8}$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1\sigma_1) & \psi_1(\vec{r}_2\sigma_2) & \ldots & \psi_1(\vec{r}_N\sigma_N) \\ . & . & & . \\ . & . & & . \\ . & . & & . \\ . & . & & . \\ \psi_N(\vec{r}_1\sigma_1) & \psi_N(\vec{r}_2\sigma_2) & \ldots & \psi_N(\vec{r}_N\sigma_N) \end{vmatrix} . \tag{L9}$$

Hartree-Fock equations

$$\psi_l(\vec{r}_i\sigma_i) = \phi_l(\vec{r}_i)\chi_l(\sigma_i). \tag{L10}$$

$$\sum_{\sigma_1\ldots\sigma_N} \int d^N\vec{r}\,\frac{1}{N!}\sum_{ss'}(-1)^{s+s'}\left[\prod_j \psi^*_{s_j}(\vec{r}_j\sigma_j)\right]\sum_l \frac{-\hbar^2\nabla_l^2}{2m}\left[\prod_{j'}\psi_{s'_{j'}}(\vec{r}_{j'}\sigma_{j'})\right]. \tag{L11}$$

$$\sum_l\sum_{\sigma_l}\int d\vec{r}_l\,\frac{1}{N!}\sum_s \psi^*_{s_l}(\vec{r}_l\sigma_l)\frac{-\hbar^2\nabla_l^2}{2m}\psi_{s_l}(\vec{r}_l\sigma_l) \tag{L12}$$

$$= \sum_l\sum_\sigma\int d\vec{r}\,\frac{1}{N}\sum_{l'}\psi^*_{l'}(\vec{r}\sigma)\frac{-\hbar^2\nabla^2}{2m}\psi_{l'}(\vec{r}\sigma) \tag{L13}$$

$$= \sum_{l=1}^N\int d\vec{r}\phi^*_l(\vec{r})\left[\frac{-\hbar^2\nabla^2}{2m}\right]\phi_l(\vec{r}). \tag{L14}$$

$$\sum_{l=1}^N\int d\vec{r}\phi^*_l(\vec{r})U(\vec{r})\phi_l(\vec{r}). \tag{L15}$$

$$\sum_{\sigma_1\ldots\sigma_N}\int d^N\vec{r}\sum_{s,s'}\frac{1}{N!}\sum_{i<j}\frac{e^2(-1)^{s+s'}}{|\vec{r}_i-\vec{r}_j|}\prod_{l,l'}\psi^*_{s_l}(l)\psi_{s'_{l'}}(l') \tag{L16}$$

$$= \sum_{\sigma_1\ldots\sigma_N}\int d^N\vec{r}\sum_{s,s'}\frac{1}{N!}\sum_{i<j}\frac{e^2(-1)^{s+s'}}{|\vec{r}_i-\vec{r}_j|}\left[\begin{array}{cc} & \psi^*_{s_i}(i)\psi^*_{s_j}(j) \\ \times & \psi_{s'_i}(i)\psi_{s'_j}(j) \\ \times & \displaystyle\prod_{l,l'\neq i,j}\psi^*_{s_l}(l)\psi_{s'_{l'}}(l')\end{array}\right] \tag{L17}$$

$$= \sum_{i<j}\sum_{\sigma_i\sigma_j}\int d\vec{r}_i d\vec{r}_j\sum_{s}\frac{1}{N!}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\left[\begin{array}{l}|\psi_{s_i}(i)|^2|\psi_{s_j}(j)|^2 \\ -\psi^*_{s_i}(i)\psi^*_{s_j}(j)\psi_{s_i}(j)\psi_{s_j}(i)\end{array}\right] \tag{L18}$$

$$= \sum_{\sigma_1\sigma_2}\int\frac{d\vec{r}_1 d\vec{r}_2}{2(N-2)!}\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\sum_{s}\left[\begin{array}{l}|\psi_{s_1}(1)|^2|\psi_{s_2}(2)|^2 \\ -\psi^*_{s_1}(1)\psi^*_{s_2}(2)\psi_{s_1}(2)\psi_{s_2}(1)\end{array}\right] \tag{L19}$$

$$= \sum_{\sigma_1\sigma_2}\int\frac{e^2 d\vec{r}_1 d\vec{r}_2}{|\vec{r}_1-\vec{r}_2|}\sum_{i<j}\left[|\psi_i(1)|^2|\psi_j(2)|^2-\psi^*_i(1)\psi^*_j(2)\psi_i(2)\psi_j(1)\right] \tag{L20}$$

$$= \int \frac{e^2 d\vec{r}_1 d\vec{r}_2}{|\vec{r}_1 - \vec{r}_2|} \sum_{i<j} \left[|\phi_i(\vec{r}_1)|^2 |\phi_j(\vec{r}_2)|^2 - \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\phi_i(\vec{r}_2)\phi_j(\vec{r}_1)\delta_{\chi_i\chi_j} \right]. \quad \text{(L21)}$$

Using second quantization

$$\hat{\mathcal{H}} = \sum_{l} \hat{c}_l^\dagger \hat{c}_{l'} \langle l|\hat{K}+\hat{U}_{\rm ion}|l'\rangle + \sum_{ll'l''l'''} \hat{c}_l^\dagger \hat{c}_{l'}^\dagger \hat{c}_{l'''} \hat{c}_{l''} \langle ll'|\hat{U}_{\rm int}|l''l'''\rangle \qquad \text{(L22)}$$

States l label $\psi_l(i) = \phi_l(\vec{r}_i)\chi_l(\sigma_i)$ which include both spatial and spin information.

Second quantization takes this form, no matter what the functions ϕ happen to be. Goal of Hartree-Fock approximation is to find best possible functions.

Using second quantization

Find expectation value in ground state

$$|G\rangle = |11111\ldots10000\ldots\rangle \tag{L23}$$

Consider

$$\langle G|\hat{c}_l^\dagger \hat{c}_{l'}|G\rangle \tag{L24}$$

- ☞ Get zero immediately unless l' is one of the states occupied in $|G\rangle$.
- ☞ Then get zero unless l creates again the state that l' has just destroyed.
- ☞ So must have $l \leq N$, $l = l'$, at which point creation and annihilation operators simply disappear.

$$\langle G|\sum_l \hat{c}_l^\dagger \hat{c}_{l'}\langle l|\hat{K}+\hat{U}_{\text{ion}}|l'\rangle|G\rangle = \sum_{l=1}^{N}\langle l|\hat{K}+\hat{U}_{\text{ion}}|l\rangle \tag{L25}$$

Pairing manipulations

Consider

$$\langle G|\hat{c}_l^\dagger \hat{c}_{l'}^\dagger \hat{c}_{l'''} \hat{c}_{l''}|G\rangle \tag{L26}$$

- Get zero immediately unless l'' and l''' are among the states occupied in $|G\rangle$.
- Then get zero unless l and l' create again the states that l'' and l''' have just destroyed.
- If l' recreates state just destroyed by l''' and then l recreates l'' formalism gives overall multiplicative factor of $+1$.
- However, if l' recreates state destroyed by l'' and then l recreates l''' formalism gives overall multiplicative factor of -1.

$$\langle G|\sum_{ll'l''l'''} \hat{c}_l^\dagger \hat{c}_{l'}^\dagger \hat{c}_{l'''} \hat{c}_{l''} \langle ll'|\hat{U}_{\text{int}}|l''l'''\rangle|G\rangle \tag{L27}$$

$$= \sum_{ll'l''l'''} ? \qquad ?\langle ll'|\hat{U}_{\text{int}}|l''l'''\rangle \tag{L28}$$

$$= \sum_{ll'} ? \qquad ? \tag{L29}$$

Final result

$$\langle\Psi|\mathcal{H}|\Psi\rangle = \sum_i \sum_{\sigma_1} \int d\vec{r}_1 \psi_i^*(1) \frac{-\hbar^2\nabla^2}{2m} \psi_i(1) + U(\vec{r}_1)|\psi_i(1)|^2$$

$$+ \int d\vec{r}_1 d\vec{r}_2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \sum_{\substack{i<j \\ \sigma_1\sigma_2}} \left[|\psi_i(1)|^2 |\psi_j(2)|^2 - \psi_i^*(1)\psi_j^*(2)\psi_i(2)\psi_j(1) \right]. \quad \text{(L30)}$$

Vary with respect to ψ

$\sum_{\sigma_1} \int d\vec{r}_1 \psi_i^*(1)\psi_j(1) = \delta_{ij}$

$$\sum_{i,j} \mathcal{E}_{ij} \sum_{\sigma_1} \int d\vec{r}_1 \psi_i^*(1)\psi_j(1) \tag{L31}$$

$$\sum_j \mathcal{E}_{ij}\psi_j(1) = \left[\begin{array}{l} -\frac{\hbar^2\nabla^2}{2m}\psi_i(1) + U(\vec{r}_1)\psi_i(1) \\ +\psi_i(1)\int d\vec{r}_2 \sum_{\sigma_2, j=1}^{N} \frac{e^2|\psi_j(2)|^2}{|\vec{r}_1 - \vec{r}_2|} \\ -\sum_{j=1}^{N}\psi_j(1)\sum_{\sigma_2}\int d\vec{r}_2 \frac{e^2\psi_j^*(2)\psi_i(2)}{|\vec{r}_1 - \vec{r}_2|} \end{array} \right]. \tag{L32}$$

$$\tilde{\psi}_i = \sum_j W_{ij}\psi_j. \tag{L33}$$

$$\int d\vec{r} \sum_{i\sigma} \tilde{\psi}_i^*(\vec{r}\sigma) \frac{-\hbar^2\nabla^2}{2m} \tilde{\psi}_i(\vec{r}\sigma) \tag{L34}$$

$$= \int d\vec{r} \sum_{i\sigma} \sum_{jj'} W_{ij}^* \psi_j^*(\vec{r}\sigma) \frac{-\hbar^2\nabla^2}{2m} W_{ij'} \psi_{j'}(\vec{r}\sigma) \tag{L35}$$

$$= \int d\vec{r} \sum_{\sigma jj'} \delta_{jj'} \psi_j^*(\vec{r}\sigma) \frac{-\hbar^2\nabla^2}{2m} \psi_j(\vec{r}\sigma) \tag{L36}$$

$$= \int d\vec{r} \sum_{j\sigma} \psi_j^*(\vec{r}\sigma) \frac{-\hbar^2\nabla^2}{2m} \psi_j(\vec{r}\sigma). \tag{L37}$$

$$\sum_{ij} \sum_{ll'} \psi_l^* W_{li}^* \mathcal{E}_{ij} W_{il'} \psi_{l'} \tag{L38}$$

$$= \sum_{ll'} \psi_l \tilde{\mathcal{E}}_{ll'} \psi_{l'}, \tag{L39}$$

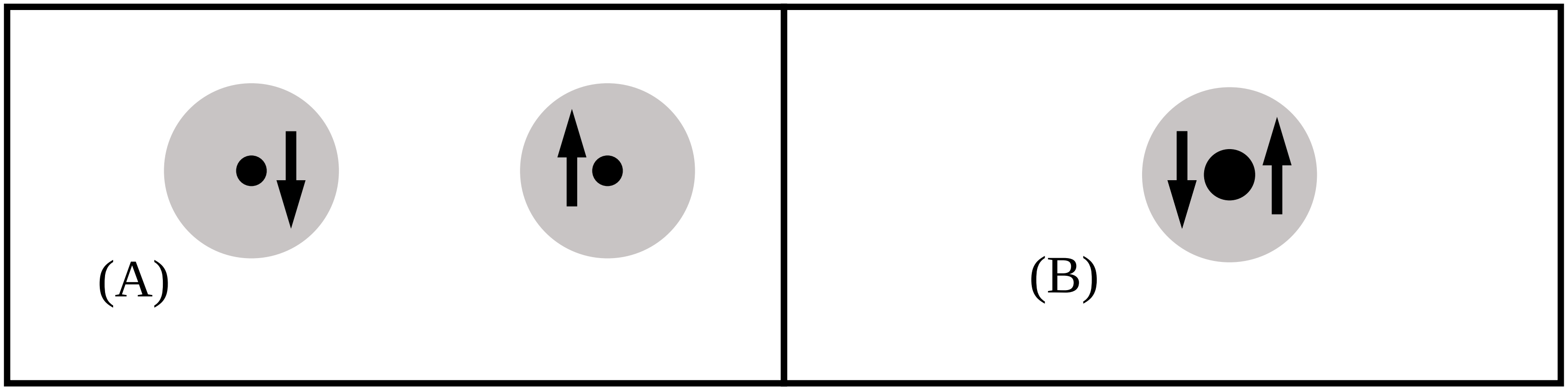
where

$$\tilde{\mathcal{E}}_{ll'} = \sum_{ij} W_{li}^* \mathcal{E}_{ij} W_{jl'} \tag{L40}$$

Final equations

$$\mathcal{E}_i\phi_i(\vec{r}) = \left[\begin{array}{l} \dfrac{-\hbar^2\nabla^2}{2m}\phi_i(\vec{r}) + U(\vec{r})\phi_i(\vec{r}) \\ +\phi_i(\vec{r})\displaystyle\int d\vec{r}\,' \sum_{j=1}^{N} \frac{e^2|\phi_j(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|} \\ -\displaystyle\sum_{j=1}^{N} \delta_{\chi_i\chi_j}\,\phi_j(\vec{r})\int d\vec{r}\,' \frac{e^2\phi_j^*(\vec{r}\,')\phi_i(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \end{array}\right]. \tag{L41}$$

Practical implementation



$$\int d\vec{r} e^{-\lambda_1|\vec{r}-\vec{r}_1|} e^{-\lambda_2|\vec{r}-\vec{r}_2|}, \tag{L42}$$

$$\gamma_l = \sum_{l'} A_{ll'} e^{-a_j\left(\vec{r}-\vec{R}_{l'}\right)^2}, \tag{L43}$$

$$\gamma_1, \gamma_2 \ldots \gamma_K, \tag{L44}$$

$$\phi_l = \sum_{k=1}^{K} B_{lk}\gamma_k, \tag{L45}$$

Practical implementation

Molecule	CH_4	NH_3	H_2O	FH	CO
Bond length (Å): Hartree–Fock	2.048	1.890	1.776	1.696	
Bond length (Å): experiment	2.050	1.912	1.809	1.733	
Ionization potential (eV): Hartree–Fock	0.546	0.428	0.507	0.650	
Ionization potential (eV): experiment	0.529	0.400	0.463	0.581	
Dipole moment (e Å): Hartree–Fock		0.653	0.785	0.764	−0.110
Dipole moment (e Å): experiment		0.579	0.728	0.716	0.044

Jellium

$$
\begin{aligned}
& \qquad\quad \textit{Kinetic energy} && \textit{Interaction with ions} \\
\mathcal{E}_l \phi_l(\vec{r}) = \; & \frac{-\hbar^2 \nabla^2}{2m} \phi_l(\vec{r}) && -\phi_l(\vec{r}) \frac{N}{\mathcal{V}} \int d\vec{r}_2 \frac{e^2}{|\vec{r}-\vec{r}_2|} \\
& +\phi_l(\vec{r}) \int d\vec{r}_2 \sum_{j=1}^{N} \frac{e^2 |\phi_j(\vec{r}_2)|^2}{|\vec{r}-\vec{r}_2|} && -\sum_{j=1}^{N} \delta_{\chi_l \chi_j} \phi_j(\vec{r}) \int d\vec{r}_2 \frac{e^2 \phi_j^*(\vec{r}_2) \phi_l(\vec{r}_2)}{|\vec{r}-\vec{r}_2|}. \\
& \qquad\quad \textit{Coulomb interaction} && \textit{Exchange interaction}
\end{aligned} \tag{L46}
$$

$$
\phi_l(\vec{r}) = \frac{e^{i\vec{k}_l \cdot \vec{r}}}{\sqrt{\mathcal{V}}}. \tag{L47}
$$

Kinetic energy

$$\frac{\hbar^2 k_l^2}{2m}\phi_l(\vec{r}). \quad \text{(L48)}$$

$|\phi_j(\vec{r}_2)|^2 = 1/\mathcal{V}$

$$e^2 \sum_{j=1}^{N} \frac{e^{i\vec{k}_j \cdot \vec{r}}}{\sqrt{\mathcal{V}}} \int \frac{d\vec{r}_2}{\mathcal{V}} \frac{e^{i(\vec{k}_l - \vec{k}_j)\cdot \vec{r}_2}}{|\vec{r} - \vec{r}_2|} \delta_{\chi_l \chi_j} \tag{L49}$$

$$= e^2 \phi_l \sum_{j=1}^{N} \int \frac{d\vec{r}'}{\mathcal{V}} \frac{e^{i(\vec{k}_l - \vec{k}_j)\cdot \vec{r}'}}{r'} \delta_{\chi_l, \chi_j} \tag{L50}$$

$$= e^2 \phi_l \sum_{j=1}^{N} \frac{1}{\mathcal{V}} \frac{4\pi}{|\vec{k}_l - \vec{k}_j|^2} \delta_{\chi_l, \chi_j} \tag{L51}$$

$$= e^2 \phi_l \int^{k_F} \frac{d\vec{k}}{(2\pi)^3} \frac{4\pi}{k_l^2 + k^2 - 2\vec{k} \cdot \vec{k}_l} \tag{L52}$$

$$= e^2 \phi_l(\vec{r}) \frac{1}{2\pi k_l} \left[\left(k_F^2 - k_l^2\right) \ln\left\{ \frac{k_F + k_l}{k_F - k_l} \right\} + 2k_l k_F \right]. \tag{L53}$$

Energy of jellium, Lindhart dielectric function

$$\mathcal{E}_l = \frac{\hbar^2 k_l^2}{2m} - \frac{2e^2}{\pi} k_F F(k_l/k_F), \tag{L54}$$

$$F(x) = \frac{1}{4x}\left[\left(1-x^2\right)\ln\left\{\frac{1+x}{1-x}\right\} + 2x\right]. \tag{L55}$$

Electron velocity diverges at Fermi surface. Hartree–Fock incorrectly omits effects of screening.

Total energy

$$\mathcal{E} = \sum_l \frac{\hbar^2 k_l^2}{2m} - \frac{e^2}{\pi} k_F F\left(\frac{k_l}{k_F}\right) \quad \text{(L56)}$$

$$= N\left[\frac{3}{5}\mathcal{E}_F - \frac{3}{4}\frac{e^2 k_F}{\pi}\right]. \quad \text{(L57)}$$

$$n(\vec{r}) = \langle \Psi | \sum_{l=1}^{N} \delta(\vec{r} - \vec{R}_l) | \Psi \rangle \tag{L58}$$

$$= N \int d\vec{r}_1 \ldots d\vec{r}_N \Psi^*(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N) \delta(\vec{r} - \vec{r}_1) \Psi(\vec{r}_1 \ldots \vec{r}_N). \tag{L59}$$

$$\mathcal{E}_1 = \langle \Psi_1 | \mathcal{H}_1 | \Psi_1 \rangle < \langle \Psi_2 | \mathcal{H}_1 | \Psi_2 \rangle \tag{L60}$$

$$\Rightarrow \mathcal{E}_1 < \langle \Psi_2 | \mathcal{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | (\hat{\mathcal{H}}_1 - \hat{\mathcal{H}}_2) | \Psi_2 \rangle \tag{L61}$$

$$\Rightarrow \mathcal{E}_1 < \mathcal{E}_2 + \int d\vec{r} n(\vec{r}) \left[U_1(\vec{r}) - U_2(\vec{r}) \right]. \tag{L62}$$

$$\mathcal{E}_2 < \mathcal{E}_1 + \int d\vec{r}\, n(\vec{r}) \left[U_2(\vec{r}) - U_1(\vec{r}) \right]. \tag{L63}$$

$$\mathcal{E}_1 + \mathcal{E}_2 < \mathcal{E}_1 + \mathcal{E}_2, \tag{L64}$$

$$\mathcal{E}[n] = T[n] + U[n] + U_{\mathrm{ee}}[n]. \tag{L65}$$

$$\int d\vec{r}\, n(\vec{r}) = N. \tag{L66}$$

$$\langle \Psi_2 | \mathcal{H}_1 | \Psi_2 \rangle = \mathcal{E}_1[n_2]. \tag{L67}$$

$$\mu = \frac{\delta E[\rho]}{\delta n(\vec{r})}, \tag{L68}$$

$$\mathcal{E}[n] = \int d\vec{r}\, n(\vec{r}) U(\vec{r}) + F_{HK}[n], \tag{L69}$$

$$F_{HK}[n] = T[n] + U_{\text{ee}}[n]. \tag{L70}$$

General derivation

$$F[n] \equiv \min_{\Psi \to n} \langle \Psi | T + U_{\text{ee}} | \Psi \rangle. \tag{L71}$$

$$\begin{aligned}
\mathcal{E}_0 &= \min_{\Psi} \langle \Psi | T + U + U_{\text{ee}} | \Psi \rangle && \text{(L72)} \\
&= \min_{n} [\min_{\Psi \to n} \langle \Psi | T + U + U_{\text{ee}} | \Psi \rangle] && \text{(L73)} \\
&= \min_{n} \left[\min_{\Psi \to n} \langle \Psi | T + U_{\text{ee}} | \Psi \rangle + \int U(\vec{r}) n(\vec{r}) d\vec{r} \right] && \text{(L74)} \\
&= \min_{n} \left[F[n] + \int U(\vec{r}) n(\vec{r}) d\vec{r} \right] && \text{(L75)} \\
&\equiv \min_{n} \mathcal{E}[n]. && \text{(L76)}
\end{aligned}$$

Thomas–Fermi theory

$$T = \mathcal{V}\int [d\vec{k}]\,\frac{\hbar^2 k^2}{2m} \tag{L77}$$

$$= \mathcal{V}\frac{\hbar^2 k_F^5}{2m5\pi^2} = \mathcal{V}\frac{\hbar^2}{2m}\frac{3}{5}(3\pi^2)^{2/3}n^{5/3}. \tag{L78}$$

$$\frac{1}{2}\int d\vec{r}_2 d\vec{r}_1 \frac{e^2 n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}. \tag{L79}$$

$$-N\frac{3}{4}\frac{e^2 k_F}{\pi} = -\mathcal{V}\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} e^2 n^{4/3}. \tag{L80}$$

$$T[n] = \int d\vec{r}\,\frac{\hbar^2}{2m}\frac{3}{5}\left(3\pi^2\right)^{2/3} n^{5/3}(\vec{r}), \tag{L81}$$

$$\mathcal{E}_{xc} = -\int d\vec{r}\,\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} e^2 n^{4/3}(\vec{r}). \tag{L82}$$

$$\mathcal{E}[n] = \frac{\hbar^2}{2m}\frac{3}{5}\left(3\pi^2\right)^{2/3}\int d\vec{r}\, n^{5/3}(\vec{r}) + \int d\vec{r}\, n(\vec{r})U(\vec{r})$$

$$+ \frac{1}{2}\int d\vec{r}_2 d\vec{r}_1 \frac{e^2 n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} - \int d\vec{r}\,\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} e^2 n^{4/3}(\vec{r}). \quad \text{(L83)}$$

$$\frac{\delta\mathcal{E}}{\delta n(\vec{r})} = \mu \quad \text{(L84)}$$

$$\Rightarrow \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} n^{2/3}(\vec{r}) + U(\vec{r}) + \int d\vec{r}_2 \frac{e^2 n(\vec{r}_2)}{|\vec{r} - \vec{r}_2|} - \left(\frac{3}{\pi}\right)^{1/3} e^2 n^{1/3}(\vec{r}) = \mu. \quad \text{(L85)}$$

Atom of charge Z has energy $-1.5375 Z^{7/3}$ Ry

Kohn–Sham equations

$$n(\vec{r}) = \sum_{l=1}^{N} |\psi_l(\vec{r})|^2. \tag{L86}$$

$$T[n] = \sum_l \frac{\hbar^2}{2m} (\nabla\psi_l)^2 . \tag{L87}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_l(\vec{r}) + \left[U(\vec{r}) + \int d\vec{r}\,' \frac{e^2 n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + \frac{\partial \mathcal{E}_{xc}(n)}{\partial n}\right]\psi_l(\vec{r}) = \mathcal{E}_l\psi_l(\vec{r}). \tag{L88}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_l(\vec{r}) + \left[U(\vec{r}) + \int d\vec{r}\,' \frac{e^2 n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} - e^2\left(\frac{3}{\pi}n(\vec{r})\right)^{1/3}\right]\psi_l(\vec{r}) = \mathcal{E}_l(\vec{r}). \tag{L89}$$

Local density approximation

Atom	LDA	Hartree–Fock	Experiment
He	−2.83	−2.86	−2.9
Li	−7.33	−7.43	−7.48
Ne	−128.12	−128.55	−128.94
Ar	−525.85	−526.82	−527.60

$$\left[\int d\vec{r}\,\hbar^2|\vec{\nabla}\psi|^2\right]\left[\int d\vec{r}\,r^2|\psi|^2\right] \geq \frac{\hbar^2}{4}; \tag{L90}$$

$$T[n] \geq \frac{\hbar^2}{8m\int d\vec{r}\,r^2 n(\vec{r})}. \tag{L91}$$

$$T[n] \geq \frac{\hbar^2}{2m}\frac{9.116}{(8\pi)^{2/3}}\int d\vec{r}\,n^{5/3}. \tag{L92}$$

$$T[n] = \frac{\hbar^2}{2m}\int d\vec{r}\,|\nabla\psi|^2 \tag{L93}$$

$$T[n] \geq \frac{\hbar^2}{2m}K_s\int d\vec{r}\,n^{5/3}, \tag{L94}$$

$$K_s = 3(\pi/2)^{4/3}, \tag{L95}$$

$$n(\vec{r}) = |\psi(\vec{r})|^2. \tag{L96}$$

$$\frac{\hbar^2}{2m}K_s\int d\vec{r}\,n^{5/3} - \int d\vec{r}\,\frac{e^2 n(\vec{r})}{r}. \tag{L97}$$

$$\lambda(1-\int d\vec{r}\,n) \quad = \quad 0 \tag{L98}$$

is

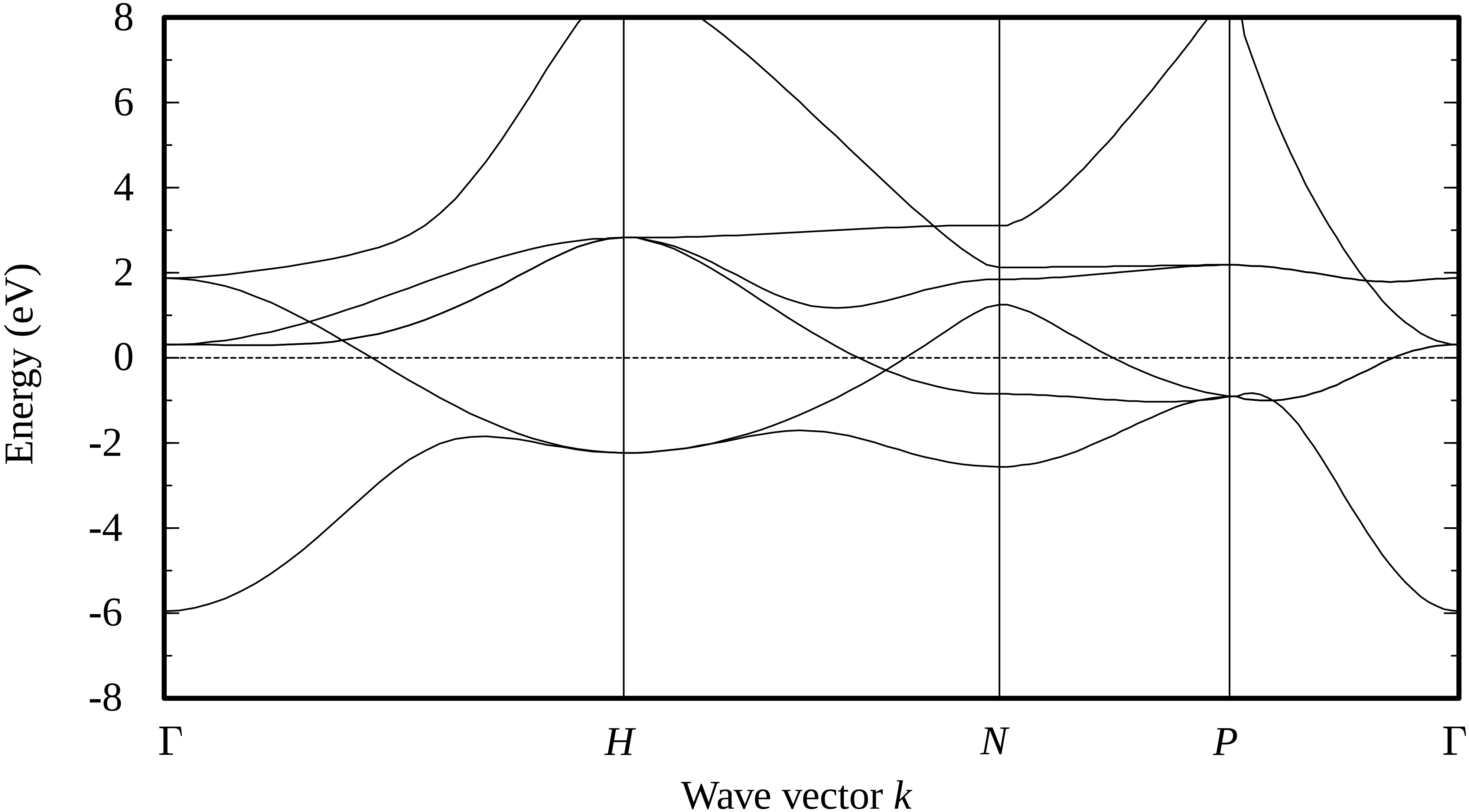
Stability of matter

$$\frac{5}{3}\frac{\hbar^2}{2m}K_s n^{2/3}(\vec{r}) - e^2/r + \lambda \quad = \quad 0. \tag{L99}$$

$$n(\vec{r}) = \begin{cases} \left\{6m[e^2/r-\lambda]/(5K_s\hbar^2)\right\}^{3/2} & \text{for} \quad r < e^2/\lambda \\ 0 & \text{else} \end{cases} . \tag{L100}$$

$$\lambda = \frac{3me^4}{5\hbar^2 K_s}\left(\frac{\pi^4}{2}\right)^{1/3}; \tag{L101}$$

$$-\frac{9me^4}{10\hbar^2 K_s}(2\pi^2)^{2/3} = -\frac{6}{5}\frac{me^4}{\hbar^2} = -\frac{12}{5}\text{Ry}. \tag{L102}$$


8
6
4
2
0
-2
-4
-6
-8
Energy (eV)
Γ
H
N
P
Γ
Wave vector k

Question: How could it ever be true that electrons in a metal think they are moving freely in an empty box?

Pseudopotentials give conceptual answer.

☞ Restrict attention to single unit cell.

☞ Let $|\vec{k}\rangle$ denote plane waves $e^{i\vec{k}\cdot\vec{r}}$.

☞ Let $|\psi_c\rangle$ denote core states.

$$|\vec{k}_{\rm ps}\rangle = |\vec{k}\rangle - \sum_c |\psi_c\rangle\langle\psi_c|\vec{k}\rangle, \tag{L1}$$

$$\hat{U}|\vec{k}_{\rm ps}\rangle = \hat{U}|\vec{k}\rangle - \sum_c \hat{U}\langle\psi_c|\vec{k}\rangle|\psi_c\rangle. \tag{L2}$$

$$(\hat{\mathcal{H}} - \mathcal{E})|\vec{k}_{\rm ps}\rangle = \left(\frac{\hat{P}^2}{2m} + \hat{U} - \mathcal{E}\right)|\vec{k}_{\rm ps}\rangle \tag{L3}$$

$$= \ ?$$

Pseudopotentials

$$? \quad = \quad \left(\frac{\hat{P}^2}{2m} + \hat{U}_{\text{ps}} - \mathcal{E}\right)|\vec{k}\rangle = (\hat{\mathcal{H}}_{\text{ps}} - \mathcal{E})|\vec{k}\rangle, \tag{L6}$$

$$\hat{U}_{\text{ps}} = \hat{U} - \sum_c (\mathcal{E}_c - \mathcal{E})|\psi_c\rangle\langle\psi_c|. \tag{L7}$$

$$(\hat{\mathcal{H}} - \mathcal{E})|\vec{k}_{\text{ps}}\rangle = (\hat{\mathcal{H}}_{\text{ps}} - \mathcal{E})|\vec{k}\rangle. \tag{L8}$$

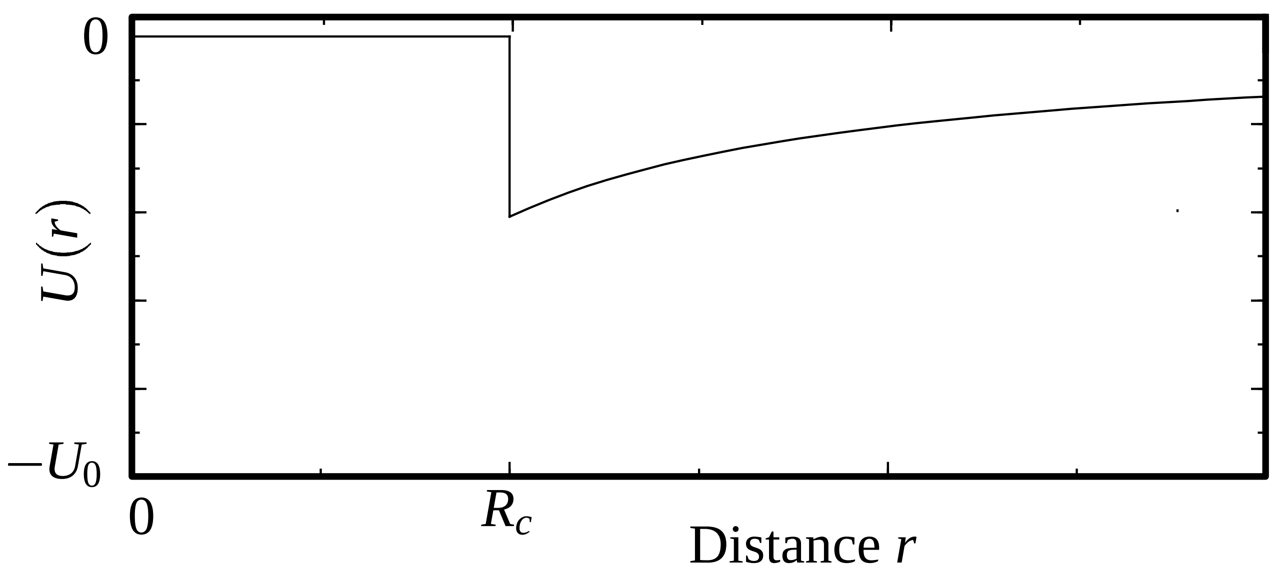


Figure 1: The Ashcroft empty core pseudopotential is zero up to a critical radius R_c, and it equals a screened Coulomb potential $-U_0 \exp[-r/d]/r$ thereafter.

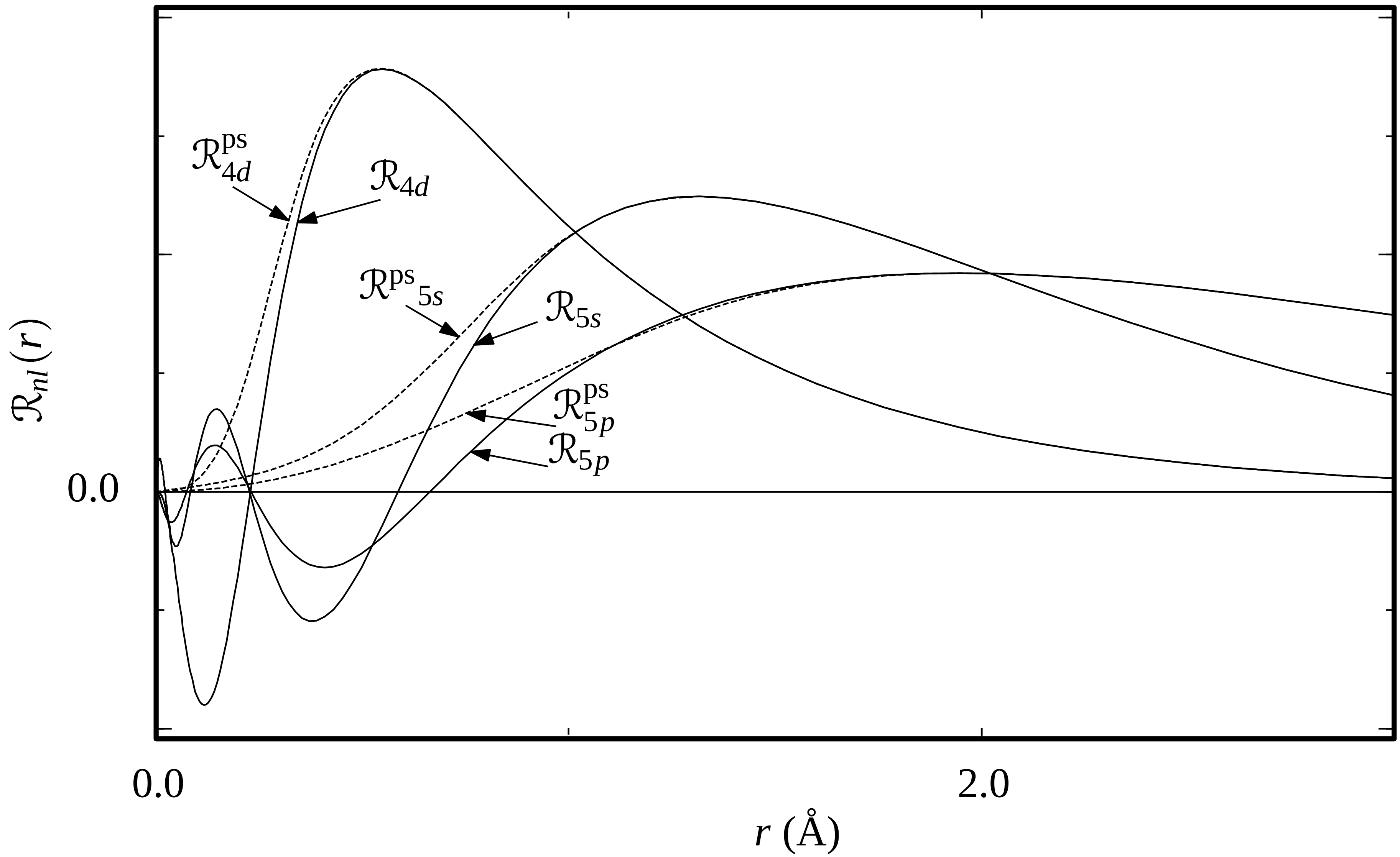


Figure 2: Real and pseudo wave functions for the 5s, 5p, and 4d levels of silver. The 5p level is not much occupied in the ground state of silver, but it can be included in the pseudopotential nevertheless.

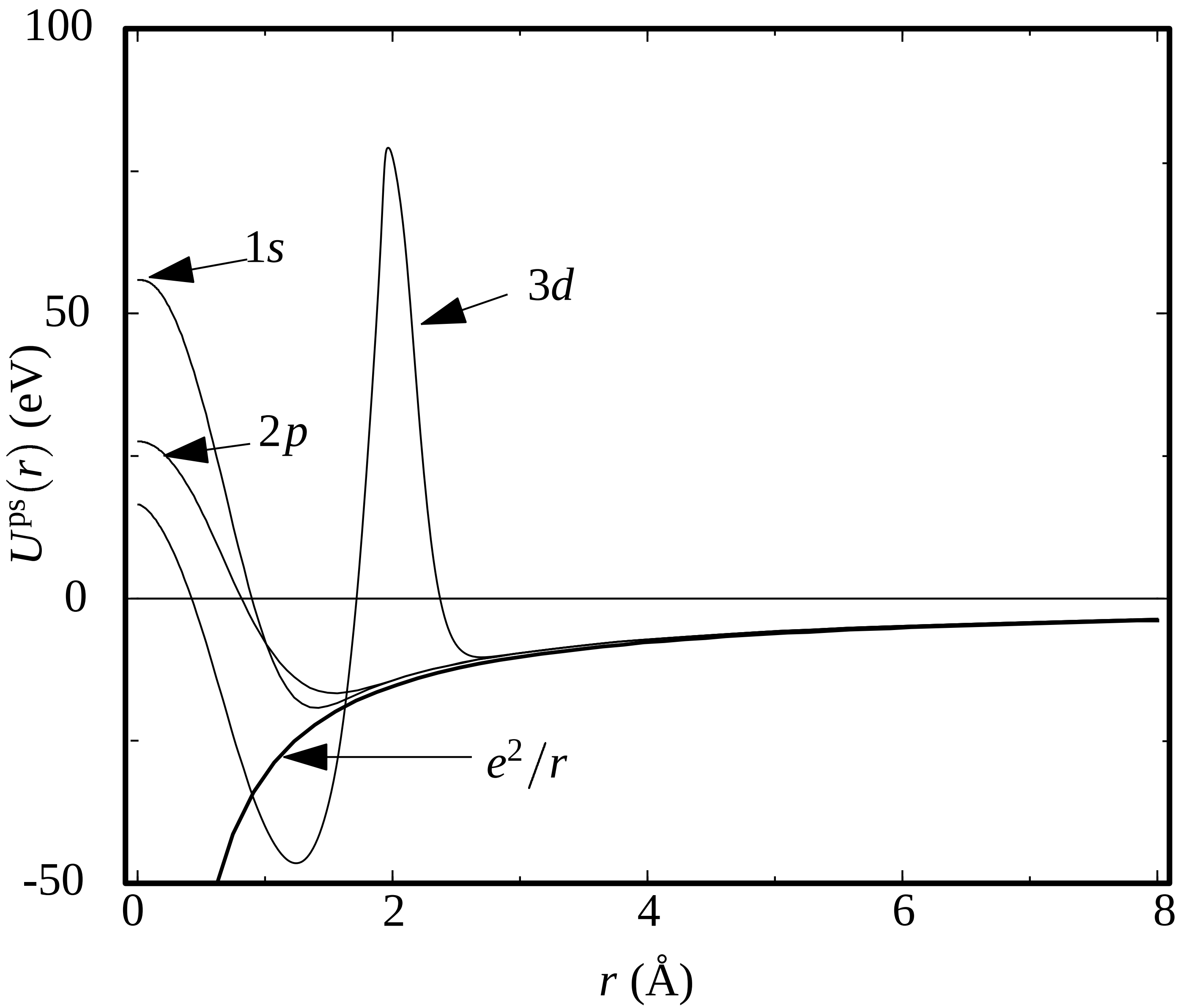


Figure 3: Pseudopotentials for the 5*s*, 5*p*, and 4*d* states of silver.

Electron density $n(\vec{r}) = \sum |\psi_i(\vec{r})|^2$ is spherically symmetrical in vicinity of nucleus

Equation for radial functions is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{l(l+1)}{r^2}\right]\mathcal{R}_{nl} + \left[\int \frac{e^2 n(r')}{|\vec{r}-\vec{r}'|}d\vec{r}' - \frac{e^2 Z}{r} + \frac{\delta \mathcal{E}_{xc}}{\delta n} - \mathcal{E}_{nl}\right]\mathcal{R}_{nl}(r) = 0. \quad \text{(L9)}$$

$$\begin{aligned} U_l^{\text{ps}}(r) = \quad & \frac{\hbar^2}{2m}\left[\frac{1}{r\mathcal{R}_{nl}^{\text{ps}}}\frac{\partial^2 r\mathcal{R}_{nl}^{\text{ps}}}{\partial r^2} - \frac{l(l+1)}{r^2}\right] \\ - \quad & \left[\int \frac{e^2 n^{\text{ps}}(r')}{|\vec{r}-\vec{r}'|}d\vec{r}' + \frac{\delta \mathcal{E}_{xc}}{\delta n^{\text{ps}}} - \mathcal{E}_{nl}\right]. \end{aligned} \quad \text{(L10)}$$

$$\psi(\vec{r}) = \sum_{lm} Y_{lm}(\theta,\phi)\psi_{lm}(r); \quad \psi_{lm}(r) = \int d\theta d\phi \sin\theta Y^*_{lm}(\theta,\phi)\psi(\vec{r}), \quad \text{(L11)}$$

Screening

$$U^{\mathrm{ps}} = \frac{4\pi Z e^2}{q^2+\kappa^2}. \tag{L12}$$

Result from later work....

$$\frac{1}{\Omega}U^{\mathrm{ps}}(q=0) = -\frac{2}{3}\mathcal{E}_F. \tag{L13}$$

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R},l} b_l e^{i\vec{k}\cdot\vec{R}} a_l^{\text{at}}(\vec{r}-\vec{R}), \tag{L14}$$

$$\langle\psi|\hat{\mathcal{H}}-\mathcal{E}|\psi\rangle. \tag{L15}$$

$$\langle\psi|\mathcal{E}|\psi\rangle = \mathcal{E}\sum_{\vec{R}\vec{R}'}\int d\vec{r}a^{\text{at}}(\vec{r}-\vec{R})a^{\text{at}}(\vec{r}-\vec{R}')\frac{e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}}{N}b^2 \tag{L16}$$

$$= b^2\mathcal{E}(1+\sum_{\vec{\delta}}\alpha e^{i\vec{k}\cdot\vec{\delta}}) \tag{L17}$$

and

$$\alpha = \int d\vec{r}\,a^{\text{at}}(\vec{r})a^{\text{at}}(\vec{r}+\vec{\delta}). \tag{L18}$$

$$\langle\psi|\hat{\mathcal{H}}|\psi\rangle = \sum_{\vec{R}\vec{R}'}\int d\vec{r}a^{\text{at}}(\vec{r}-\vec{R})[-\frac{\hbar^2}{2m}\nabla^2+U(\vec{r})]a^{\text{at}}(\vec{r}-\vec{R}')\frac{e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}}{N}b^2 \tag{L19}$$

$$= \sum_{\vec R \vec R'} \int d\vec r a^{\rm at}(\vec r - \vec R) \left\{ \begin{array}{cc} & [-\frac{\hbar^2}{2m}\nabla^2 + U^{\rm at}(\vec r - \vec R')]a^{\rm at}(\vec r - \vec R') \\ + & [U(\vec r) - U^{\rm at}(\vec r - \vec R')]a^{\rm at}(\vec r - \vec R') \end{array} \right\} \frac{e^{i\vec k\cdot(\vec R - \vec R')}}{N} b^2 \quad \text{(L20)}$$

$$= \int d\vec r \sum_{\vec R \vec R'} \mathcal{E}^{\rm at} \frac{a^{\rm at}(\vec r - \vec R) a^{\rm at}(\vec r - \vec R')}{N} e^{i\vec k\cdot(\vec R - \vec R')} b^2$$

$$+ \int d\vec r \sum_{\vec R \vec R'} a^{\rm at}(\vec r - \vec R)[U(\vec r) - U^{\rm at}(\vec r - \vec R')]a^{\rm at}(\vec r - \vec R') \frac{e^{i\vec k\cdot(\vec R - \vec R')}}{N} b^2. \quad \text{(L21)}$$

$$\mathcal{E}(1 + \sum_{\vec\delta} \alpha e^{i\vec k\cdot\vec\delta}) = \mathcal{E}^{\rm at} \sum_{\vec\delta} \alpha e^{i\vec k\cdot\vec\delta} + U + (\mathfrak{t} - \alpha\mathcal{E}^{\rm at}) \sum_{\vec\delta} e^{i\vec k\cdot\vec\delta}, \quad \text{(L22)}$$

where

$$U = \mathcal{E}^{\rm at} + \int d\vec r a^{\rm at}(\vec r)[U(\vec r) - U^{\rm at}(\vec r)]a^{\rm at}(\vec r) \quad \text{(L23)}$$

and

$$\mathfrak{t} = \alpha\mathcal{E}^{\rm at} + \int d\vec r a^{\rm at}(\vec r)[U(\vec r) - U^{\rm at}(\vec r + \vec\delta)]a^{\rm at}(\vec r + \vec\delta). \quad \text{(L24)}$$

$$\mathcal{E} = U + \mathfrak{t} \sum_{\vec{\delta}} e^{i\vec{k}\cdot\vec{\delta}}. \quad \text{(L25)}$$

$$\vec{K} = l_1\vec{b}_1 + l_2\vec{b}_2 + l_3\vec{b}_3 \tag{L26}$$

$$\sum_{i=1}^{N} \lambda_i^r \hat{e}_i(\hat{e}_i \cdot \vec{a}_1). \tag{L27}$$

$$\hat{\mathcal{H}} = \frac{\hat{P}^2}{2m} + U(\hat{R}). \tag{L28}$$

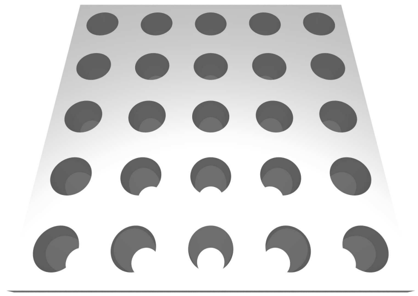
$\hbar^2 K_{\max}^2/2m = \mathcal{E}_{\max}$

$$\hat{\mathcal{H}}\psi = \sum_{\vec{K}'} \left\{ \left[\mathcal{E}^0_{\vec{k}+\vec{K}'} - \mathcal{E}_{\max} \right] \delta_{\vec{K}\vec{K}'} + U_{\vec{K}-\vec{K}'} \right\} \psi_{n\vec{k}}(\vec{K}'), \tag{L29}$$

$$1 + \hat{\mathcal{H}}\, dt/\hbar. \tag{L30}$$

$$\psi_{n+1} = (1 + \hat{\mathcal{H}} dt/\hbar)\psi_n \Rightarrow \frac{\psi_{n+1} - \psi_n}{dt} = \frac{1}{\hbar}\hat{\mathcal{H}}\psi_n, \tag{L31}$$

Linear Augmented Plane Waves (LAPW)



$$\phi_{\mathcal{E}\vec{k}} = e^{i\vec{k}\cdot\vec{r}}$$

$$-\frac{1}{2m}\hbar^2\nabla^2\phi_{\mathcal{E}\vec{k}} + U(r)\phi_{\mathcal{E}\vec{k}} = \mathcal{E}\phi_{\mathcal{E}\vec{k}}$$

$$\psi_{\mathcal{E}} = Y_{lm}\mathcal{R}_{l\mathcal{E}}(r), \tag{L32}$$

$$\frac{-\hbar^2}{2mr^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\mathcal{R}_{l\mathcal{E}}(r) + [U(r) + \frac{\hbar^2 l(l+1)}{2mr^2}]\mathcal{R}_{l\mathcal{E}}(r) = \mathcal{E}\mathcal{R}_{l\mathcal{E}}(r). \tag{L33}$$

$$\phi_{\mathcal{E}\vec{k}} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} A_{lm}Y_{lm}(\hat{r})\mathcal{R}_{l\mathcal{E}}(r), \tag{L34}$$

$$e^{i\vec{k}\cdot\vec{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr) Y^*_{lm}(\hat{k}) Y_{lm}(\hat{r}). \tag{L35}$$

$$\phi_{\mathcal{E}\vec{k}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{i^l j_l(kR_h) Y^*_{lm}(\hat{k})}{\mathcal{R}_{l\mathcal{E}}(R_h)} Y_{lm}(\hat{r}) \mathcal{R}_{l\mathcal{E}}(r). \tag{L36}$$

$$\psi_{\vec{k}} = \sum_{\vec{K}} b_{\vec{k}+\vec{K}} \phi_{\mathcal{E},\vec{k}+\vec{K}}. \tag{L37}$$

$$\langle \psi | \hat{\mathcal{H}} - \mathcal{E} | \psi \rangle, \tag{L38}$$

$$0 = \sum_{\vec{K}} \langle \phi_{\mathcal{E}\vec{q}} | \hat{\mathcal{H}} - \mathcal{E} | \phi_{\mathcal{E}\vec{q}+\vec{K}} \rangle b_{\vec{q}+\vec{K}}, \tag{L39}$$

where

$$\langle \phi_{\mathcal{E}\vec{q}} | \hat{\mathcal{H}} - \mathcal{E} | \phi_{\mathcal{E}\vec{q}'} \rangle = \left(\frac{\hbar^2 \vec{q}\cdot\vec{q}'}{2m} - \mathcal{E}\right) \Omega \delta_{\vec{q},\vec{q}'} + \mathcal{U}_{\vec{q},\vec{q}'} \tag{L40}$$

$$\mathcal{U}_{\vec{q},\vec{q}'} = 4\pi R_h^2 \left\{ \begin{array}{ll} - & \left(\frac{\hbar^2 \vec{q}\cdot\vec{q}'}{2m} - \mathcal{E}\right) \frac{j_1(|\vec{q}-\vec{q}'|R_h)}{|\vec{q}-\vec{q}'|} \\ + & \sum_{l=0}^{\infty} \frac{\hbar^2}{2m} (2l+1) P_l(\hat{q}\cdot\hat{q}') j_l(qR_h) j_l(q'R_h) \frac{\mathcal{R}'_{l\mathcal{E}}(R_h)}{\mathcal{R}_{l\mathcal{E}}(R_h)} \end{array} \right\}. \quad \text{(L41)}$$

$$\chi_{lm}(\mathcal{E},r) = \begin{cases} i^l Y_l^m(\hat{r})[\mathcal{R}_{l\mathcal{E}}(r) + (\frac{r}{R_h})^l p_{l\mathcal{E}}] & \text{for } r < R_h \\ i^l Y_l^m(\hat{r})(\frac{R_h}{r})^{l+1} & \text{for } r > R_h. \end{cases} \quad \text{(L42)}$$

$$\begin{aligned} \mathcal{R}_{l\mathcal{E}}(R_h) + p_{l\mathcal{E}} &= 1 \\ \mathcal{R}'_{l\mathcal{E}}(R_h) + l\frac{p_{l\mathcal{E}}}{R_h} &= -\frac{l+1}{R_h}. \end{aligned} \quad \text{(L43)}$$

$$p_{l\mathcal{E}} = \frac{-(l+1)/R_h - \left.\frac{\partial \mathcal{R}_{l\mathcal{E}}}{\partial r}\right|_{R_h}}{l/R_h - \left.\frac{\partial \mathcal{R}_{l\mathcal{E}}}{\partial r}\right|_{R_h}} = \frac{\mathcal{D}_l(\mathcal{E}) + l + 1}{\mathcal{D}_l(\mathcal{E}) - l} \quad \text{(L44a)}$$

with

$$\mathcal{D}_l(\mathcal{E}) = \frac{R_h}{\mathcal{R}_{l\mathcal{E}}(R_h)} \left.\frac{\partial \mathcal{R}_{l\mathcal{E}}}{\partial r}\right|_{R_h}. \quad \text{(L44b)}$$

$$\psi(\vec{r}) = \sum_{lm} B_{lm}^{n\vec{k}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \chi_{lm}(\mathcal{E}, \vec{r} - \vec{R}) \quad \text{(L45)}$$

$$0 = \sum_{lm} B_{lm}^{n\vec{k}} \left[p_{l\varepsilon} i^l Y_l^m(\hat{r}) \left(\frac{r}{R_h} \right)^l + \sum_{\vec{R}\neq 0} i^l Y_l^m\left(\widehat{\vec{r}-\vec{R}}\right) \left(\frac{R_h}{|\vec{r}-\vec{R}|} \right)^{l+1} e^{i\vec{k}\cdot\vec{R}} \right]. \tag{L46}$$

$$\sum_{\vec{R}\neq 0} i^l Y_l^m(\widehat{\vec{r}-\vec{R}}) \left(\frac{R_h}{|\vec{r}-\vec{R}|} \right)^{l+1} e^{i\vec{k}\cdot\vec{R}} = -\sum_{l'm'} \frac{\mathcal{S}_{ll'mm'}^{\vec{k}}}{2(2l'+1)} \left(\frac{r}{R_h} \right)^{l'} i^{l'} Y_{l'}^{m'}(\hat{r}). \tag{L47}$$

$$0 = \sum_{lm} B_{lm}^{n\vec{k}} \left[p_{l\varepsilon} i^l Y_l^m(\hat{r}) \left(\frac{r}{R_h} \right)^l - \sum_{l'm'} \frac{\mathcal{S}_{ll'mm'}^{\vec{k}}}{2(2l'+1)} \left(\frac{r}{R_h} \right)^{l'} i^{l'} Y_{l'}^{m'}(\hat{r}) \right] \tag{L48}$$

$$\Rightarrow 0 = \sum_{lml'm'} B_{lm}^{n\vec{k}} \left[p_{l\varepsilon} \delta_{ll'} \delta_{mm'} - \frac{\mathcal{S}_{ll'mm'}^{\vec{k}}}{2(2l'+1)} \right] \left(\frac{r}{R_h} \right)^{l'} i^{l'} Y_{l'}^{m'}(\hat{r}). \tag{L49}$$

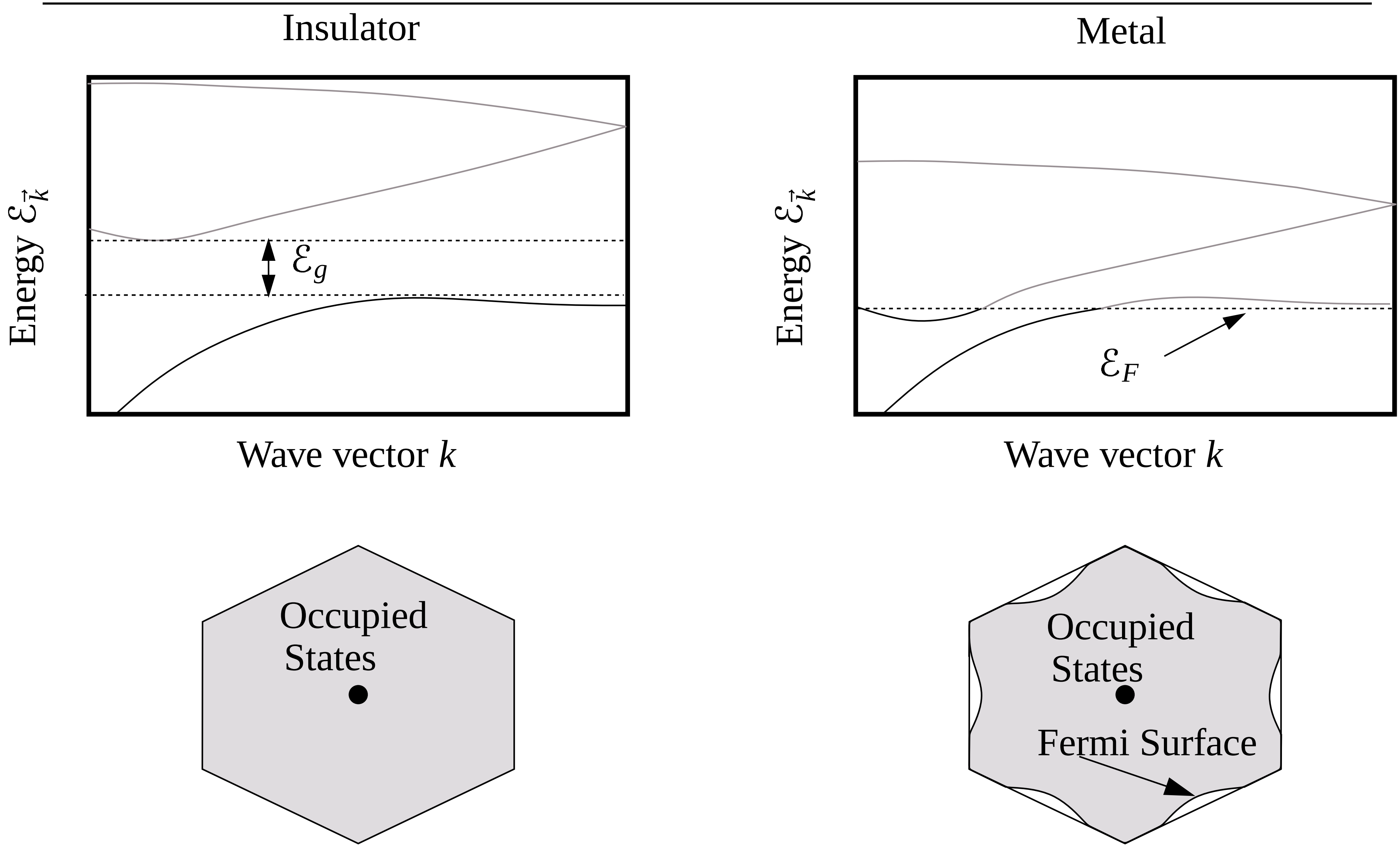
$$0 = \sum_{lm} \left[2(2l+1) p_{l\varepsilon} \delta_{ll'} \delta_{mm'} - \mathcal{S}_{ll'mm'}^{\vec{k}} \right] B_{lm}^{n\vec{k}}. \tag{L50}$$

Definition of Metals, Insulators, and Semiconductors

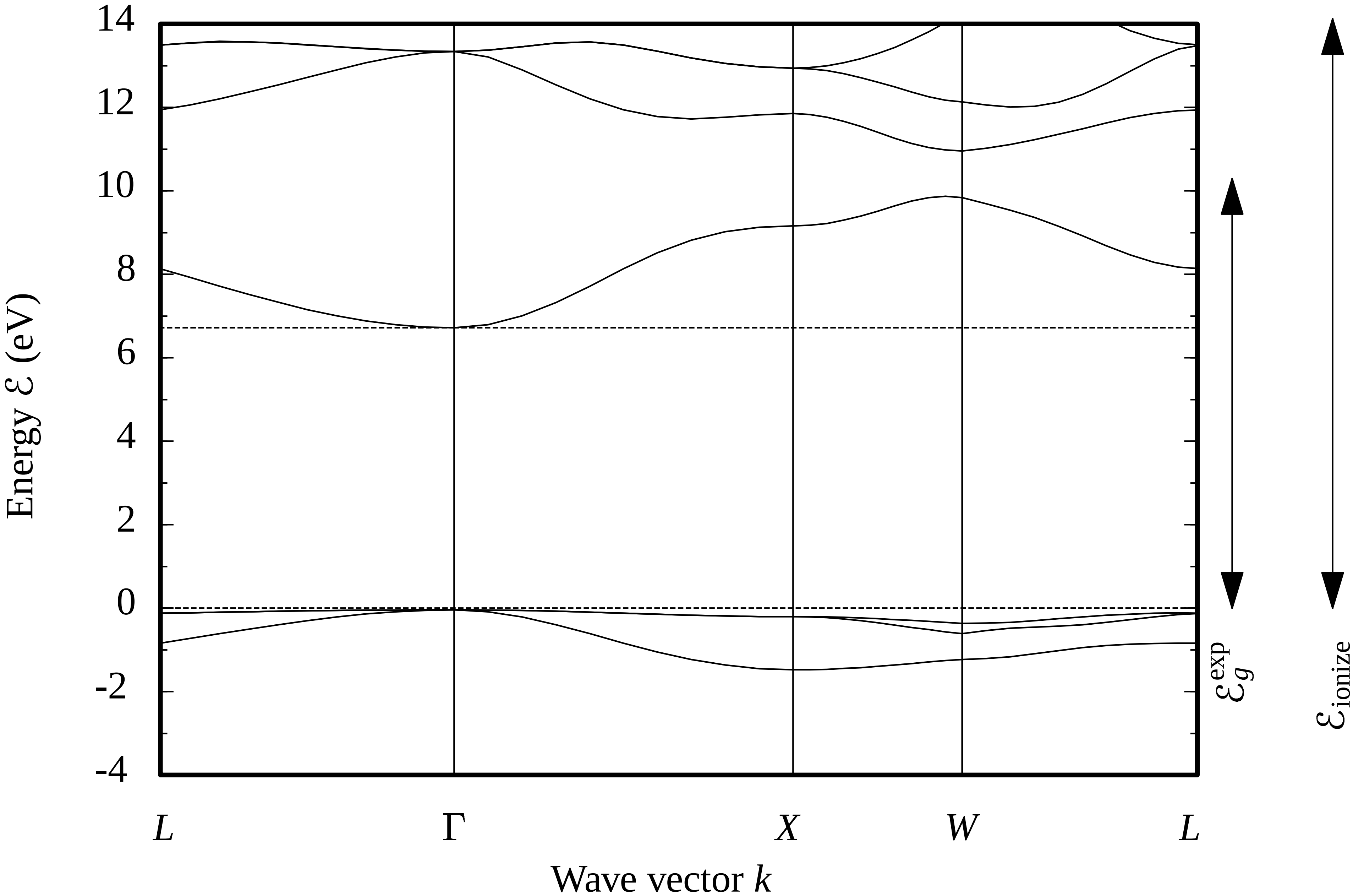
Wilson's theory:

- ☞ Insulator: All bands are either full or empty.
- ☞ Metal: At least one band is partially occupied.
- ☞ Semiconductor: Insulator where energy gap is less than around 1 eV.
- ☞ Semimetal: Metal with very small population of conduction electrons.

Definition of Metals, Insulators, and Semiconductors

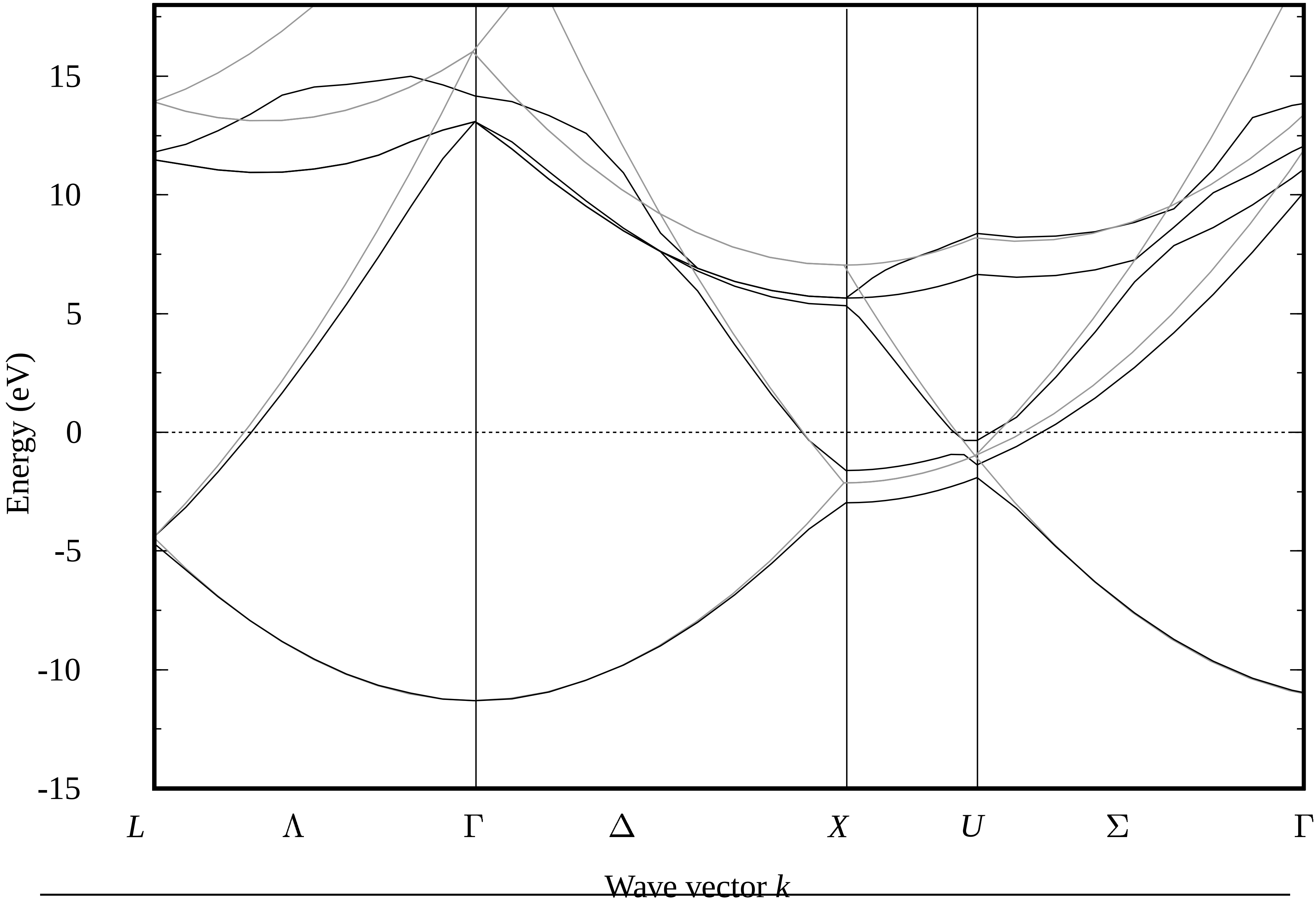


Noble Gases

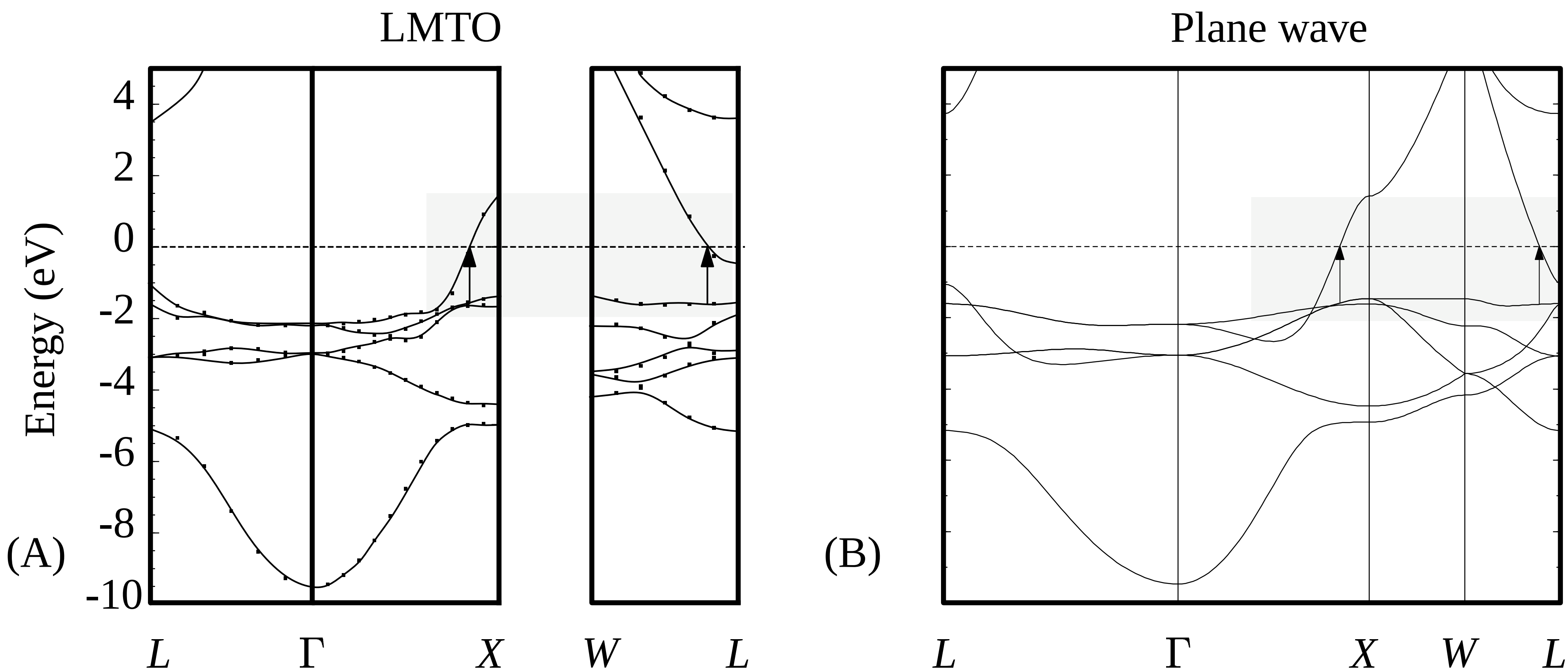


14
12
10
8
6
4
2
0
-2
-4
Energy $\mathcal{E}$ (eV)
L
Γ
X
W
L
Wave vector k
$\mathcal{E}_g^{\mathrm{exp}}$
$\mathcal{E}_{\mathrm{ionize}}$

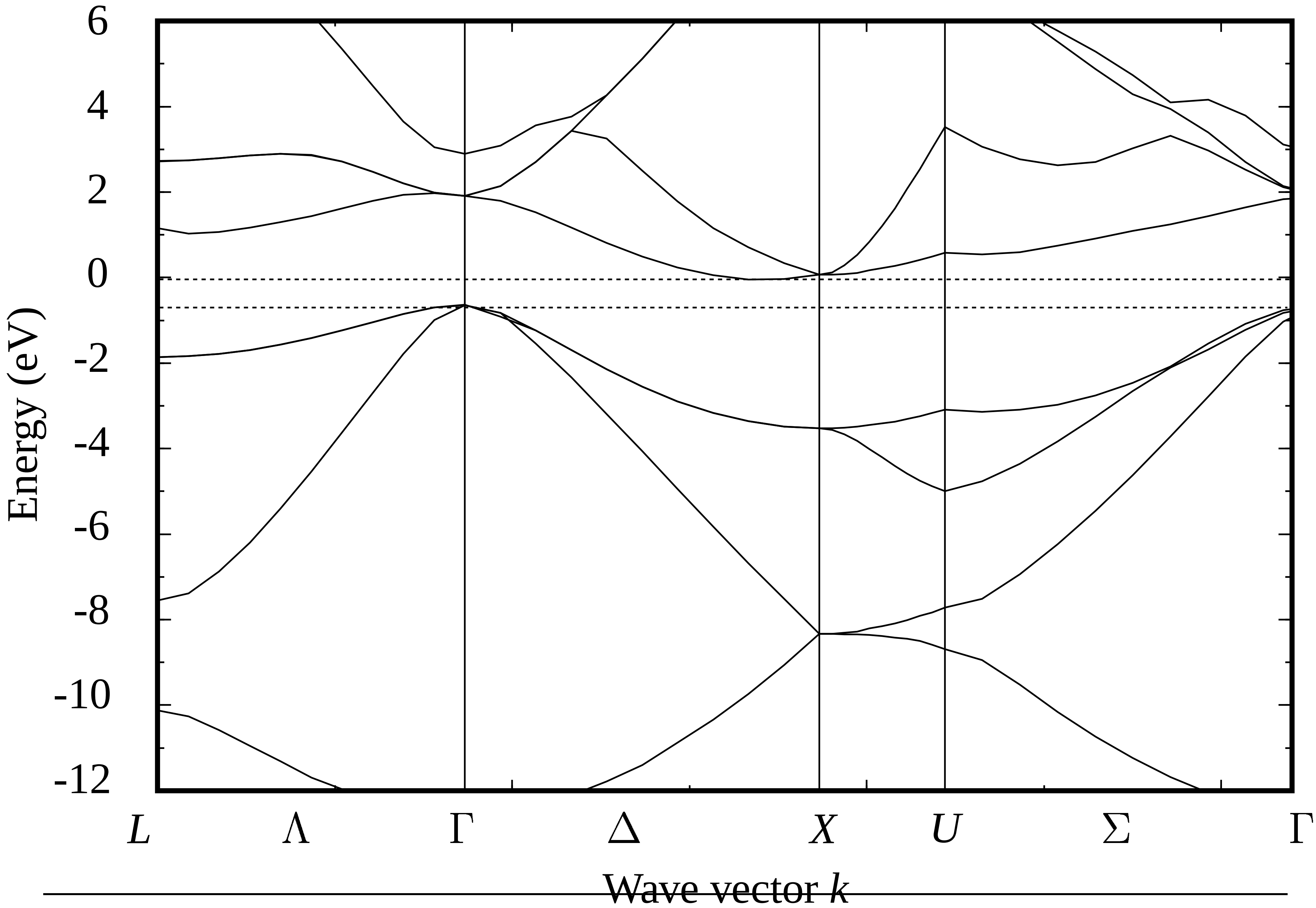
Nearly Free Electron Metals



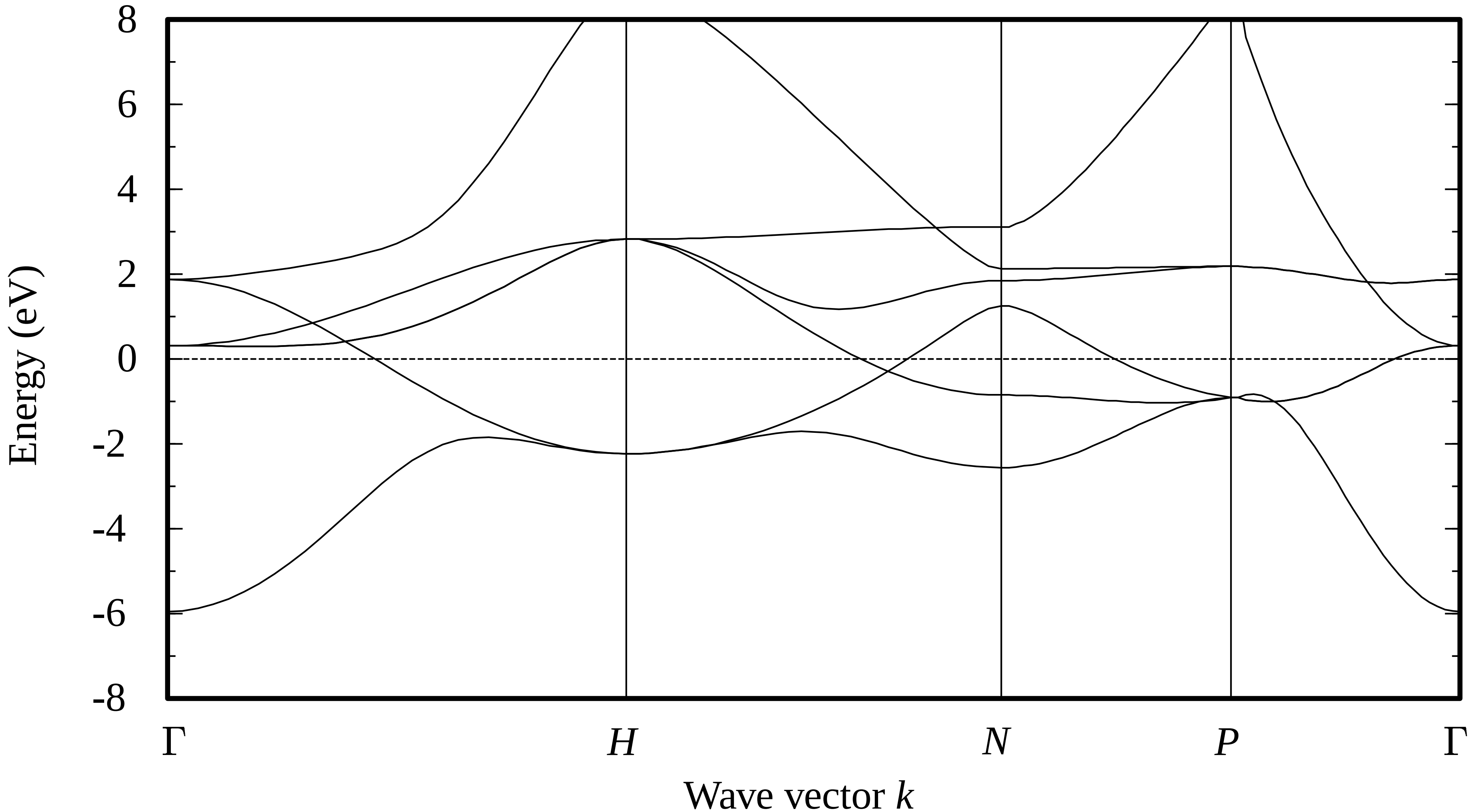
Nearly Free Electron Metals



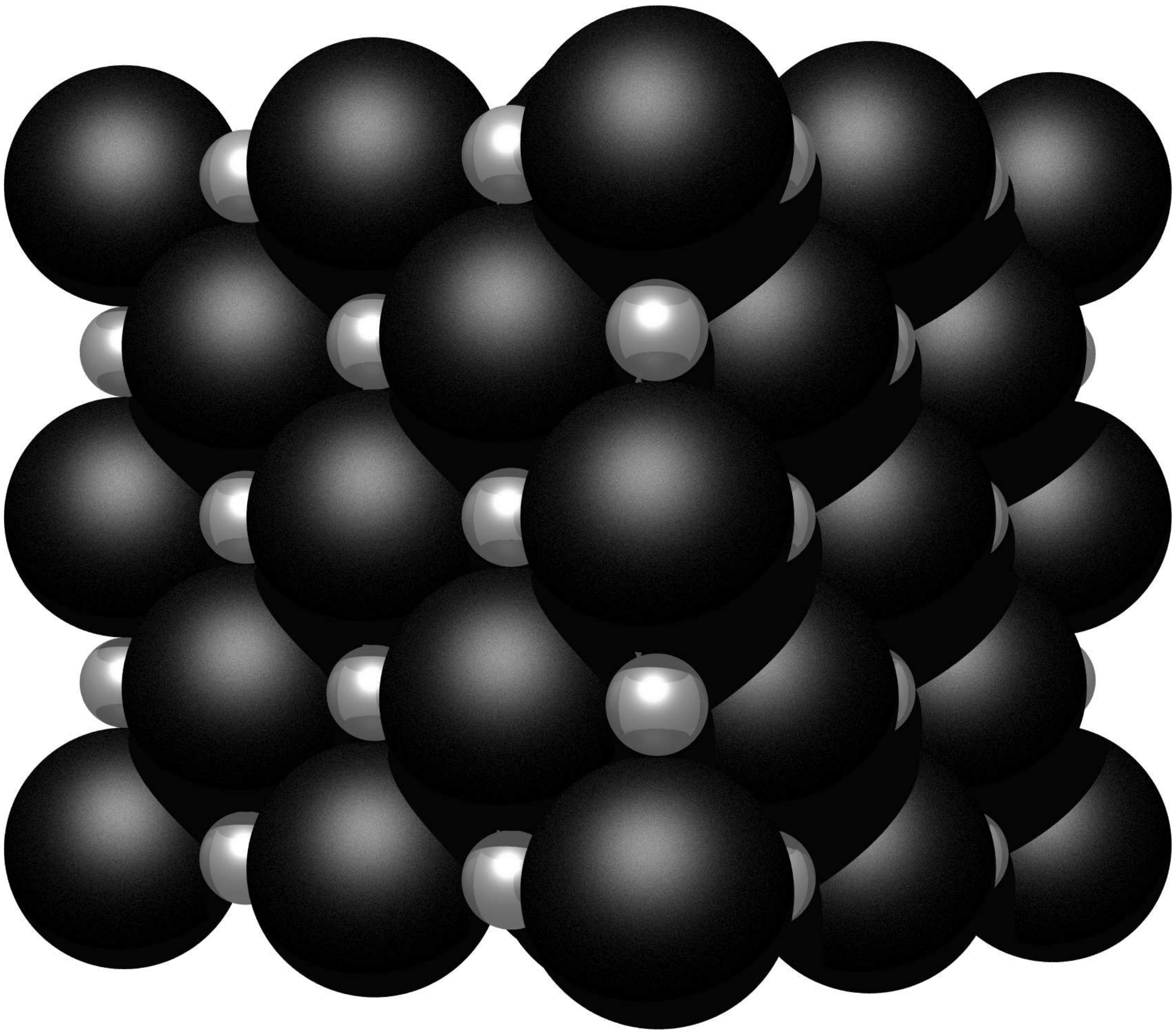
Semiconductors



Transition Metals



Cohesion of Solids



Cohesion of Solids

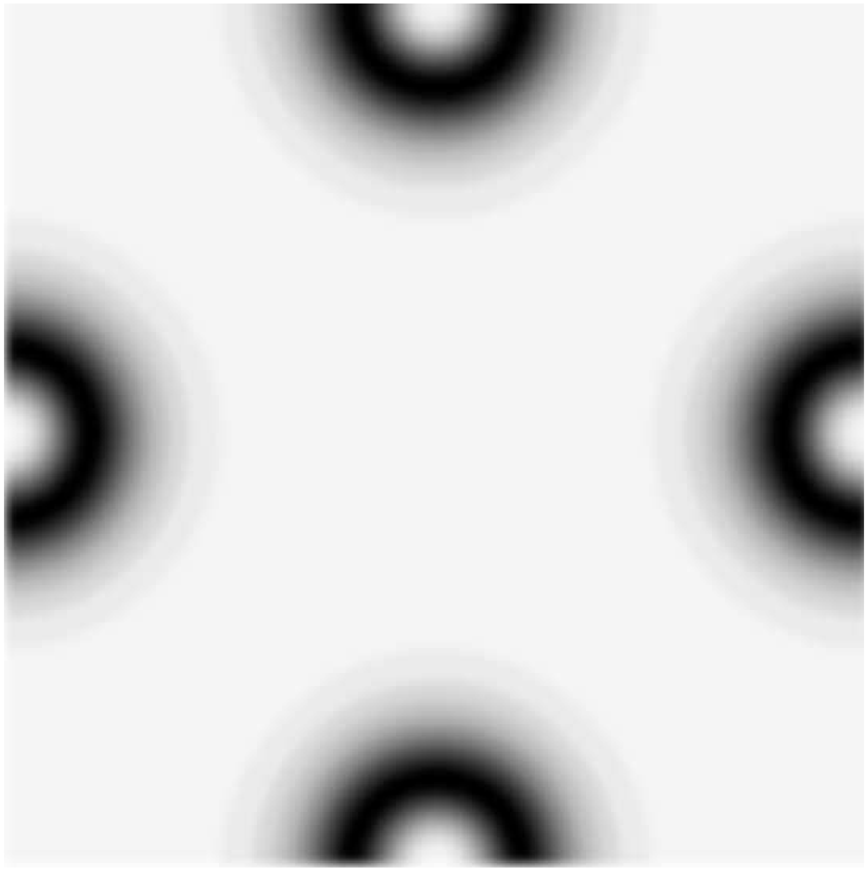
Solids divide into 5 rough classes for purposes of studying cohesion

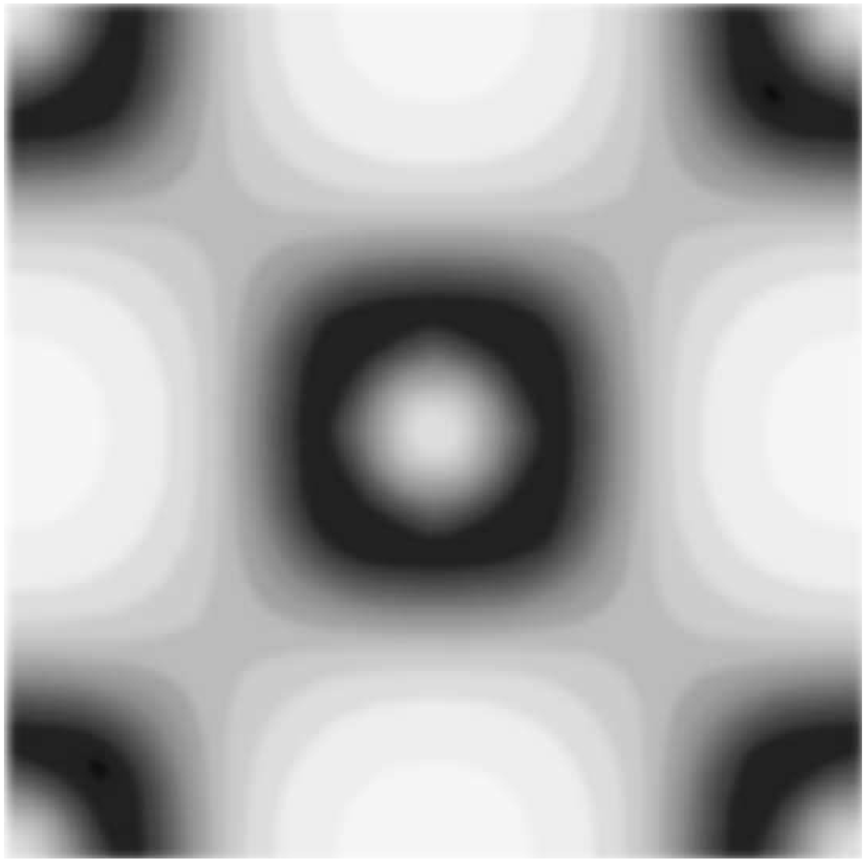
- ☞ Molecular
- ☞ Ionic
- ☞ Covalent
- ☞ Metallic
- ☞ Hydrogen bonded

Goal is to obtain conceptual and semi-quantitative estimates of cohesive energies, falling back upon elaborate calculations only as necessary.

Cohesive energy has nothing to do with the strength of solids. It allows one to decide what the ground state structure ought to be.

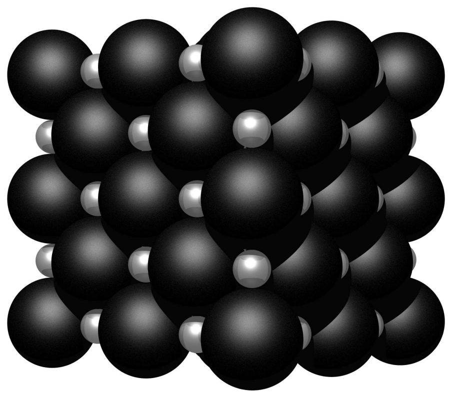
Cohesion of Solids





Radii of Atoms

Semi-empirical procedure, assigning atoms a radius and modifying it slightly according to the number and type of neighbors



Radii of Atoms

El.	Z	M	I	R_1
Ac	3+	1.88		
Am	3+	1.81		
Ar	0		1.86	
Ag	1+	1.45	1.26	1.53
Al	3+	1.43	0.50	1.25
As	3−	1.39	2.22	1.21
Au	1+	1.44	1.37	1.52
Ba	2+	2.24	1.35	1.98
Be	2+	1.13	0.35	0.89
Bi	3−	1.70		1.52
B	3+	0.98	0.20	0.80
Br	1−		1.95	1.14
C	4+	0.92	0.15	0.77
	4−		2.60	
Ca	2+	1.97	0.99	1.74
Cd	2+	1.57	0.97	1.49
Ce	3+	1.83	1.01	1.65
Co	2−	1.25		
Cl	1−		1.81	0.99
Cr	3+	1.36		
Cs	1+	2.73	1.67	2.35
Cu	1+	1.28	0.96	1.35
Dy	3+	1.77		1.59
Er	3+	1.76		1.57
Eu	2+	2.04		1.85
F	1−		1.36	0.72
Fe	2−	1.27		
Ga	3+	1.41	0.62	1.27
Ge	4+	1.37	0.53	1.22
Ge	4−		2.72	
Gd	3+	1.80		1.61
H	1−	0.78	2.08	
He	0			
Hf	4+	1.58		
Hg	2+	1.57	1.10	1.49
Ho	3+	1.77		1.58
I	1−		2.16	1.33
In	3+	1.66	0.81	1.44
Ir	2−	1.36		
K	1+	2.38	1.33	2.03
Kr	0		2.00	
La	3+	1.88	1.15	1.69
Li	1+	1.56	0.68	1.23
Lu				1.56
Mg	2+	1.60	0.65	1.36

Radii of Atoms

El.	Z	M	I	R_1
Mn	4+	1.30		
Mo	2−	1.40		
N	3−	0.88	1.71	0.74
Na	1+	1.91	0.97	1.57
Nb	3−	1.47		
Nd	3+	1.83		1.64
Ne	0		1.58	
Ni	2−	1.25		
Np	2−	1.56		
O	2−	0.89	1.40	0.74
Os	2−	1.35		
P	3−	1.28	2.12	1.10
Pa	3−	1.63		
Pb	4+	1.75	0.84	1.43
Pd	2−	1.38		

El.	Z	M	I	R_1
Po	2−	1.76		1.53
Pr	3+	1.83		1.65
Pt	2−	1.39		
Pu	3−	1.58		
Rb	1+	2.55	1.48	2.16
Re	2−	1.38		
Rh	2−	1.35		
Ru	2−	1.34		
S	2−	1.27	1.84	1.04
Sb	3−	1.59	2.45	1.41
Sc	3+	1.64	0.81	1.44
Se	2−	1.40	1.98	1.17
Si	4+	1.32	0.41	1.17
Si	4−		2.71	
Sm	3+	1.80		1.66
Sn	4+	1.62	0.71	1.40

El.	Z	M	I	R_1
Sn	4−		2.94	
Sr	2+	2.15	1.13	1.91
Ta	3−	1.47		
Tb	3+	1.78		1.59
Te	2−	1.60	2.21	1.37
Th	4+	1.80		
Ti	4+	1.46	0.68	
Tl	3+	1.72	0.95	1.46
Tm	3+	1.75		1.56
U	2−	1.56		
V	3−	1.35		
W	2−	1.41		
Xe	0		2.17	
Y	3+	1.80	0.93	1.62
Yb	2+	1.94		1.70
Zn	2+	1.39	0.74	1.31
Zr	4+	1.60	0.80	

Radii of Atoms

Ion Type	He	Ne	Ar	Kr	Xe
(inert core)			Cu^+	Ag^+	Au^+
Born exponent n	5	7	9	10	12

I is ionic radius: $R = I[z/6]^{1/(n-1)}$

R_1 is covalent radius: $R = R_1 - 0.13\ln[Z/z]$: for $Z < 0$, use $8 - |Z|$.

Cristobalite

According to Wykoff, quartz in the β-cristobalite form is cubic ($a = 7.12$ Å) and has a basis with eight silicon atoms and sixteen oxygens, which in units of $a/8$ are at

Si:	(000)	(440)	(404)	(044)	(222)	(266)	(626)	(662)
O:	(111)	(551)	(515)	(155)	(177)	(537)	(573)	(133)
	(717)	(357)	(313)	(753)	(771)	(331)	(375)	(735)

The nearest-neighbor distance for this structure is 1.54 Å. The silicon has four neighboring oxygens, so $Z = z = 4$, while each oxygen has two neighboring silicons, and $Z = 6$, $z = 2$. According to table, the covalent radius of silicon is 1.17 Å, and that of oxygen is $0.74 - 0.14 = 0.60$ Å, which sum to 1.77 Å. The discrepancy is more than 10%; structure is wrong.

Energy produced by simple sums.

$$\mathcal{E} = \frac{1}{2}\sum_{ij}\phi(r_{ij}) \quad \text{(L1)}$$

Lennard–Jones potential

$$\phi(r) = -4\epsilon\left[\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right]. \quad \text{(L2)}$$

Origin from dipole moments.

$$\phi(r) = [\vec{p}_1\cdot\vec{p}_2 - 3(\vec{p}_1\cdot\hat{r})(\vec{p}_2\cdot\hat{r})]/r^3, \quad \text{(L3)}$$

Dipole moments induced by fluctuations

$$\phi \sim -\frac{\alpha_1\alpha_2}{r^6}, \quad \text{(L4)}$$

Repulsive term of form r^{12} because...because...well, it has to be something!.

Thermodynamic properties from

$$P\mathcal{V}/k_BT = 1 - b_2/\mathcal{V}\ldots \tag{L5}$$

where

$$b_2 = \frac{1}{2}\int d\vec{r}\,[1-e^{-\beta\phi(r)}]. \tag{L6}$$

Theory of solids obtained from measurements performed purely on gases.

Noble Gas	He	Ne	Ar	Kr	Xe
ϵ (eV)	$8.6\cdot 10^{-4}$	0.0031	0.0104	0.0104	0.0200
σ (Å)	2.56	2.74	3.40	3.65	3.98

$$\mathcal{E}/N = \frac{1}{2} 4\epsilon \sum_{\vec{R}\neq 0}\left[(\frac{\sigma}{R})^{12} - (\frac{\sigma}{R})^{6}\right]. \tag{L7}$$

Noble Gases

$$\mathcal{E}/N = 2\epsilon \sum_{\vec{R}} (\frac{\sigma}{d})^{12} (\frac{d}{R})^{12} - (\frac{\sigma}{d})^{6} (\frac{d}{R})^{6} \tag{L8}$$

$$\equiv 2\epsilon[A_{12}(\frac{\sigma}{d})^{12} - A_6(\frac{\sigma}{d})^{6}] \text{ with } A_l \equiv \sum_{\vec{R}\neq 0} \left(\frac{d}{R}\right)^l . \tag{L9}$$

Lattice sums:

Crystal	fcc	bcc	hcp
A_6	14.4519	12.2519	14.4548
A_{12}	12.1319	9.1142	12.1353
$A_6^2/2A_{12}$	8.6078	8.2349	8.6088

Nearest–neighbor spacing in equilibrium:

$$d_0 = \sigma(\frac{2A_{12}}{A_6})^{1/6}, \tag{L10}$$

Cohesive energy:

$$\mathcal{E}/N = -\epsilon \frac{A_6^2}{2A_{12}}, \tag{L11}$$

Bulk modulus:

$$B = \mathcal{V} \frac{\partial^2 \mathcal{E}}{\partial \mathcal{V}^2}. \tag{L12}$$

$$B = \frac{4\epsilon}{\sigma^3} A_{12} \left(\frac{A_6}{A_{12}} \right)^{5/2}. \tag{L13}$$

Noble Gases

Noble Gas	Ne	Ar	Kr	Xe
Experimental d_0 (Å)	3.13	3.75	3.99	4.33
d_0 from Eq. (L10) (Å)	2.99	3.71	3.98	4.34
Experimental $\mathcal{E}/N$ (eV/atom)	-0.02	-0.08	-0.11	-0.17
$\mathcal{E}/N$ from Eq. (L11)	-0.027	-0.089	-0.120	-0.172
Experimental B (dyne/cm^2)	$1.1 \cdot 10^{10}$	$2.7 \cdot 10^{10}$	$3.5 \cdot 10^{10}$	$3.6 \cdot 10^{10}$
B from Eq. (L13)	$1.81 \cdot 10^{10}$	$3.18 \cdot 10^{10}$	$3.46 \cdot 10^{10}$	$3.81 \cdot 10^{10}$

Ionic Crystals

Atom	Electron affinity (eV)	Atom	First ionization potential (eV)
H	0.75	Li	5.32
F	3.40	Na	5.14
Cl	3.61	K	4.34
Br	3.36	Rb	4.18
I	3.06	Cs	3.90

Computing sums over particles interacting with $1/r$ potentials is very tricky because mathematically the sums candiverge or are ambiguous. Physically, ambiguities in the sums correspond to putting varying values of surface charge at outer surfaces of crystal, and the mathematical resolution corresponds to having no net surface charge.

$$\frac{e^2}{d}\sum_{\vec{R}\neq 0}\left[\frac{d}{R}-\frac{d}{|\vec{R}+\vec{d}|}\right]-\frac{e^2}{d}\equiv\frac{e^2}{d}[dS(0)-dS(\vec{d})-1], \qquad \text{(L14)}$$

$$S(\vec{d}) = \sum_{\vec{R}\neq\vec{0}}\frac{1}{|\vec{d}-\vec{R}|}=\int_0^\infty\frac{2\,d\rho}{\sqrt{\pi}}\sum_{\vec{R}\neq\vec{0}}e^{-\rho^2|\vec{d}-\vec{R}|^2} \qquad \text{(L15)}$$

$$= \int_0^\infty\frac{2\,d\rho}{\sqrt{\pi}}\int\frac{d\vec{k}}{\rho^3\sqrt{\pi}^3}\sum_{\vec{R}\neq\vec{0}}e^{-k^2/\rho^2+2i\vec{k}\cdot(\vec{d}-\vec{R})} \qquad \text{(L16)}$$

$$= \int_0^\infty\frac{2\,d\rho}{\sqrt{\pi}}\int\frac{d\vec{k}}{\rho^3\sqrt{\pi}^3}\left[\left\{\sum_{\vec{K}}\frac{(2\pi)^3}{\Omega}\delta(2\vec{k}-\vec{K})\right\}-1\right]e^{-k^2/\rho^2+2i\vec{k}\cdot\vec{d}} \qquad \text{(L17)}$$

$$= \int_0^\infty \frac{2\,d\rho}{\sqrt{\pi}} \left[\frac{\pi^3}{\rho^3 \sqrt{\pi}^3} \sum_{\vec K} \frac{1}{\Omega} e^{-K^2/4\rho^2 + i\vec K\cdot\vec d} - e^{-d^2\rho^2} \right] \tag{L18}$$

$$= \sum_{\vec K} \frac{4\pi}{\Omega K^2} e^{i\vec K\cdot\vec d} - \frac{1}{d}. \tag{L19}$$

$$S(\vec d) = \int_g^\infty \frac{2\,d\rho}{\sqrt{\pi}} \sum_{\vec R\neq\vec 0} e^{-\rho^2(\vec d-\vec R)^2}$$

$$+ \int_0^g \frac{2\,d\rho}{\sqrt{\pi}} \left[\frac{(\pi)^3}{\rho^3 \sqrt{\pi}^3} \sum_{\vec K\neq 0} \frac{1}{\Omega} e^{-K^2/4\rho^2 + i\vec K\cdot\vec d} - e^{-d^2\rho^2} \right] \tag{L20}$$

$$= \int_g^\infty \frac{2\,d\rho}{\sqrt{\pi}} \sum_{\vec R\neq 0} e^{-\rho^2(\vec d-\vec R)^2} + \sum_{\vec K\neq 0} \frac{4\pi}{\Omega K^2} e^{-K^2/4g^2 + i\vec K\cdot\vec d} - \int_0^g \frac{2\,d\rho}{\sqrt{\pi}} e^{-\rho^2 d^2}.$$

(L21)

$$dS(\vec{d}) - dS(0) + 1 \equiv \alpha \tag{L22}$$

$$\frac{\mathcal{E}}{N_{\text{ion pairs}}} = -\alpha\frac{e^2}{d} = -\alpha\frac{14.4\,\text{eV}}{[d/\text{Å}]}, \tag{L23}$$

α is the Madelung constant.

Structure	Madelung constant α
Cesium chloride	1.76268
Sodium chloride	1.74757
Wurtzite	1.638704
Zincblende	1.63806

Add repulsive term C/d^{12} because...because...well, it has to be something!.

$$\frac{\mathcal{E}}{N_{\text{ion pairs}}} = -\alpha\frac{e^2}{d} + \frac{C}{d^{12}}. \tag{L24}$$

$$d_0 = \left[\frac{12C}{e^2\alpha}\right]^{1/11}, \tag{L25}$$

$$\frac{\mathcal{E}}{N_{\text{ion pairs}}} = -\frac{11}{12}\alpha\frac{e^2}{d}. \tag{L26}$$

Compound	Experimental d_0 (Å)	Experimental $\mathcal{E}/N_{\text{ion pairs}}$ (eV)	Eq. (L26) $\mathcal{E}/N_{\text{ion pairs}}$ (eV)
LiF	2.01	10.83	11.45
LiCl	2.57	8.85	8.98
LiBr	2.75	8.51	8.39
LiI	3.01	7.92	7.66
NaCl	2.82	8.18	8.18
NaF	2.32	9.62	9.96
NaBr	2.99	7.81	7.72
NaI	3.24	7.32	7.13
KF	2.67	8.55	8.63
KCl	3.15	7.42	7.33
KBr	3.30	7.16	6.99
KI	3.53	6.74	6.53
RbF	2.83	8.18	8.16
RbCl	3.29	7.17	7.01
RbBr	3.44	6.90	6.70
RbI	3.67	6.52	6.28
AgCl	2.77	9.53	8.32
AgBr	2.89	9.40	7.99

$$\mathcal{E}_{\rm el} \equiv - \int d\vec{r}\, n(\vec{r}) \sum_{\vec{R}} \frac{e^2}{|\vec{r}-\vec{R}|} + \frac{e^2}{2} \sum_{\vec{R}\neq\vec{R}'} \frac{1}{|\vec{R}-\vec{R}'|} + \frac{1}{2} \int d\vec{r}_2 d\vec{r}_1 \frac{e^2 n(\vec{r}_1) n(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}. \tag{L27}$$

$$\frac{\mathcal{E}_{\rm el}}{N} = -\frac{\alpha}{2}\frac{e^2}{r_s}, \tag{L28}$$

$$r_s = [\frac{3}{4\pi}\frac{\mathcal{V}}{N}]^{1/3} \tag{L29}$$

Madelung constants for metals

bcc	fcc	hcp	sc	Diamond
1.791 86	1.791 75	1.791 68	1.760 12	1.670 85

$$\frac{\mathcal{E}_{\rm kin}}{N} = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m} = \frac{3}{5}\frac{\hbar^2}{2m}(\frac{9\pi}{4})^{2/3}\frac{1}{r_s^2} \tag{L30}$$

$$\frac{\mathcal{E}_{\rm ex}}{N} = -\frac{3}{4\pi}e^2 k_F = -\frac{3}{4\pi}e^2\left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s}. \qquad \text{(L31)}$$

$$\frac{\mathcal{E}}{N} = \left[-\frac{24.35}{(r_s/a_0)} + \frac{30.1}{(r_s/a_0)^2} - \frac{12.5}{(r_s/a_0)}\right]\text{eV/atom}. \qquad \text{(L32)}$$

Get general (wrong) prediction

$$\frac{r_s}{a_0} = 1.6, \qquad \text{(L33)}$$

Metals

Element	Z	n (10^{22} cm^{-3})	k_F (10^8 cm^{-1})	$\mathcal{E}_F$ (eV)	T_F (10^4 K)	v_F (10^8 cm s^{-1})	r_s/a_0
Li	1	4.60	1.11	4.68	5.43	1.28	3.27
Na	1	2.54	0.91	3.15	3.66	1.05	3.99
K	1	1.32	0.73	2.04	2.37	0.85	4.95
Rb	1	1.08	0.68	1.78	2.06	0.79	5.30
Cs	1	0.85	0.63	1.52	1.76	0.73	5.75
Cu	1	8.49	1.36	7.04	8.17	1.57	2.67
Ag	1	5.86	1.20	5.50	6.38	1.39	3.02
Au	1	5.90	1.20	5.53	6.42	1.39	3.01
Be	2	24.72	1.94	14.36	16.67	2.25	1.87
Mg	2	8.62	1.37	7.11	8.26	1.58	2.65
Ca	2	4.66	1.11	4.72	5.48	1.29	3.26
Sr	2	3.49	1.01	3.89	4.52	1.17	3.59
Ba	2	3.15	0.98	3.64	4.22	1.13	3.71
Zn	2	13.13	1.57	9.42	10.93	1.82	2.31
Cd	2	9.26	1.40	7.47	8.66	1.62	2.59
Hg	2	16.22	1.69	10.84	12.59	1.95	2.15
Al	3	18.07	1.75	11.66	13.53	2.02	2.07
Ga	3	15.31	1.65	10.44	12.11	1.92	2.19
In	3	11.50	1.50	8.62	10.01	1.74	2.41
Sn	4	14.83	1.64	10.22	11.86	1.89	2.22
Pb	4	13.19	1.57	9.45	10.97	1.82	2.30
Sb	5	16.54	1.70	10.99	12.75	1.97	2.14
Bi	5	14.04	1.61	9.85	11.43	1.86	2.26
Mn	4	32.61	2.13	17.28	20.05	2.46	1.70
Fe	2	16.90	1.71	11.15	12.94	1.98	2.12
Co	2	18.18	1.75	11.70	13.58	2.03	2.07
Ni	2	18.26	1.76	11.74	13.62	2.03	2.07

$$U(r) = \begin{cases} 0 & \text{for } r < R_c \\ -Ze^2/r & \text{for } r > R_c. \end{cases} \tag{L34}$$

$$\frac{\mathcal{E}_{ps}}{N} = \int_0^{R_c} d\vec{r}\,\frac{N}{\mathcal{V}}\frac{e^2}{r} = \frac{N}{\mathcal{V}}2\pi e^2 R_c^2 \tag{L35}$$

$$= \frac{3}{4\pi r_s^3}2\pi e^2 R_c^2 = 41\frac{a_0 R_c^2}{r_s^3}\text{eV}/\text{atom} \tag{L36}$$

$$\Rightarrow \frac{\mathcal{E}}{N} = \left[-\frac{24.35}{(r_s/a_0)} + \frac{30.1}{(r_s/a_0)^2} - \frac{12.5}{(r_s/a_0)} + 41\frac{a_0 R_c^2}{r_s^3}\right]\text{eV}/\text{atom}. \tag{L37}$$

$$r_s/a_0 = \sqrt{11.9[R_c/\text{Å}]^2 + .667} + 0.817. \tag{L38}$$

Use of Pseudopotentials

Element	R_c (Å)	r_s/a_0, measured	r_s/a_0, Eq. (L38)
Li	0.92	3.27	4.09
Na	0.96	3.99	4.23
K	1.20	4.95	5.04
Rb	1.38	5.30	5.65
Cs	1.55	5.75	6.23

Calculated radii r_s are all about 10% too large because electronic structure has not been computed in accurate way.

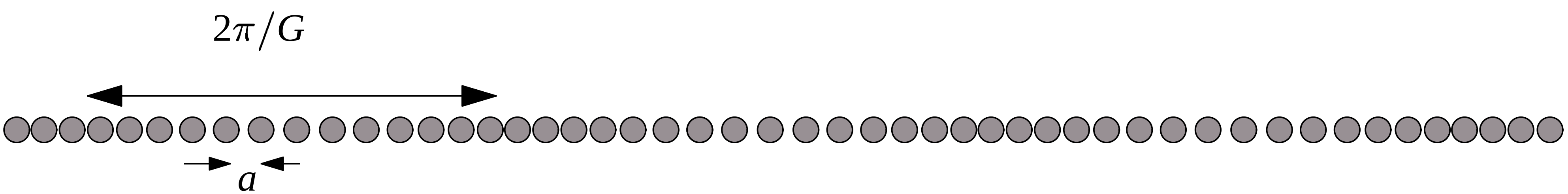
Peierls Distortion

Perfectly periodic one–dimensional chain of ions is always unstable against small displacements of ions caused by interaction with electrons.

Displacement of ion at location n is Δ_n.

$$\frac{1}{2} a Y \Delta_n^2. \tag{L39}$$

$$\Delta_n = \Delta_G \cos Gna. \tag{L40}$$



$$U \cos Gx = (\Delta_G u_0 / a) \cos Gx. \tag{L41}$$

$$\mathcal{E} = \frac{1}{2}(\mathcal{E}_k^0 + \mathcal{E}_{k-G}^0) \pm \sqrt{(\mathcal{E}_k^0 - \mathcal{E}_{k-G}^0)^2/4 + |U|^2}. \tag{L42}$$

$$L\int_{-k_F}^{k_F}\frac{dk}{\pi}\left\{\tfrac{1}{2}(\mathcal{E}^0_{k-G}-\mathcal{E}^0_k)-\sqrt{(\mathcal{E}^0_{k-G}-\mathcal{E}^0_k)^2/4+|U|^2}\right\} \quad \text{(L43)}$$

$$= \quad L\int_{-k_F}^{k_F}\frac{dk}{\pi}\left\{\frac{\hbar^2}{4m}([k-2k_F]^2-k^2)\right.$$

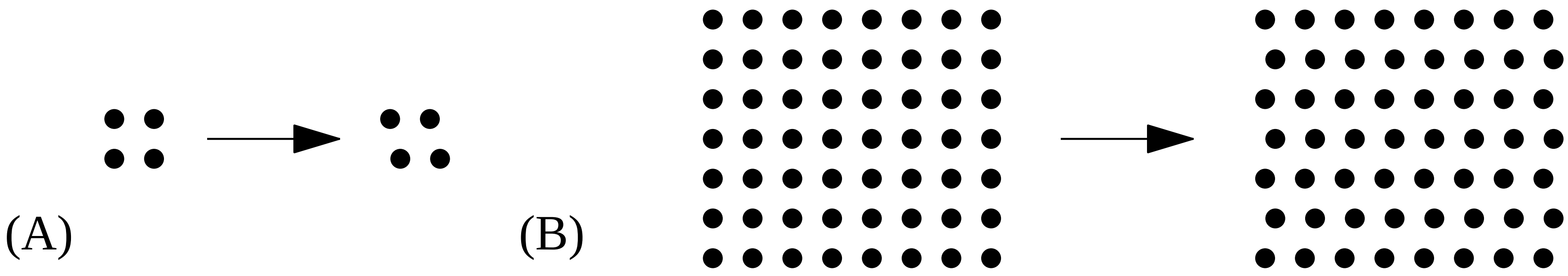
$$\left.-\sqrt{(\frac{\hbar^2}{4m}([k-2k_F]^2-k^2))^2+|U^2|}\right\} \quad \text{(L44)}$$

$$= \quad \frac{2L}{\pi}k_F\left\{2\mathcal{E}^0_{k_F}-\sqrt{|U|^2/4+(2\mathcal{E}^0_{k_F})^2}-\frac{|U|^2}{8\mathcal{E}^0_{k_F}}\sinh^{-1}(4\mathcal{E}^0_{k_F}/|U|)\right\}. \quad \text{(L45)}$$

$$\frac{L}{4}\Delta_G^2 Y. \quad \text{(L46)}$$

$$\Delta_{2k_F}=\frac{8a\mathcal{E}^0_{k_F}}{|u_0|}\exp\left\{\frac{-\pi\mathcal{E}^0_{k_F}a^2Y/k_F}{|u_0|^2}\right\}. \quad \text{(L47)}$$

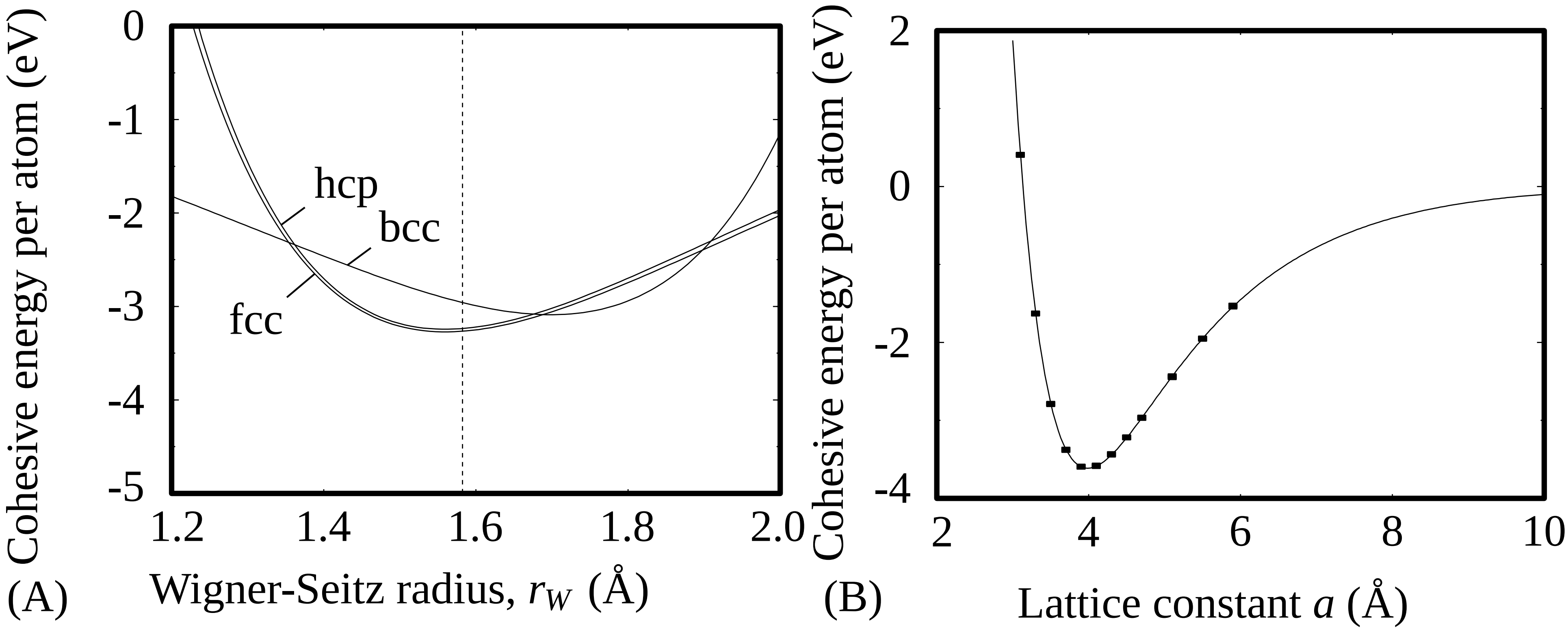
Structural Phase Transitions



Hydrogen-Bonded Solids

H_2O

Cohesive Energy from Band Calculations



Results of computing cohesive energies with full–fledged band structure codes takes a universal form. It's not quite clear why! The energies of almost all solids with respect to uniform contraction and compression take a universal form described by just a few constants.

$$\frac{4\pi}{3} r_W^3 = \frac{\mathcal{V}}{N}. \tag{L48}$$

$$a_* = \eta(\frac{r_W}{r_{W0}} - 1), \tag{L49}$$

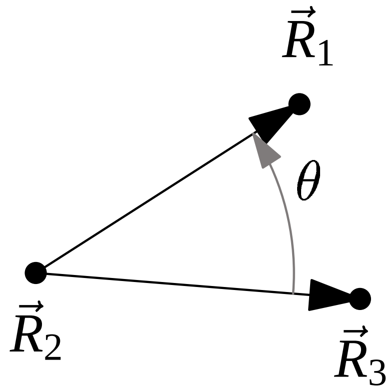
$$\mathcal{E}(r_W) = \mathcal{E}_0 e^{-a_*} \left(-1 - a_* - 0.05 a_*^3\right). \tag{L50}$$

Cohesive Energy from Band Calculations

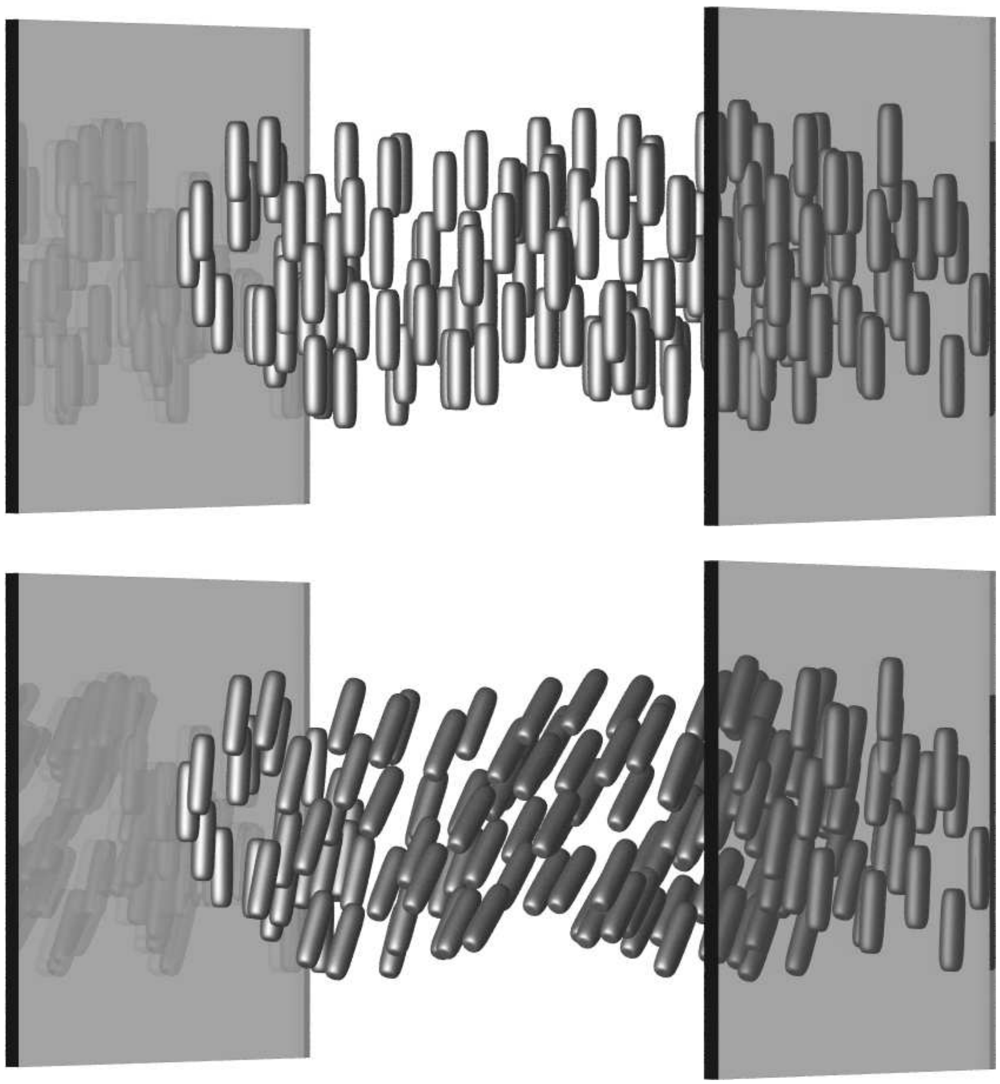
El.	r_{W0} (Å)	η	$\mathcal{E}_0$ (eV)	El.	r_{W0} (Å)	η	$\mathcal{E}_0$ (eV)	El.	r_{W0} (Å)	η	$\mathcal{E}_0$ (eV)
Ag	1.60	5.94	2.96	Fe	1.41	5.16	4.29	Pt	1.53	6.47	5.85
Al	1.58	4.71	3.34	Gd	1.99	4.27	4.14	Rb	2.75	4.18	0.86
Au	1.59	6.75	3.78	Ge	1.76	5.05	3.87	Re	1.52	6.15	8.10
Ba	2.46	4.41	1.86	Hf	1.74	4.66	6.35	Ru	1.48	6.04	6.62
Be	1.25	4.01	3.33	In	1.84	5.11	2.60	Si	1.68	4.88	4.64
Ca	2.18	4.52	1.83	Ir	1.50	6.52	6.93	Ta	1.62	4.92	8.09
Cd	1.73	8.08	1.16	K	2.57	3.94	0.94	Th	1.99	4.12	5.93
Ce	2.02	3.11	4.77	Li	1.72	3.10	1.65	Ti	1.62	4.76	4.86
Co	1.39	5.31	4.39	Mg	1.77	5.60	1.53	Tl	1.90	5.74	1.87
Cr	1.42	5.59	4.10	Mo	1.55	5.85	6.81	V	1.49	4.81	5.30
Cs	2.98	4.17	0.83	Na	2.08	3.70	1.13	W	1.56	5.69	8.66
Cu	1.41	5.30	3.50	Nb	1.63	4.84	7.47	Y	1.99	4.23	4.39
Dy	1.96	4.85	3.10	Ni	1.38	5.11	4.44	Yb	1.99	3.94	1.60
Er	1.94	4.94	3.30	Pb	1.93	6.37	2.04	Zn	1.54	7.16	1.35
Eu	2.27	4.75	1.80	Pd	1.52	6.41	3.94	Zr	1.77	4.48	6.32

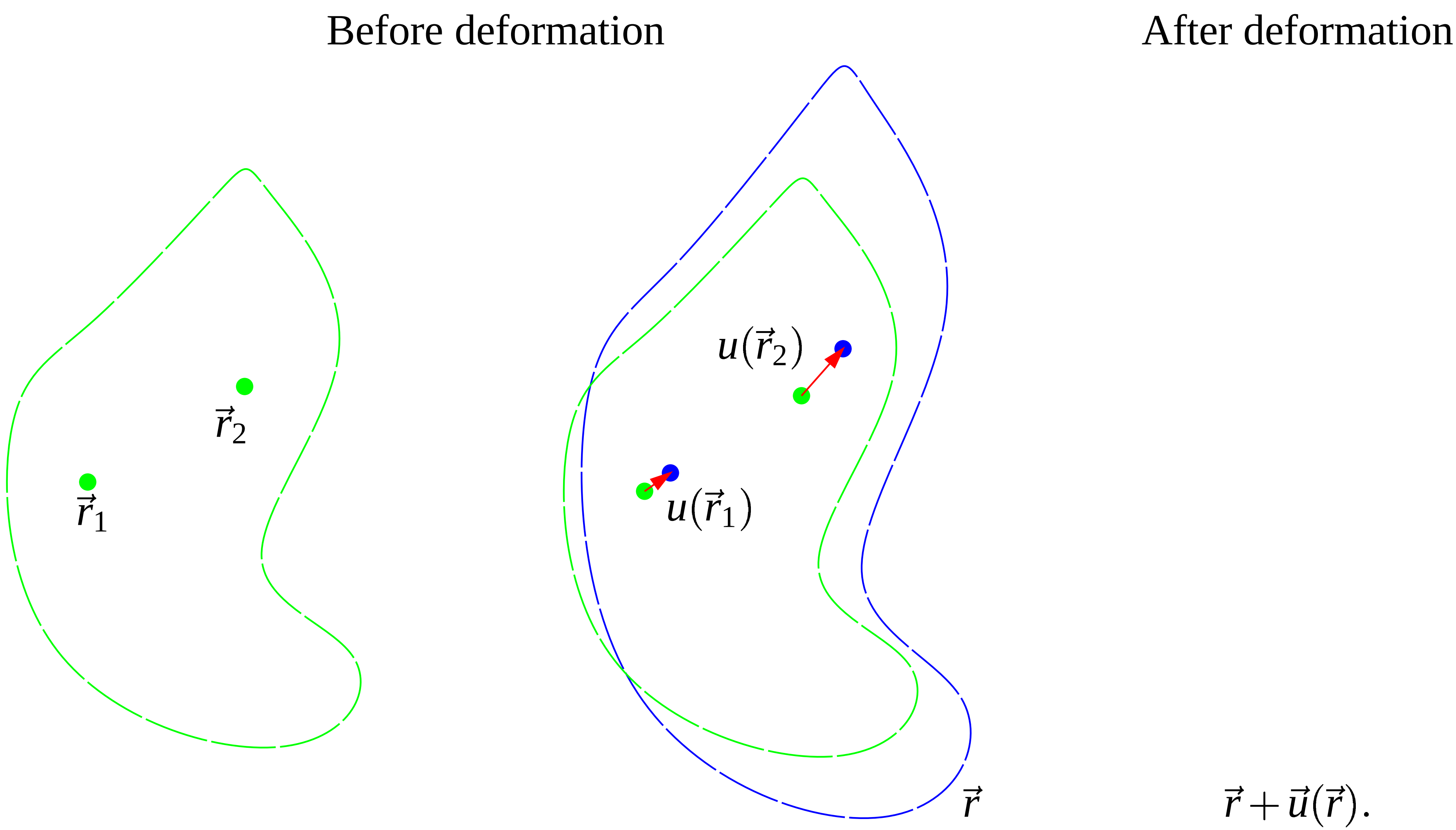
$$\mathcal{E} = \langle \Psi | \hat{\mathcal{H}}(\vec{R}_1 \ldots \vec{R}_N) | \Psi \rangle \tag{L51}$$

$$\vec{F}_l = -\frac{\partial \mathcal{E}}{\partial \vec{R}_l}. \tag{L52}$$



Elasticity





$$\vec{r} \qquad \vec{r}+\vec{u}(\vec{r}). \tag{L1}$$

Many ways to derive elasticity. Could derive from theory of atoms and their interactions. However, this approach is not historically accurate, and not fully general.

Most general approach modeled by Landau; construct free energy simply by considering symmetry and using fact that deformations are small:

- $\vec{u}$ vanishes in equilibrium
- Free energy invariant under translation.
- Smallest allowed powers or $\vec{u}$
- Derivatives of lowest allowed order
- Uniform rotation costs no energy.

Unique (?) free energy consistent with these constraints:

$$\mathcal{F} = \int d\vec{r}\, \tfrac{1}{2} \sum_{\alpha\beta\gamma\delta} E_{\alpha\beta\gamma\delta} \frac{\partial u_\alpha(\vec{r})}{\partial r_\beta} \frac{\partial u_\gamma(\vec{r})}{\partial r_\delta}. \quad \text{(L2)}$$

45 independent $E_{\alpha\beta\gamma\delta}$ after considering symmetry under interchange of indices.

$$u_\alpha = \phi \sum_{\beta\mu} \epsilon^{\alpha\beta\mu} r_\beta n_\mu. \quad \text{(L3)}$$

$$\sum_{\alpha\beta\gamma\delta\mu\mu'} \int d\vec{r}\,\epsilon^{\alpha\beta\mu} n_\mu E_{\alpha\beta\gamma\delta} \epsilon^{\gamma\delta\mu'} n_{\mu'} = 0 \tag{L4}$$

$$\Rightarrow \quad E_{\alpha\beta\gamma\delta} - E_{\beta\alpha\gamma\delta} - E_{\alpha\beta\delta\gamma} + E_{\beta\alpha\delta\gamma} = 0. \tag{L5}$$

Strain tensor

Define strain tensor

$$e_{\alpha\beta} \equiv \tfrac{1}{2}[\frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha}] \quad \text{(L6)}$$

$$\omega_{\alpha\beta} \equiv \tfrac{1}{2}[\frac{\partial u_\alpha}{\partial r_\beta} - \frac{\partial u_\beta}{\partial r_\alpha}]. \quad \text{(L7)}$$

$$\begin{aligned}\mathfrak{F} = \sum_{\alpha\beta\gamma\delta} \int d\vec{r} \quad & \tfrac{1}{8} \quad e_{\alpha\beta}[E_{\alpha\beta\gamma\delta} + E_{\beta\alpha\gamma\delta} + E_{\alpha\beta\delta\gamma} + E_{\beta\alpha\delta\gamma}]e_{\gamma\delta} \\ & + \tfrac{1}{8} \quad \omega_{\alpha\beta}[E_{\alpha\beta\gamma\delta} - E_{\beta\alpha\gamma\delta} - E_{\alpha\beta\delta\gamma} + E_{\beta\alpha\delta\gamma}]\omega_{\gamma\delta}.\end{aligned} \quad \text{(L8)}$$

$$\mathfrak{F} = \sum_{\alpha\beta\gamma\delta} \int d\vec{r}\, \tfrac{1}{2} e_{\alpha\beta}\, C_{\alpha\beta\gamma\delta}\, e_{\gamma\delta}, \quad \text{(L9)}$$

$$C_{\alpha\beta\gamma\delta} = \tfrac{1}{4}[E_{\alpha\beta\gamma\delta} + E_{\beta\alpha\gamma\delta} + E_{\alpha\beta\delta\gamma} + E_{\beta\alpha\delta\gamma}]. \quad \text{(L10)}$$

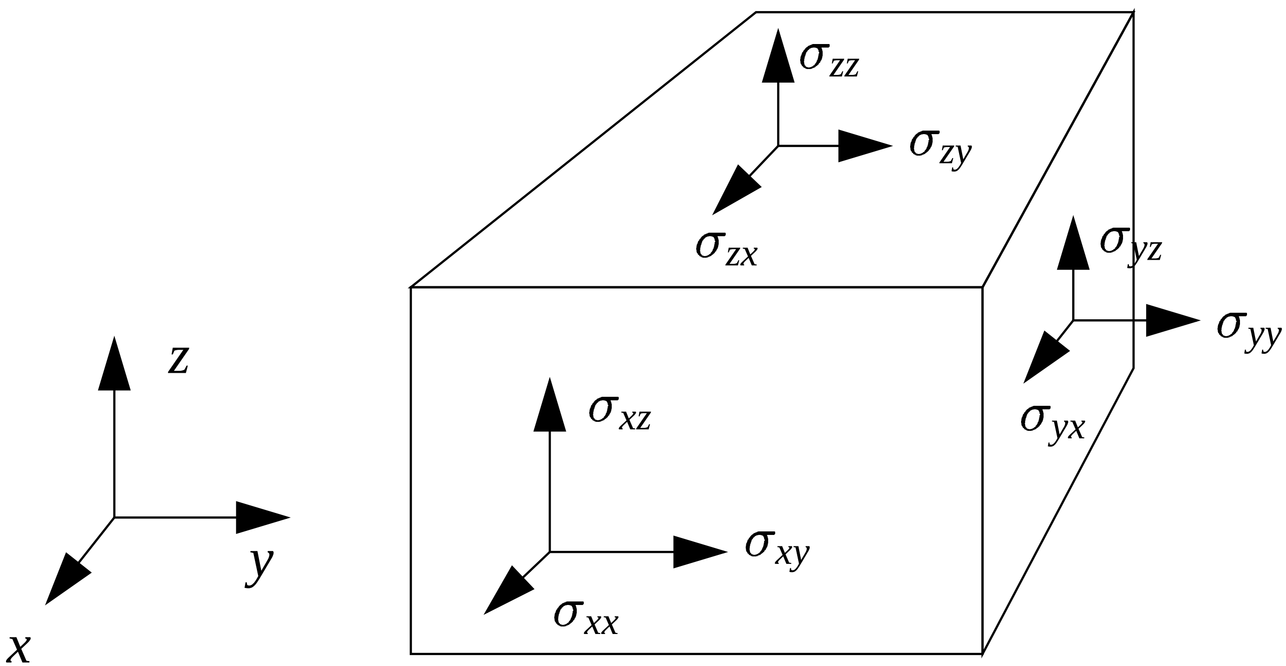
$$\alpha \leftrightarrow \beta,\ \gamma \leftrightarrow \delta \text{ and also } \alpha\beta \leftrightarrow \gamma\delta. \quad \text{(L11)}$$

Stress Tensor

$$\mathcal{F} = \sum_{\alpha\beta} \int d\vec{r}\, \tfrac{1}{2} e_{\alpha\beta}\, \sigma_{\alpha\beta}, \tag{L12}$$

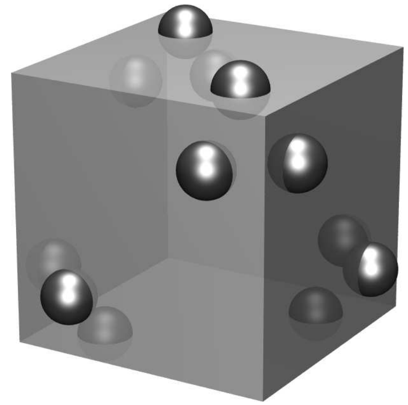
where the stress tensor is

$$\sigma_{\alpha\beta} = \sum_{\gamma\delta} C_{\alpha\beta\gamma\delta}\, e_{\gamma\delta}. \tag{L13}$$



Equation of motion

Solids of Cubic Symmetry



C_{xyyy} vanishes because it multiplies ? ? but ? ? flips sign when $x \to -x$.

Also invariant under $x \to y \to z \to x$

Three parameters survive:

C_{xxxx}

C_{xxyy}

C_{xyxy}

Solids of Cubic Symmetry

$$\mathfrak{F} = \int d\vec{r}\,\frac{1}{2}\left\{\begin{array}{rl} C_{xxxx} & [e_{xx}^2+e_{yy}^2+e_{zz}^2] \\ +2C_{xxyy} & [e_{xx}e_{yy}+e_{yy}e_{zz}+e_{zz}e_{xx}] \\ +4C_{xyxy} & [e_{xy}^2+e_{yz}^2+e_{zx}^2] \end{array}\right\}. \tag{L14}$$

$$\begin{array}{cccccc} e_{xx} & e_{yy} & e_{zz} & 2e_{yz} & 2e_{zx} & 2e_{xy} \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ e_1 & e_2 & e_3 & e_4 & e_5 & e_6 \end{array} \tag{L15}$$

$$\begin{array}{ccccccc} C_{xxxx} & C_{xxyy} & C_{xxzz} & C_{yzxx} & C_{zxxx} & C_{xyxx} & \text{etc.} \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \\ C_{11} & C_{12} & C_{13} & C_{41} & C_{51} & C_{61} & \text{etc.} \end{array} \tag{L16}$$

Solids of Cubic Symmetry

$$\mathfrak{F} = \int d\vec{r}\, \tfrac{1}{2} \sum_{\alpha\beta=1}^{6} e_\alpha C_{\alpha\beta} e_\beta . \tag{L17}$$

Cauchy relation: $C_{44} = C_{12}$

Solids of Cubic Symmetry

Element	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)	Element	C_{11} (GPa)	C_{44} (GPa)	C_{12} (GPa)
Al	108	28.3	62	Li (195K)	13.4	9.6	11.3
Ar (80 K)	2.77	0.98	1.37	Mo	459	111	168
Ag	123	45.3	92	Na	7.59	4.30	6.33
Au	190	42.3	161	Ne (6 K)	1.62	0.93	0.85
Cs (78 K)	2.47	2.06	1.48	Ni	247	122	153
Ca	16	12	8	Nb	245	28.4	132
Cr	346	100	66	O (54.4 K)	2.60	0.275	2.06
Cu	169	75.3	122	Pd	224	71.6	173
C (diamond)	1040	550	170	Pt	347	76.5	251
Fe	230	117	135	Rb	2.96	1.60	2.44
Ge (undoped)	129	67.1	48	Si (undoped)	165	79.2	64
Ge (*n*-doped,10^{19} Sb)	128.8	65.5	47.7	Si (*n*-doped, 10^{19} As)	162.2	78.7	65.4
Ge (*p*-doped,10^{20} Ga)	118.0	65.3	39.0	Sr	14.7	5.74	9.9
He^3 (0.4 K, 24 cm^3/mole)	0.0235	0.01085	0.0197	Ta	262	82.6	156
He^4 (1.6 K, 12 cm^3/mole)	0.0311	0.0217	0.0281	Th	76	46	49
Ir	600	270	260	W	517	157	203
K	3.71	1.88	3.15	V	230	43.2	120
Kr (115 K)	2.85	1.35	1.60	Xe (156 K)	2.98	1.48	1.90
Pb	48.8	14.8	41.4				

$$B = \mathcal{V}\partial^2\mathcal{F}/\partial\mathcal{V}^2$$

$$e_{xx} = e_{yy} = e_{zz} = \delta\mathcal{V}/3\mathcal{V}$$

$$\mathcal{F} = \tfrac{1}{6}\mathcal{V}\left[C_{11} + 2C_{12}\right]\left[\delta\mathcal{V}/\mathcal{V}\right]^2, \tag{L18}$$

$$B = \tfrac{1}{3}\left[C_{11} + 2C_{12}\right]. \tag{L19}$$

Isotropic Solids

Distinguish between rotating all mass points and rotating a pattern of distortion in mass points that otherwise remain fixed.

$$e_{\alpha\beta}(\vec{r}) = \sum_{\gamma\delta} R^*_{\alpha\gamma} e'_{\gamma\delta}(\vec{r}\,')R_{\delta\beta} \tag{L20a}$$

with

$$\vec{r}\,' = R\vec{r} \text{ and } R = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & \sqrt{2} \end{pmatrix}. \tag{L20b}$$

$$\begin{aligned} 0 &= (2C_{xyxy} + C_{xxyy} - C_{xxxx})(e_{yy} - 2e_{xy} - e_{xx})(e_{yy} + 2e_{xy} - e_{xx}) && \text{(L21)} \\ \Rightarrow C_{xxxx} &= C_{xxyy} + 2C_{xyxy}. && \text{(L22)} \end{aligned}$$

$$\mathcal{F} = \frac{1}{2}\int d\vec{r}\,\lambda\Big(\sum_{\alpha} e_{\alpha\alpha}\Big)^2 + 2\mu\sum_{\alpha\beta} e^2_{\alpha\beta}. \tag{L23}$$

Kinetic energy:

$$T = \int d\vec{r}\,\frac{1}{2}\rho|\dot{\vec{u}}(\vec{r})|^2, \tag{L24}$$

Equation of motion:

$$\rho\ddot{u}_\alpha(\vec{r}) = -\frac{\delta\mathcal{F}}{\delta u_\alpha(\vec{r})} = \sum_\beta \frac{\partial}{\partial r_\beta}\sigma_{\alpha\beta}(\vec{r}), \tag{L25}$$

$$\sigma_{\alpha\beta} = \sum_{\gamma\delta} C_{\alpha\beta\gamma\delta}\, e_{\gamma\delta}. \tag{L26}$$

$$\int_{\mathcal{V}} d\vec{r}\,\rho\ddot{u}_\alpha = \int d\Sigma \sum n_\beta \sigma_{\beta\alpha} \tag{L27}$$

Stress figure

$$\sigma_{\alpha\beta} = \lambda\delta_{\alpha\beta}\sum_\gamma e_{\gamma\gamma} + 2\mu e_{\alpha\beta} \tag{L28}$$

$$\Rightarrow e_{\alpha\beta} = \frac{-\lambda\delta_{\alpha\beta}}{2\mu(3\lambda+2\mu)}\sum_{\gamma}\sigma_{\gamma\gamma} + \frac{1}{2\mu}\sigma_{\alpha\beta}. \quad \text{(L29)}$$

$$\rho\frac{\partial^2\vec{u}}{\partial t^2} = (\lambda+\mu)\nabla(\nabla\cdot\vec{u}) + \mu\nabla^2\vec{u}. \quad \text{(L30)}$$

$$\mathcal{S} = Ye_{zz} \quad \text{(L31)}$$

with

$$Y = \frac{\mu(3\lambda+2\mu)}{\lambda+\mu}; \quad \text{(L32)}$$

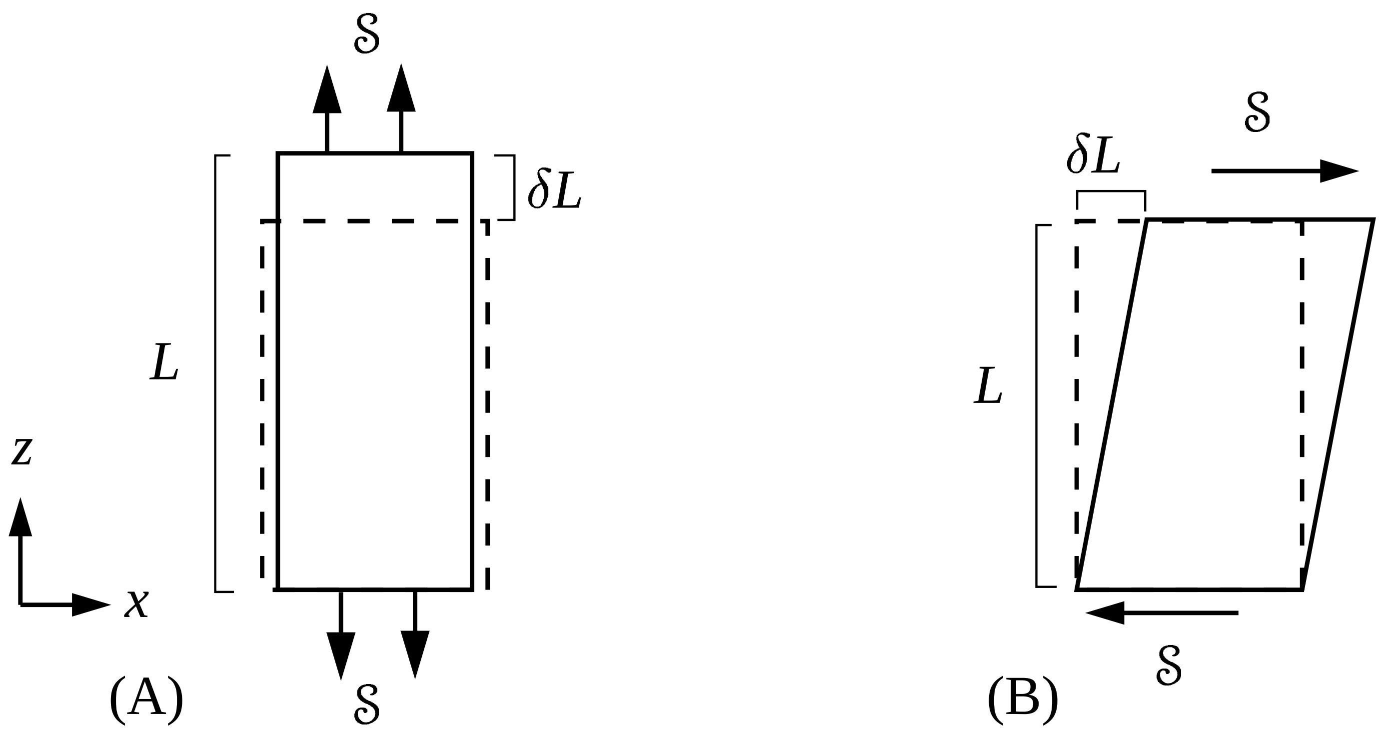
$$e_{xx} = e_{yy} = \frac{-\lambda}{2\mu(3\lambda+2\mu)}\mathcal{S}, \quad \text{(L33)}$$

$$\nu = \frac{\lambda}{2(\lambda+\mu)}. \quad \text{(L34)}$$

Isotropic Solids

$$\mathcal{S} = 2Ge_{yz} = G\frac{\partial u_y}{\partial z} \tag{L35}$$

$$\mathcal{S} = \frac{\delta L}{L}Y = e_{zz}Y \qquad\qquad \mathcal{S} = \frac{\delta L}{L}G = 2e_{xz}G$$



Isotropic Solids

Material	Young's Modulus Y (GPa)	Poisson Ratio ν
Lead (cast)	5	0.5
Tin (cast)	27	0.3
Glass	55	0.16
Aluminum (cast)	68	0.3
Copper (cast)	76	0.4
Zinc (cast)	76	0.3
Copper (soft, wrought)	100	0.4
Iron (cast)	110	0.3
Copper (hard drawn)	120	0.4
Iron (wrought)	200	0.3
Carbon steel	200	0.3
Tungsten	400	0.3

$$\Delta(\vec{r},t) = \vec{\nabla}\cdot\vec{u}(\vec{r},t) \text{ and } \vec{w}(\vec{r},t) = \vec{\nabla}\times\vec{u}(\vec{r},t). \tag{L36}$$

$$\rho\frac{\partial^2\Delta}{\partial t^2} = (\lambda+2\mu)\nabla^2\Delta, \tag{L37}$$

$$\rho\frac{\partial^2\vec{w}}{\partial t^2} = \mu\nabla^2\vec{w}, \tag{L38}$$

$\vec{u}$ is of form $\vec{u}_0 e^{i\vec{k}\cdot i\vec{r}-i\omega t}$

$$c_l = \sqrt{\frac{\lambda+2\mu}{\rho}}, \tag{L39}$$

$$c_t = \sqrt{\frac{\mu}{\rho}}. \tag{L40}$$

Director $\hat{n}$.

$$(\hat{n}\cdot\vec{\nabla})\hat{n} \tag{L41a}$$

$$\vec{\nabla}\cdot\hat{n} \tag{L41b}$$

$$\hat{n}\cdot\vec{\nabla}\times\hat{n}. \tag{L41c}$$

$$\frac{\partial n_\alpha}{\partial r_\beta}\frac{\partial n_\gamma}{\partial r_\delta}, \tag{L42}$$

$$\mathfrak{F} = \int d\vec{r}\,\mathfrak{F}(\vec{r}) = \tfrac{1}{2}\int d\vec{r}\sum_{\alpha\beta\gamma\delta} C_{\alpha\beta\gamma\delta}\frac{\partial n_\alpha}{\partial r_\beta}\frac{\partial n_\gamma}{\partial r_\delta}. \tag{L43}$$

$$0 = \frac{\partial}{\partial r_\alpha}1 = \frac{\partial}{\partial r_\alpha}(\hat{n}\cdot\hat{n}) \tag{L44}$$

$$= 2n_z\frac{\partial}{\partial r_\alpha}n_z = 2\frac{\partial}{\partial r_\alpha}n_z \tag{L45}$$

$$\frac{\partial n_\gamma}{\partial r_\delta} \to \frac{\partial n_\gamma}{\partial r_\delta} + \theta[\sum_\beta \frac{\partial n_\gamma}{\partial r_\beta} R_{\beta\delta} - R_{\gamma\beta} \frac{\partial n_\beta}{\partial r_\delta}] \tag{L46}$$

$$R = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{L47}$$

$$\begin{aligned} 0 = & \sum_{\alpha\gamma\delta} \left[\frac{\partial n_\alpha}{\partial y} \frac{\partial n_\gamma}{\partial r_\delta} C_{\alpha x\gamma\delta} - \frac{\partial n_\alpha}{\partial x} \frac{\partial n_\gamma}{\partial r_\delta} C_{\alpha y\gamma\delta} \right] \\ - & \sum_{\beta\gamma\delta} \left[\frac{\partial n_x}{\partial r_\beta} \frac{\partial n_\gamma}{\partial r_\delta} C_{y\beta\gamma\delta} - \frac{\partial n_y}{\partial r_\beta} \frac{\partial n_\gamma}{\partial r_\delta} C_{x\beta\gamma\delta} \right]. \end{aligned} \tag{L48}$$

$$\frac{\partial n_x}{\partial z} \frac{\partial n_y}{\partial y}, \tag{L49}$$

$$0 = -C_{yzyy} + C_{yxxz} + C_{xyxz}. \tag{L50}$$

$$\left[\frac{\partial n_x}{\partial x}+\frac{\partial n_y}{\partial y}\right]^2 \tag{L51a}$$

$$\left[\frac{\partial n_x}{\partial z}\right]^2+\left[\frac{\partial n_y}{\partial z}\right]^2 \tag{L51b}$$

$$\left[\frac{\partial n_y}{\partial x}-\frac{\partial n_x}{\partial y}\right]^2 \tag{L51c}$$

$$\left[\frac{\partial n_y}{\partial x}-\frac{\partial n_x}{\partial y}\right]\left[\frac{\partial n_y}{\partial y}+\frac{\partial n_x}{\partial x}\right] \tag{L51d}$$

$$\frac{\partial n_y}{\partial x}\frac{\partial n_x}{\partial y}-\frac{\partial n_y}{\partial y}\frac{\partial n_x}{\partial x}. \tag{L51e}$$

$$(\vec{\nabla}\cdot\hat{n})^2 \tag{L52a}$$

$$|\hat{n}\times(\vec{\nabla}\times\hat{n})|^2 \tag{L52b}$$

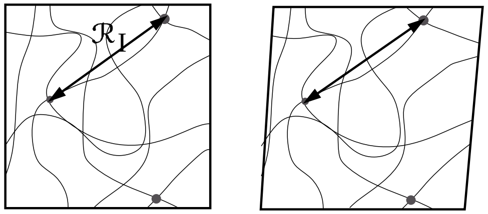
$$(\hat{n}\cdot(\vec{\nabla}\times\hat{n}))^2 \tag{L52c}$$

$$\hat{n}\cdot(\vec{\nabla}\times\hat{n})\vec{\nabla}\cdot\hat{n} \tag{L52d}$$

$$\tfrac{1}{2} \qquad \vec{\nabla}\cdot\left[(\hat{n}\cdot\vec{\nabla})\hat{n}-\hat{n}(\vec{\nabla}\cdot\hat{n})\right]. \tag{L52e}$$

$$\mathfrak{F}=\underbrace{\frac{K_1}{2}(\vec{\nabla}\cdot\hat{n})^2}_{\text{splay}} \quad +\underbrace{\frac{K_2}{2}(\hat{n}\cdot(\vec{\nabla}\times\hat{n}))^2}_{\text{twist}} \quad +\underbrace{\frac{K_3}{2}(\hat{n}\times(\vec{\nabla}\times\hat{n}))^2}_{\text{bend}}. \tag{L53}$$

$$\mathcal{F} \quad = \quad \mathcal{F}_0 + k_B T \Big[\sum_{j=1}^{N_\mathrm{p}} \frac{\mathcal{R}_j^2}{\mathcal{R}_\mathrm{I}{}^2} + N \frac{\mathcal{R}_\mathrm{I}^2}{(\mathcal{V})^{2/3}} - \mathcal{V}|B|n^2 + \mathcal{V}Cn^3 + \ldots \Big]. \tag{L54}$$



$$\mathcal{R}_j^\alpha \to \mathcal{R}_j^\alpha + \sum_\beta \mathcal{R}_j^\beta \frac{\partial u_\alpha}{\partial r_\beta}. \tag{L55}$$

$$\mathcal{V} = \mathcal{V} \sum_{\alpha\beta\gamma} \epsilon_{\alpha\beta\gamma} \left(\delta_{x\alpha} + \frac{\partial u_\alpha}{\partial x} \right) \left(\delta_{y\beta} + \frac{\partial u_\beta}{\partial y} \right) \left(\delta_{z\gamma} + \frac{\partial u_\gamma}{\partial z} \right) \tag{L56}$$

$$\Rightarrow \sum_\alpha \frac{\partial u_\alpha}{\partial r_\alpha} = \frac{1}{2} \sum_{\alpha\beta} \left[\frac{\partial u_\alpha}{\partial r_\beta} \frac{\partial u_\beta}{\partial r_\alpha} - \frac{\partial u_\alpha}{\partial r_\alpha} \frac{\partial u_\beta}{\partial r_\beta} \right]. \tag{L57}$$

$$\mathfrak{F} = \frac{k_B T}{\mathcal{R}_{\rm I}^2} \sum_j \sum_\alpha \left[(\mathcal{R}_j^\alpha)^2 + 2 \sum_\beta \mathcal{R}_j^\alpha \frac{\partial u_\alpha}{\partial r_\beta} \mathcal{R}_j^\beta + \sum_{\beta\beta'} \frac{\partial u_\alpha}{\partial r_\beta} \frac{\partial u_\alpha}{\partial r_{\beta'}} \mathcal{R}_j^\beta \mathcal{R}_j^{\beta'} \right]. \tag{L58}$$

$$\sum_{j=1}^{N_{\rm p}} \mathcal{R}_j^\alpha \mathcal{R}_j^\beta = N_{\rm p} \frac{\mathcal{R}_{\rm I}^2}{3} \delta_{\alpha\beta} \tag{L59}$$

$$\Rightarrow \mathfrak{F} = \frac{k_B T N_{\rm p}}{3} [3 + 2 \sum_\beta \frac{\partial u_\beta}{\partial r_\beta} + \sum_{\alpha\beta} \frac{\partial u_\alpha}{\partial r_\beta} \frac{\partial u_\alpha}{\partial r_\beta}] \tag{L60}$$

$$\Rightarrow \mathfrak{F} = \frac{k_B T N_{\rm p}}{3} \left[\sum_{\alpha\beta} \frac{\partial u_\alpha}{\partial r_\beta} \frac{\partial u_\alpha}{\partial r_\beta} + \sum_{\alpha\beta} \left(\frac{\partial u_\alpha}{\partial r_\beta} \frac{\partial u_\beta}{\partial r_\alpha} - \frac{\partial u_\alpha}{\partial r_\alpha} \frac{\partial u_\beta}{\partial r_\beta} \right) \right] \tag{L61}$$

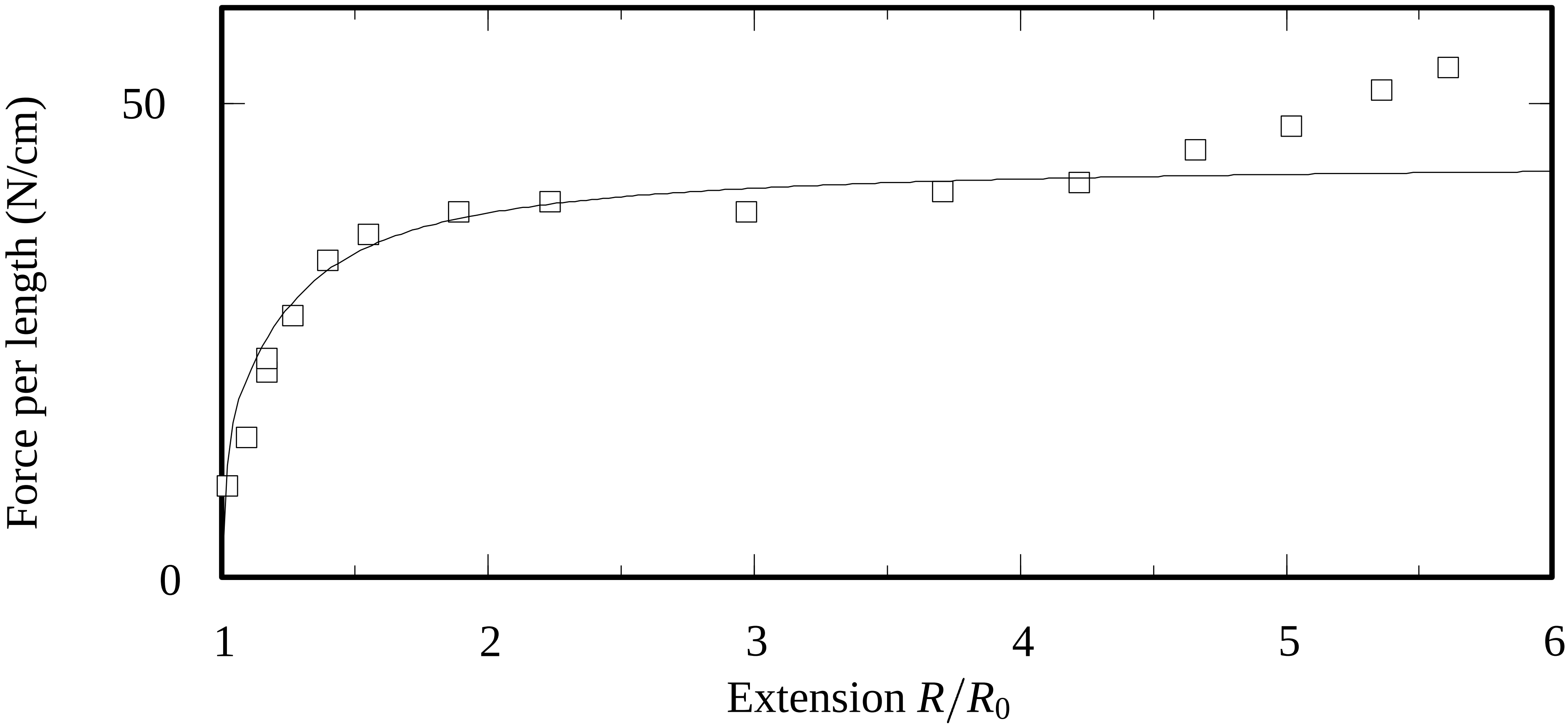
$$= \frac{k_B T N_{\rm p}}{3} \sum_{\alpha\beta} \left[2 e_{\alpha\beta}^2 - (\sum_\alpha e_{\alpha\alpha})^2 \right] \tag{L62}$$

$$= \frac{2 k_B T N_{\rm p}}{3} \sum_{\alpha\beta} e_{\alpha\beta}^2 . \tag{L63}$$

Rubber

$$\mathfrak{F} = \frac{2k_B T N_\mathrm{p}}{3}\left[\left(\sum_{\alpha\beta}[e_{\alpha\beta}+\delta_{\alpha\beta}]^2\right)-3\right]. \tag{L64}$$

$$\mathfrak{F} = \frac{2k_B T N_\mathrm{p}}{3}\left[2\left(\frac{R}{R_0}\right)^2+\left\{\left(\frac{R_0}{R}\right)^2\right\}^2-3\right]. \tag{L65}$$



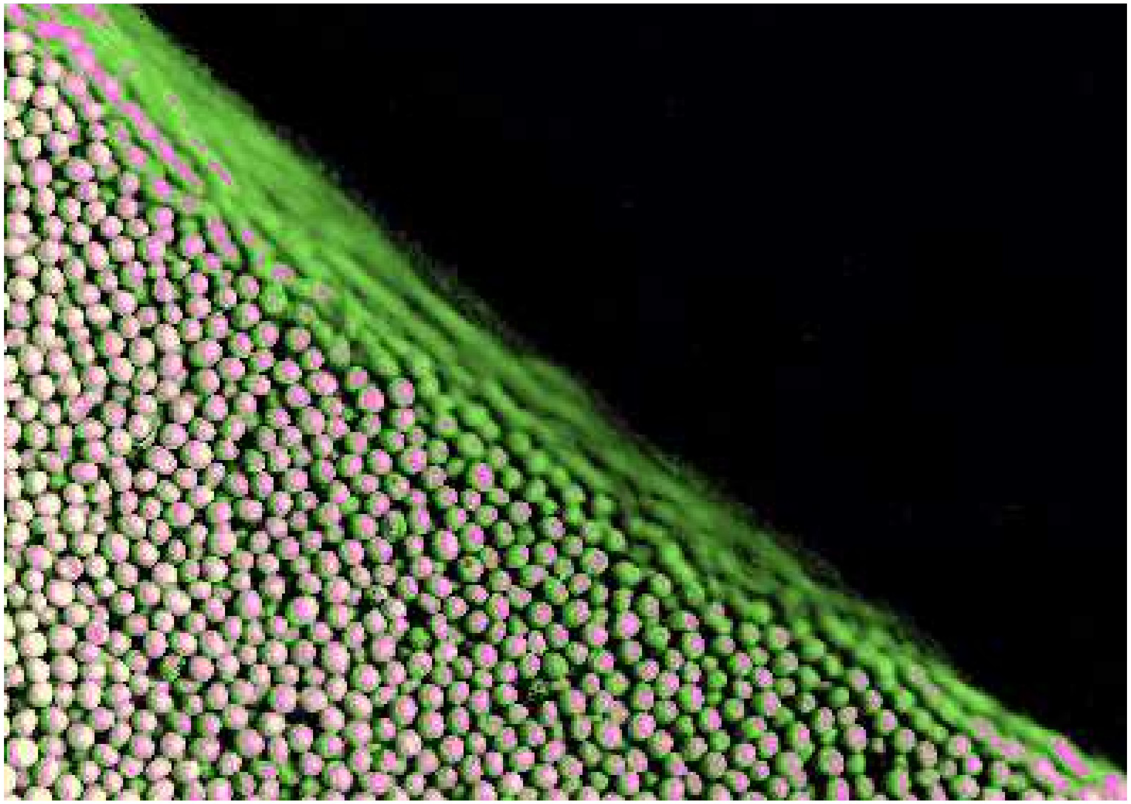
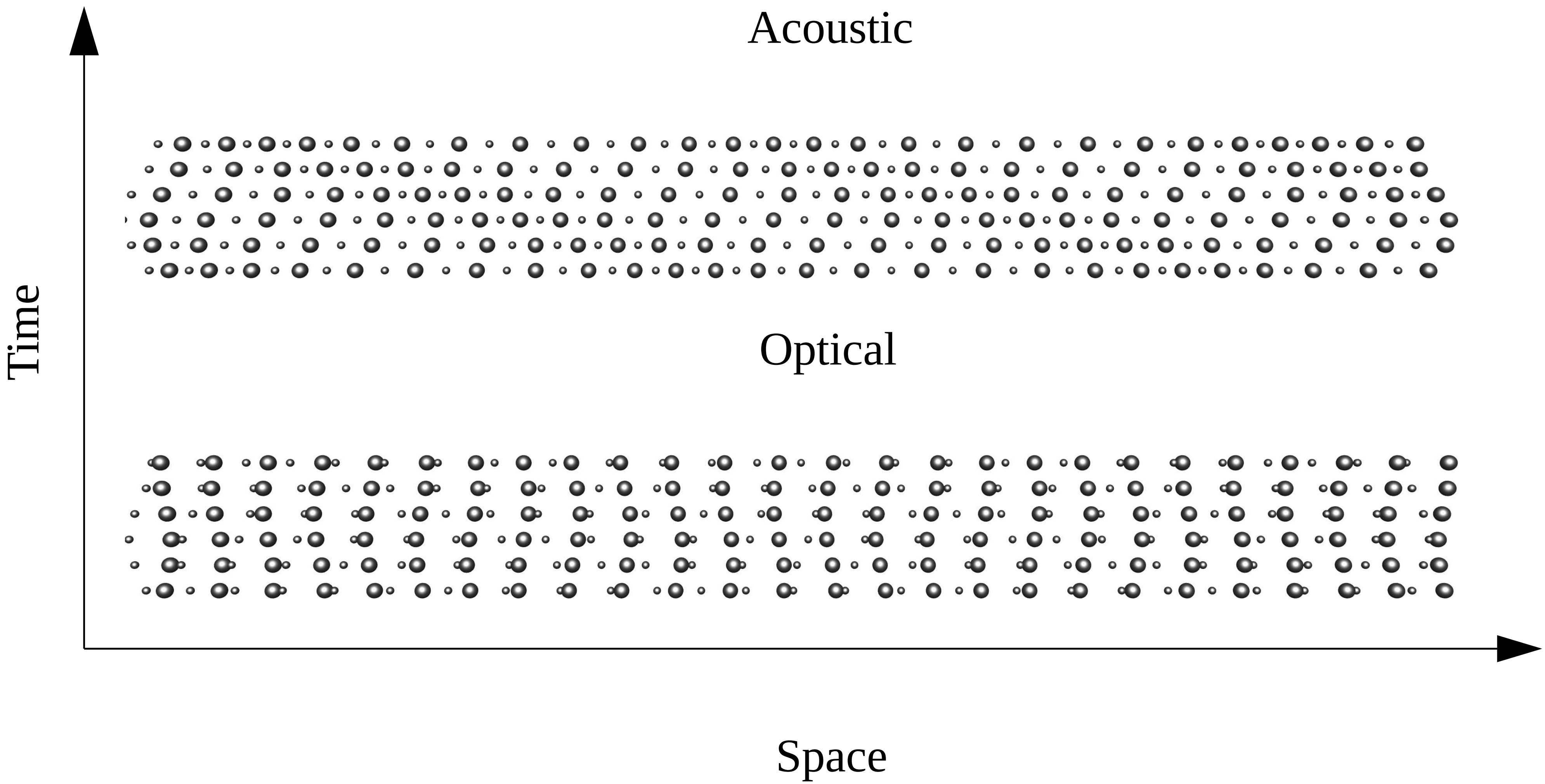


Figure 1: Avalanche in mustard seeds: Jaeger, University of Chicago

University of Chicago Granular Group

Duke University Granular Page

Phonons



Definitions

- Phonons
- Goldstone modes
- Acoustic branch
- Optical branch
- Density of phonon states
- Einstein model
- Debye model, Debye frequency, Debye temperature
- Grüneisen parameter
- Inelastic scattering, scattering length, inelastic structure factor
- Debye–Waller factor
- Kohn anomalies
- Mössbauer effect

Vibrations of a Classical Lattice

Find energy when atoms move small distances from equilibrium. Must keep changes to second order.

$$\mathcal{E}(\vec{u}^1, \vec{u}^2 \ldots \vec{u}^N), \tag{L1}$$

$$\mathcal{E} = \mathcal{E}_c + \sum_{\substack{\alpha \\ l}} \frac{\partial \mathcal{E}}{\partial u^l_\alpha} u^l_\alpha + \frac{1}{2} \sum_{\substack{\alpha\beta \\ ll'}} u^l_\alpha \Phi^{ll'}_{\alpha\beta} u^{l'}_\beta + \ldots. \tag{L2}$$

$$\Phi^{ll'}_{\alpha\beta} = \frac{\partial^2 \mathcal{E}}{\partial u^l_\alpha \partial u^{l'}_\beta} \tag{L3}$$

$$M\ddot{\vec{u}}^l = -\sum_{l'} \Phi^{ll'} \vec{u}^{l'}. \tag{L4}$$

In a crystal, because of translational invariance,

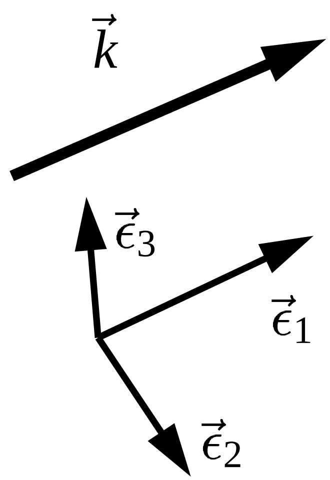
$$\sum_{l'} \Phi^{ll'} = 0. \tag{L5}$$

Polarization $\vec{\epsilon}$

$$\vec{u}^l = \vec{\epsilon} e^{i\vec{k}\cdot\vec{R}^l - i\omega t}. \tag{L6}$$

$$M\omega^2\vec{\epsilon} = \sum_{l'} \Phi^{ll'} e^{i\vec{k}\cdot(\vec{R}^l - \vec{R}^{l'})}\vec{\epsilon} \tag{L7a}$$

$$= \Phi(\vec{k})\vec{\epsilon}, \text{ with } \Phi(\vec{k}) = \sum_{l'} e^{i\vec{k}\cdot(\vec{R}^l - \vec{R}^{l'})}\Phi^{ll'}. \tag{L7b}$$



Normal Modes

$$\omega^2_{\vec{k}\nu} = \frac{\Phi_\nu(\vec{k})}{M}. \tag{L8}$$

$$\Phi(\vec{k}+\vec{K}) = \Phi(\vec{k}), \tag{L9}$$

- Can restrict $\vec{k}$ to the first Brillouin zone.
- Phonons, like electrons, are waves in a periodic potential.
- $\vec{k}$ in Brillouin zone completely exhausts all phonon states.

Example in One Dimension

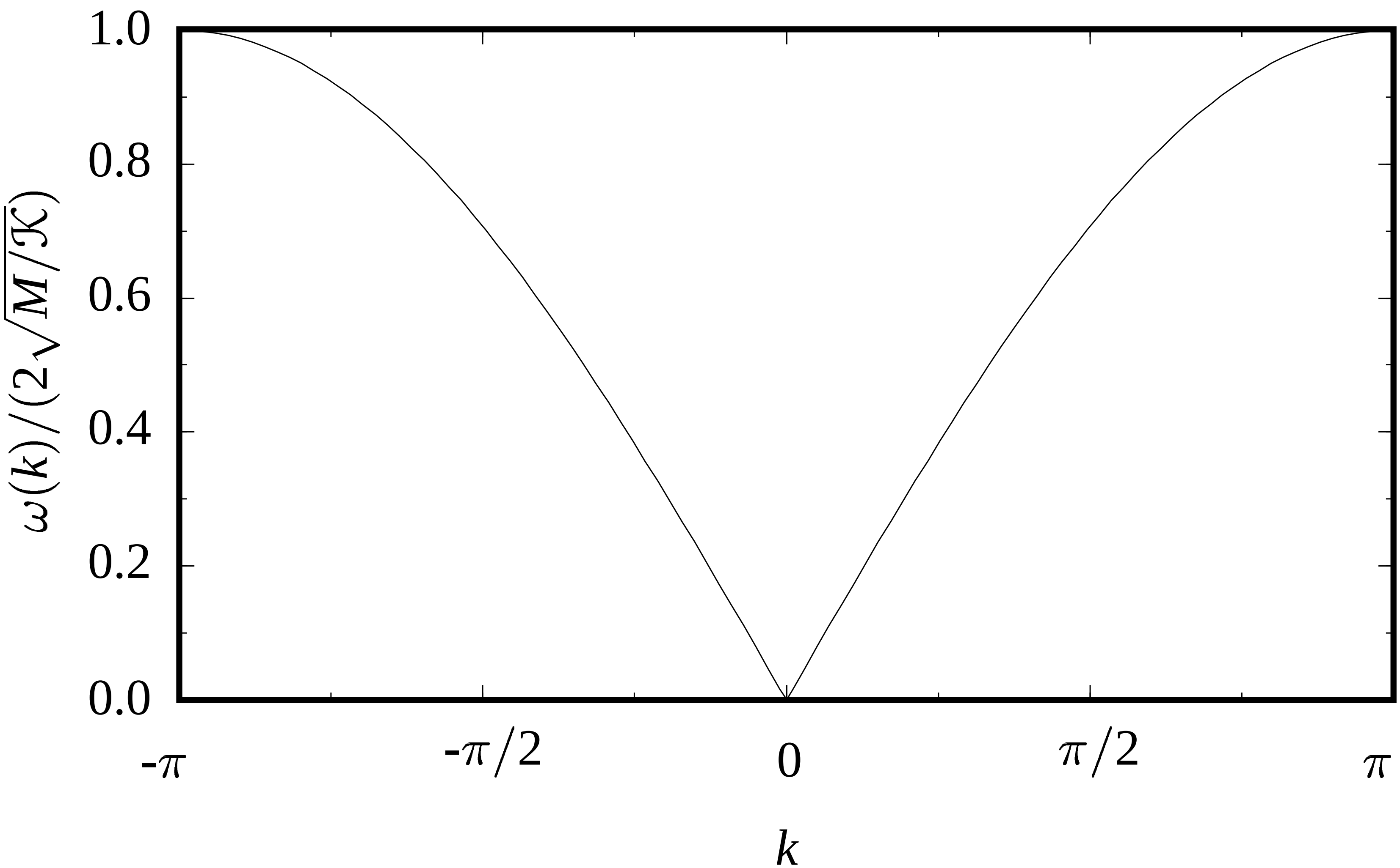
$$M\ddot{u}^l = \mathcal{K}(u^{l+1} - 2u^l + u^{l-1}). \tag{L10}$$

Substituting $u \propto \exp(ikl - i\omega t)$ gives

$$M\omega^2 = ? \qquad ? \tag{L11}$$

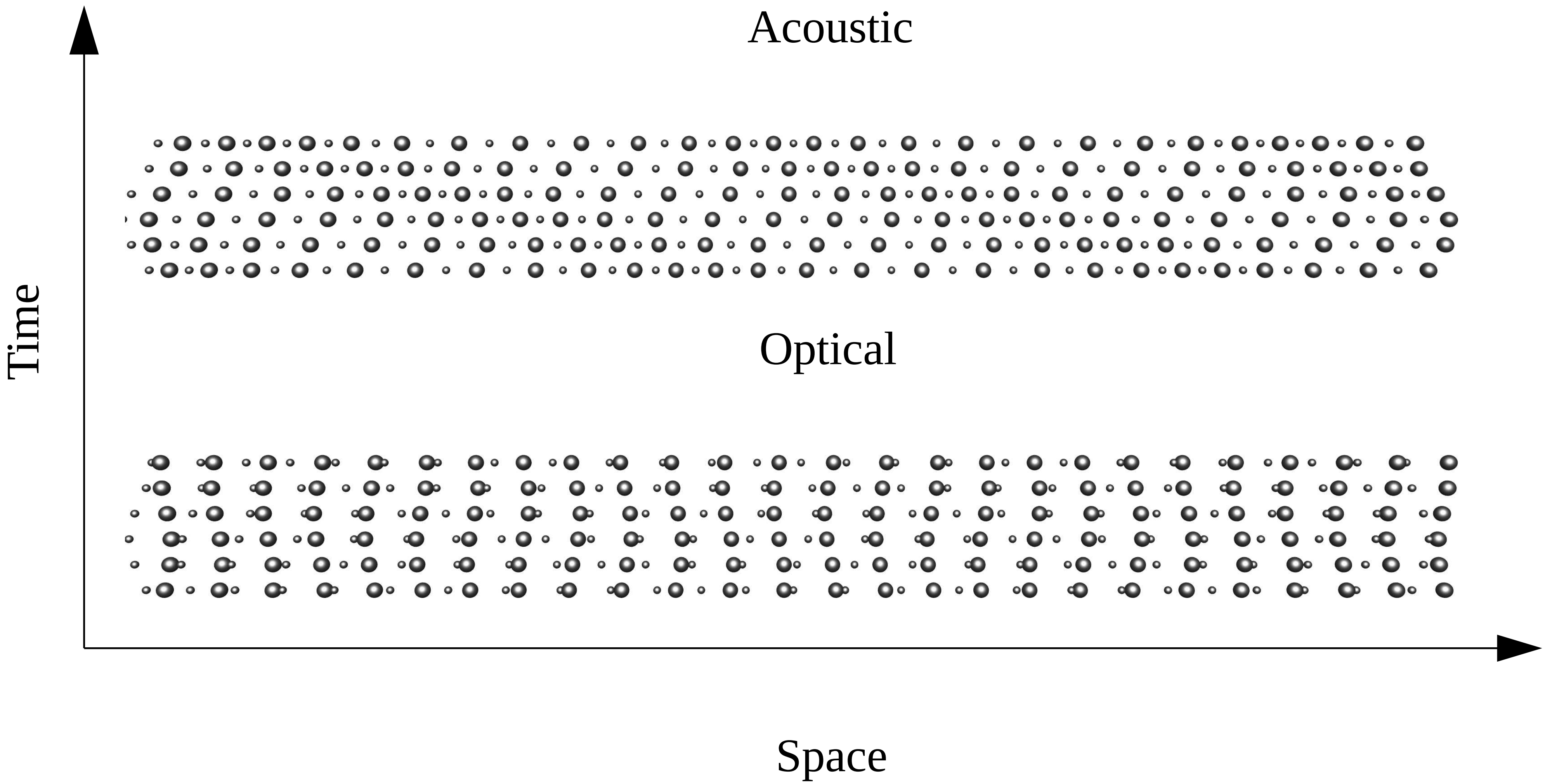
$$\Rightarrow \omega = ? \qquad ? \tag{L12}$$

Example in One Dimension



Linear dispersion as $\vec{k} = \rightarrow 0$ is generic, example of Goldstone mode.

Lattice with a Basis



$$M_n \ddot{\vec{u}}^{ln} = -\sum_{l'n'} \Phi^{lnl'n'} \vec{u}^{l'n'}, \tag{L13}$$

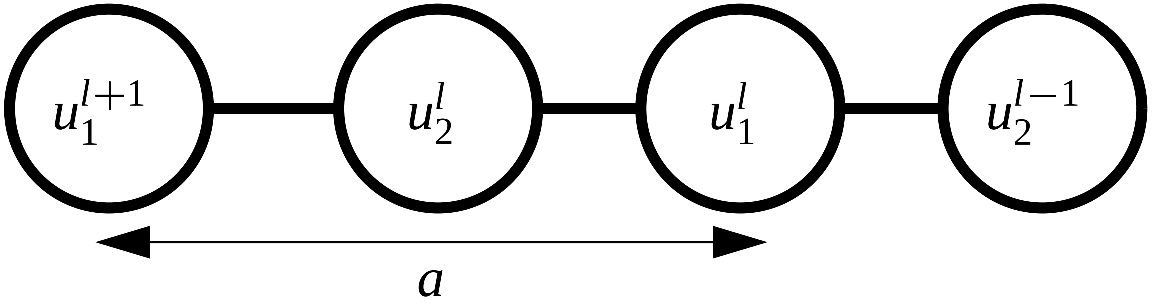
Lattice with a Basis

$$\vec{u}^{ln} = \vec{\epsilon}^{n} e^{i\vec{k}\cdot\vec{R}^{ln} - i\omega t}, \tag{L14}$$

$$\Rightarrow M_n \omega^2 \vec{\epsilon}^{n} = \sum_{n'} \Phi^{nn'}(\vec{k}) \vec{\epsilon}^{n'}. \tag{L15}$$

$$M_p \omega^2 \epsilon_p = \sum_{p'}^{3N} \Phi_{pp'}(\vec{k}) \epsilon_{p'}. \tag{L16}$$

One–dimensional example with basis



$$M_1\ddot{u}_1^l = \mathcal{K}(u_2^l - 2u_1^l + u_2^{l-1}) \quad \text{(L17a)}$$

$$M_2\ddot{u}_2^l = \mathcal{K}(u_1^{l+1} - 2u_2^l + u_1^l) \quad \text{(L17b)}$$

$$\Rightarrow -\omega^2 M_1\epsilon_1 e^{ikla} = \mathcal{K}(\epsilon_2 - 2\epsilon_1 + \epsilon_2 e^{-ika})e^{ikla} \quad \text{(L18a)}$$

$$-\omega^2 M_2\epsilon_2 e^{ikla} = ? \qquad ? \quad \text{(L18b)}$$

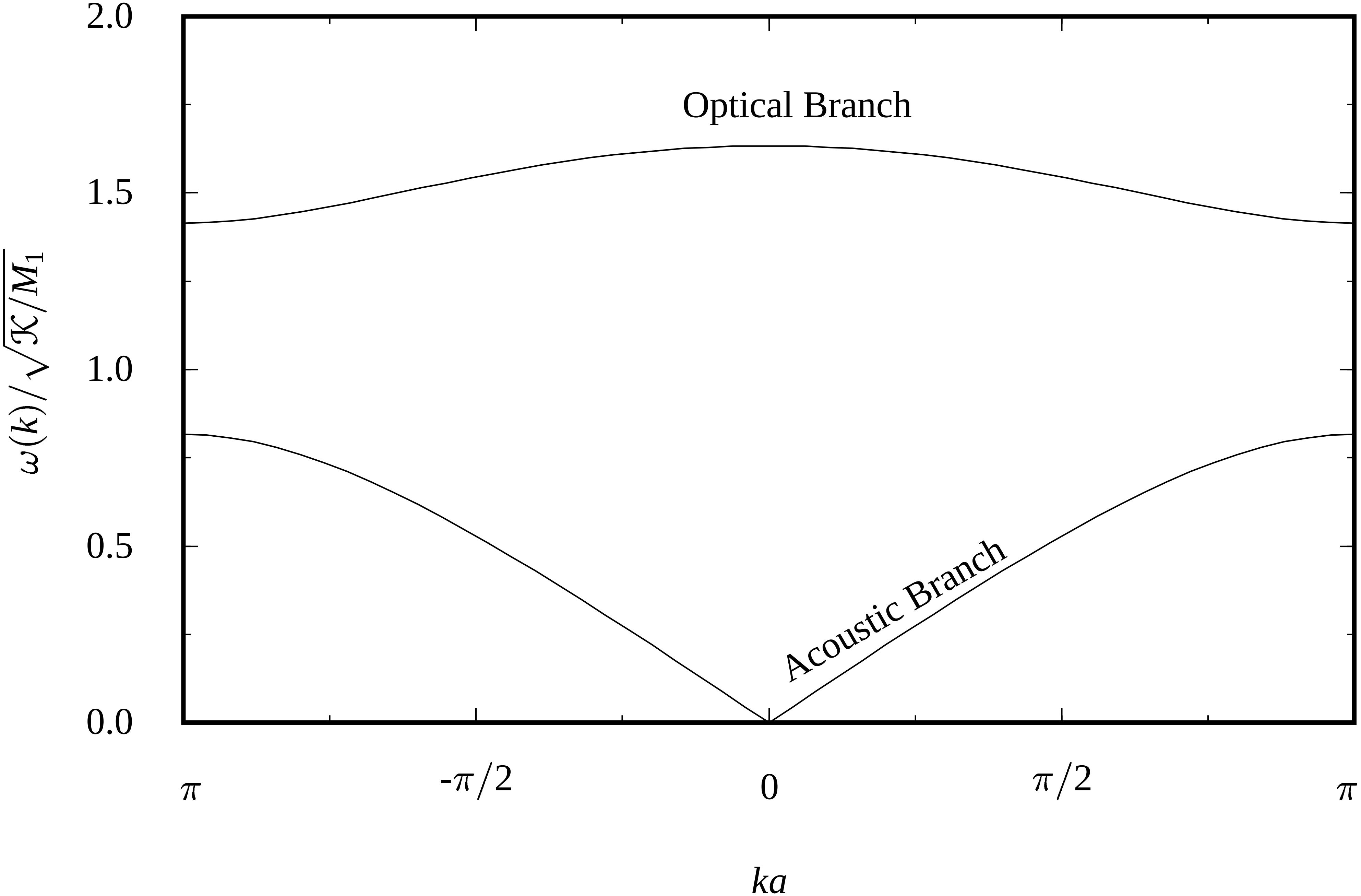
$$\Rightarrow \omega = \sqrt{\mathcal{K}}\sqrt{\frac{M_1 + M_2 \pm \sqrt{M_1^2 + 2M_1M_2\cos ka + M_2^2}}{M_1M_2}}. \quad \text{(L19)}$$

One–dimensional example with basis

$$\omega(k) = \sqrt{\frac{\mathcal{K}}{2(M_1+M_2)}}ka, \qquad \epsilon_1 = 1; \epsilon_2 = 1+ika/2, \tag{L20a}$$

$$\omega(k) = \sqrt{\frac{2\mathcal{K}(M_1+M_2)}{M_1M_2}}, \qquad \epsilon_1 = M_2; \epsilon_2 = -M_1(1+ika/2). \tag{L20b}$$

One–dimensional example with basis



Diamond Lattice

$$U = \frac{1}{2} \sum_{lnl'n'} \phi_{nn'}(|\vec{u}^{ln} + \vec{R}^{ln} - \vec{u}^{l'n'} - \vec{R}^{l'n'}|). \quad \text{(L21)}$$

$$U \approx \frac{1}{4} \sum_{lnl'n'} [\vec{u}^{ln} - \vec{u}^{l'n'}] \mathbf{f}^{lnl'n'} [\vec{u}^{ln} - \vec{u}^{l'n'}], \quad \text{(L22)}$$

$$\mathbf{f}^{lnl'n'}_{\alpha\beta} = \frac{\partial^2}{\partial r_\alpha r_\beta} \phi_{nn'}(|\vec{r}|)\Big|_{\vec{r}=\vec{R}^{ln}-\vec{R}^{l'n'}} \quad \text{(L23)}$$

$$= \left\{ \frac{r_\alpha r_\beta}{r^2} [\phi''_{nn'}(r) - \frac{1}{r}\phi'_{nn'}(r)] + \frac{\delta_{\alpha\beta}}{r} \phi'_{nn'}(r) \right\} \Big|_{\vec{r}=\vec{R}^{ln}-\vec{R}^{l'n'}}. \quad \text{(L24)}$$

$$\sum_{l'n'} \frac{\vec{r}}{r} \phi'_{nn'}(r)\Big|_{\vec{r}=\vec{R}^{ln}-\vec{R}^{l'n'}} = 0. \quad \text{(L25)}$$

$$\Phi^{lnl'n'} = \sum_{l''n''} \mathbf{f}^{lnl''n''} (\delta_{ll'}\delta_{nn'} - \delta_{l'l''}\delta_{n'n''}). \quad \text{(L26)}$$

$$f_1 - f_2 = \phi''(d) - \frac{1}{d}\phi'(d) \qquad \text{(L27)}$$

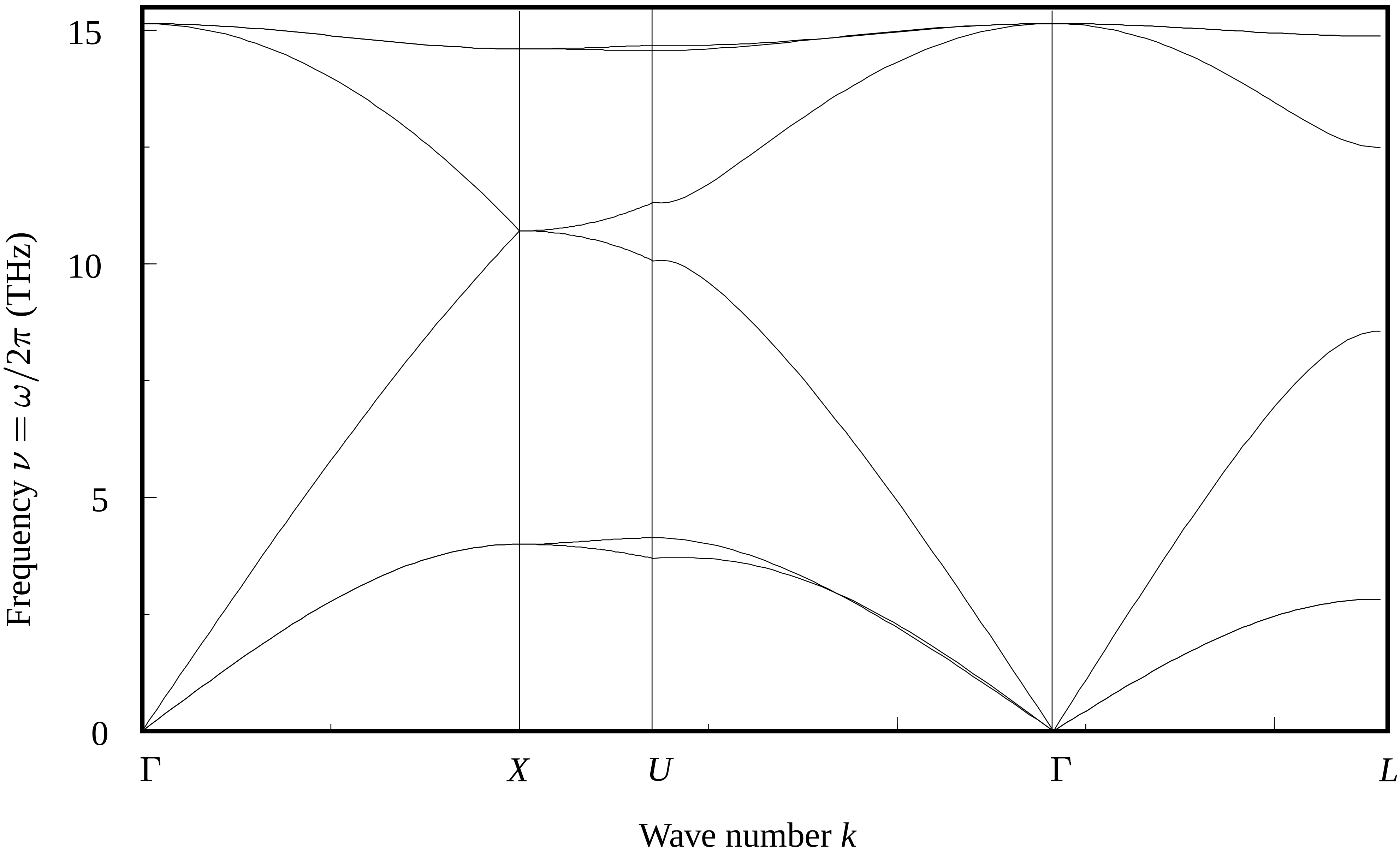
and

$$f_2 = \frac{1}{d}\phi'(d) \qquad \text{(L28)}$$

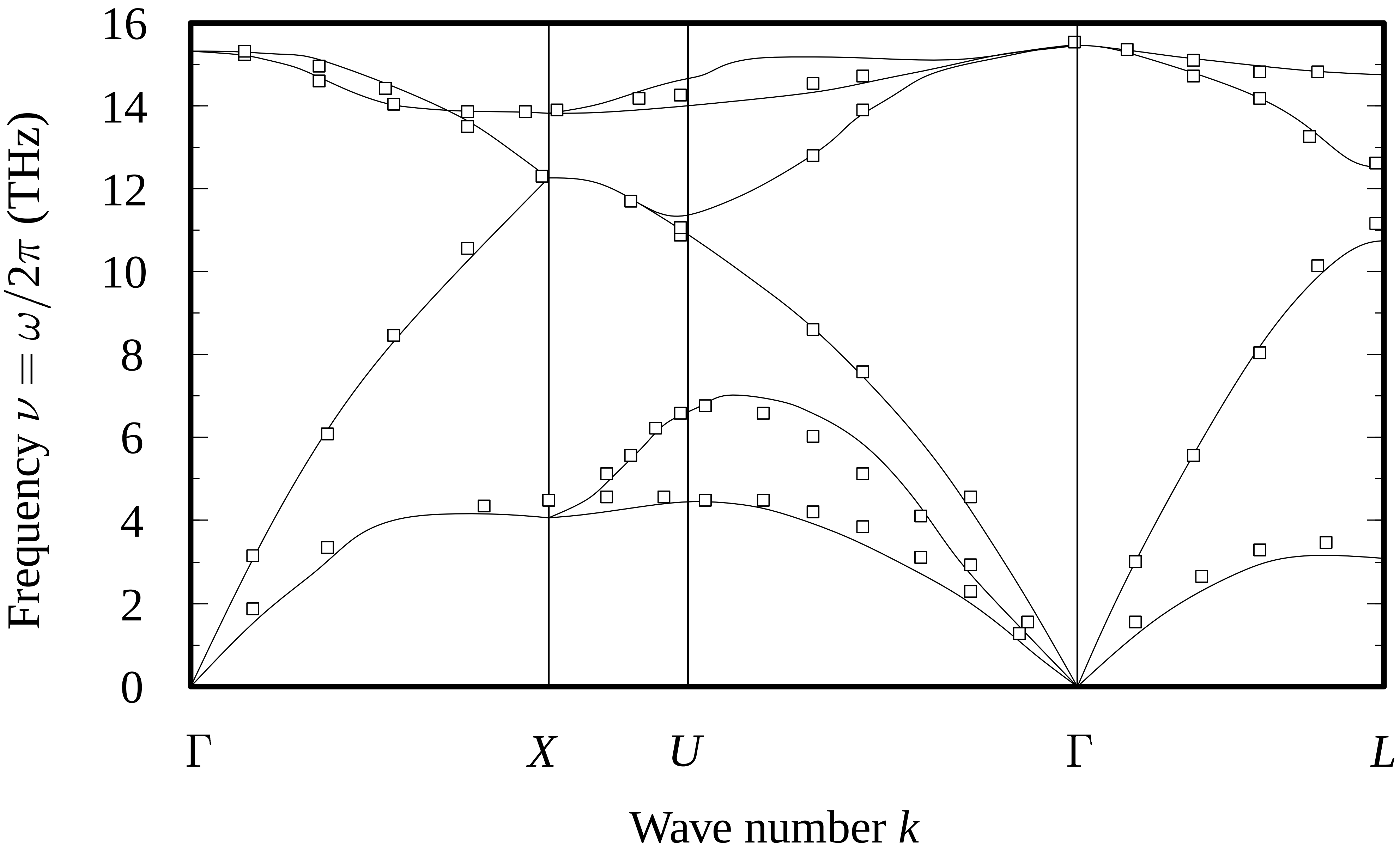
$$\Rightarrow \mathbf{f}^{lnl'n'}_{\alpha\beta} = \frac{r_\alpha r_\beta}{r^2}[f_1 - f_2] + \delta_{\alpha\beta} f_2\Big|_{\vec{r}=\vec{R}^{ln}-\vec{R}^{l'n'}}. \qquad \text{(L29)}$$

$$\Phi^{nn'}(\vec{k}) = \sum_{l'} \Phi^{0nl'n'} e^{i\vec{k}\cdot(\vec{R}^{0n}-\vec{R}^{l'n'})} \qquad \text{(L30)}$$

Comparison with Experiment



Comparison with Experiment



$$\hbar\omega_{\vec{k}\nu}(n+\tfrac{1}{2}); \tag{L31}$$

$$\hat{\mathcal{H}} = \frac{\hat{P}^2}{2M} + \frac{1}{2}M\omega^2\hat{R}^2 \tag{L32}$$

Raising and lowering operators

$$\hat{a}^\dagger = \sqrt{\frac{M\omega}{2\hbar}}\hat{R} - i\sqrt{\frac{1}{2\hbar M\omega}}\hat{P} \tag{L33a}$$

$$\hat{a} = \sqrt{\frac{M\omega}{2\hbar}}\hat{R} + i\sqrt{\frac{1}{2\hbar M\omega}}\hat{P}. \tag{L33b}$$

$$\hat{\mathcal{H}} = \hbar\omega\left(\hat{a}^\dagger a + \tfrac{1}{2}\right) = \hbar\omega\left(\hat{n} + \tfrac{1}{2}\right) \tag{L34}$$

$$\hat{R} = \sqrt{\frac{\hbar}{2M\omega}}(\hat{a} + \hat{a}^\dagger). \tag{L35}$$

$$\hat{\mathcal{H}} = \sum_l \frac{\hat{P}^{l\,2}}{2M} + \tfrac{1}{2}\sum_{ll'} \hat{u}^l \Phi^{ll'} \hat{u}^{l'} \ldots . \tag{L36}$$

$$\hat{a}_{\vec{k}\nu} = \frac{1}{\sqrt{N}} \sum_{l=1}^{N} e^{-i\vec{k}\cdot\vec{R}^l} \vec{\epsilon}^{\,*}_{\vec{k}\nu} \cdot \left[\sqrt{\frac{M\omega_{\vec{k}\nu}}{2\hbar}}\hat{u}^l + i\sqrt{\frac{1}{2\hbar M\omega_{\vec{k}\nu}}}\hat{P}^l\right] \tag{L37a}$$

$$\hat{a}^\dagger_{\vec{k}\nu} = \frac{1}{\sqrt{N}} \sum_{l=1}^{N} e^{i\vec{k}\cdot\vec{R}^l} \vec{\epsilon}_{\vec{k}\nu} \cdot \left[\sqrt{\frac{M\omega_{\vec{k}\nu}}{2\hbar}}\hat{u}^l - i\sqrt{\frac{1}{2\hbar M\omega_{\vec{k}\nu}}}\hat{P}^l\right]. \tag{L37b}$$

$$\hat{u}^l = \frac{1}{\sqrt{N}} \sum_{\vec{k}\nu} \left[\hat{u}_{\vec{k}\nu} e^{i\vec{k}\cdot\vec{R}^l} + \hat{u}^\dagger_{\vec{k}\nu} e^{-i\vec{k}\cdot\vec{R}^l}\right] \text{ with } \hat{u}_{\vec{k}\nu} \equiv \sqrt{\frac{\hbar}{2M\omega_{\vec{k}\nu}}}\vec{\epsilon}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu} \tag{L38a}$$

and

$$\hat{P}^l = \frac{1}{\sqrt{N}} \sum_{\vec{k}\nu} \left[\hat{P}_{\vec{k}\nu} e^{i\vec{k}\cdot\vec{R}^l} + \hat{P}^\dagger_{\vec{k}\nu} e^{-i\vec{k}\cdot\vec{R}^l}\right] \text{ with } \hat{P}_{\vec{k}\nu} = -i\sqrt{\frac{\hbar M\omega_{\vec{k}\nu}}{2}}\vec{\epsilon}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}. \tag{L38b}$$

$$[\hat{P}^l, \hat{R}^l] = -i\hbar$$

$$[\hat{a}_{\vec{k}\nu}, \hat{a}^{\dagger}_{\vec{k}\nu}] = 1. \tag{L39}$$

$$\omega_{\vec{k}\nu} = \omega_{-\vec{k}\nu}. \tag{L40}$$

$$\sum_{l} \frac{\hat{P}^{l\,2}}{2M} = \sum_{\vec{k}\nu} \frac{\hbar\omega_{\vec{k}\nu}}{4} \left\{ \begin{array}{l} [\hat{a}_{\vec{k}\nu}\hat{a}^{\dagger}_{\vec{k}\nu} + \hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}] \\ -[\hat{a}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}\vec{\epsilon}_{\vec{k}\nu}\cdot\vec{\epsilon}_{-\vec{k}\nu} + \hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}^{\dagger}_{\vec{k}\nu}\vec{\epsilon}^{*}_{\vec{k}\nu}\cdot\vec{\epsilon}^{*}_{-\vec{k}\nu}] \end{array} \right\} \tag{L41a}$$

$$\sum_{ll'} \tfrac{1}{2}\hat{u}^{l}\Phi^{ll'}\hat{u}^{l'} = \sum_{\vec{k}\nu} \frac{\hbar\omega_{\vec{k}\nu}}{4} \left\{ \begin{array}{l} [\hat{a}_{\vec{k}\nu}\hat{a}^{\dagger}_{\vec{k}\nu} + \hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}] \\ +[\hat{a}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}\vec{\epsilon}_{\vec{k}\nu}\cdot\vec{\epsilon}_{-\vec{k}\nu} + \hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}^{\dagger}_{\vec{k}\nu}\vec{\epsilon}^{*}_{\vec{k}\nu}\cdot\vec{\epsilon}^{*}_{-\vec{k}\nu}] \end{array} \right\} \tag{L41b}$$

Don't assume $\vec{\epsilon}^{*}_{\vec{k}\nu} = \vec{\epsilon}_{-\vec{k}\nu}$, as it leads to problems for longitudinal modes.

$$\hat{\mathcal{H}} = \sum_{\vec{k}\nu} \frac{\hbar\omega_{\vec{k}\nu}}{2}[\hat{a}_{\vec{k}\nu}\hat{a}^{\dagger}_{\vec{k}\nu} + \hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}] = \sum_{\vec{k}\nu} \hbar\omega_{\vec{k}\nu}(\hat{a}^{\dagger}_{\vec{k}\nu}\hat{a}_{\vec{k}\nu} + \tfrac{1}{2}). \tag{L42}$$

$$\hat{\mathcal{H}} = \sum_i \hbar\omega_i(\hat{n}_i + \tfrac{1}{2}). \tag{L43}$$

$$\hat{a}_{\vec{k}\nu}(t) = e^{i\hat{\mathcal{H}}t/\hbar}\hat{a}_{\vec{k}\nu}e^{-i\hat{\mathcal{H}}t/\hbar} \tag{L44}$$

so that

$$\frac{\partial \hat{a}_{\vec{k}\nu}(t)}{\partial t} = e^{i\hat{\mathcal{H}}t/\hbar} i[\hat{\mathcal{H}}, \hat{a}_{\vec{k}\nu}]e^{-i\mathcal{H}t/\hbar}/\hbar \tag{L45}$$

$$= -i\omega_{\vec{k}\nu}\hat{a}_{\vec{k}\nu} \tag{L46}$$

$$\Rightarrow \hat{a}_{\vec{k}\nu}(t) = \hat{a}_{\vec{k}\nu}e^{-i\omega_{\vec{k}\nu}t}. \tag{L47}$$

$$\hat{u}^l(t) = \frac{1}{\sqrt{N}}\sum_{\vec{k}\nu}[\hat{u}_{\vec{k}\nu}e^{i\vec{k}\cdot\vec{R}^l - i\omega_{\vec{k}\nu}t} + \hat{u}^\dagger_{\vec{k}\nu}e^{-i\vec{k}\cdot\vec{R}^l + i\omega_{\vec{k}\nu}t}]. \tag{L48}$$

Testing ground for quantum mechanics

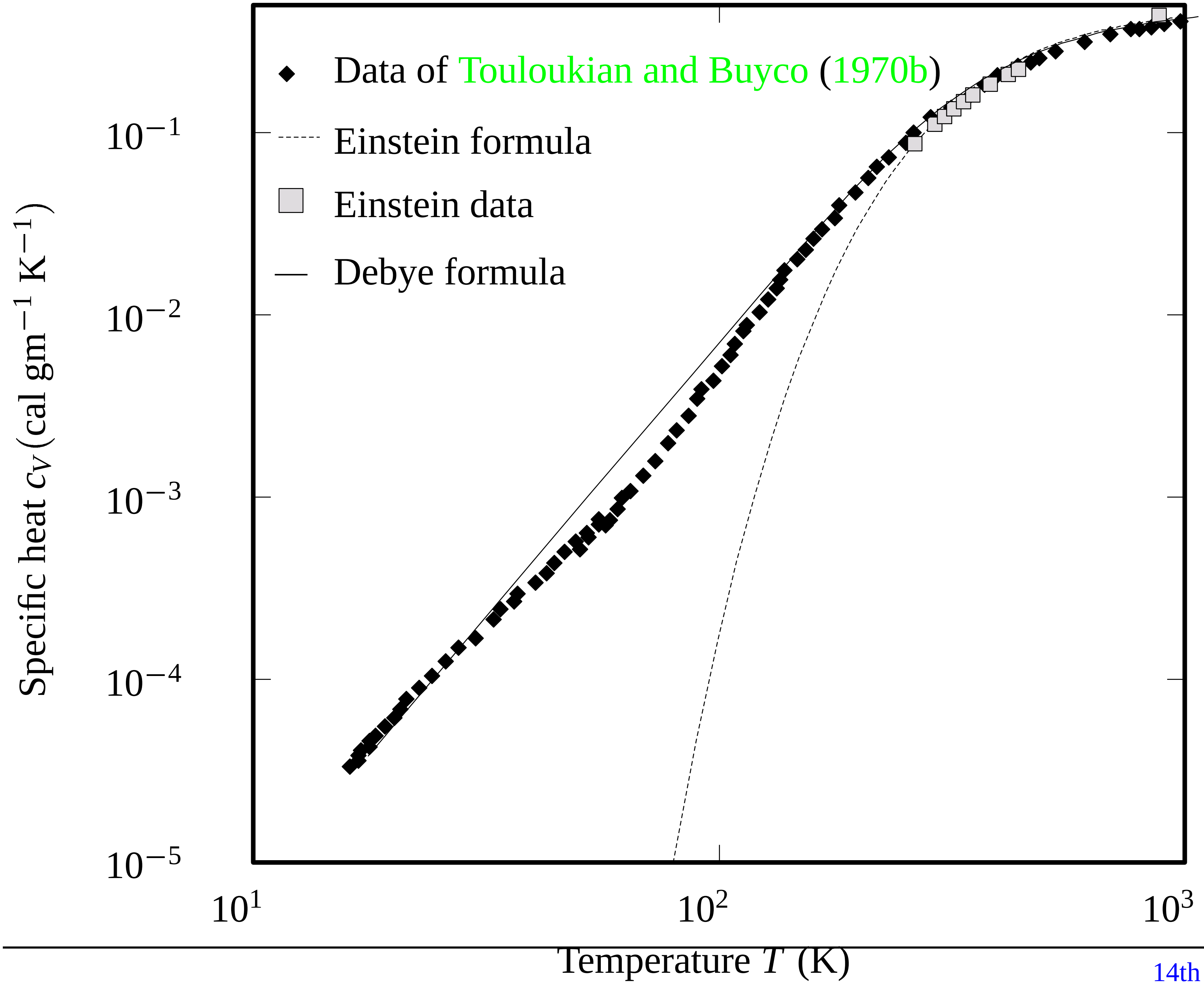
Einstein model

$$\mathcal{E} = \frac{3N\hbar\omega_0}{e^{\hbar\beta\omega_0} - 1} \tag{L49}$$

$$\Rightarrow C_{\mathcal{V}} = \frac{\partial \mathcal{E}}{\partial T}\Big|_{\mathcal{V}} = \frac{3N(\hbar\omega_0)^2 e^{\hbar\beta\omega_0}/(k_B T^2)}{[e^{\hbar\beta\omega_0} - 1]^2}. \tag{L50}$$

Residual ray of diamond $\omega_0 = 1.71 \cdot 10^{14}\mathrm{s}^{-1}$ leads to

Phonon Specific Heat



$$\mathcal{E} = \sum_i \hbar\omega_i (l_i + \tfrac{1}{2}). \tag{L51}$$

$$Z = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \ldots e^{-\beta \sum_i \hbar\omega_i (l_i + 1/2)} \tag{L52}$$

$$= \prod_{i=1}^{\infty} \left\{ \sum_{l=0}^{\infty} e^{-\beta\hbar\omega_i (n+1/2)} \right\} \tag{L53}$$

$$= \prod_{i=1}^{\infty} \left\{ \frac{e^{-\beta\hbar\omega_i/2}}{1 - \exp(-\beta\hbar\omega_i)} \right\} \tag{L54}$$

$$\Rightarrow \mathfrak{F} = -k_B T \ln Z = \sum_i \frac{\hbar\omega_i}{2} + k_B T \ln(1 - e^{-\beta\hbar\omega_i}) \tag{L55}$$

$$\Rightarrow \mathcal{E} = \frac{\partial \beta \mathfrak{F}}{\partial \beta} = \sum_i \frac{\hbar\omega_i}{2} + \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i} - 1} = \sum_i \hbar\omega_i (n_i + \tfrac{1}{2}) \tag{L56}$$

with

$$n_i \equiv \frac{1}{e^{\beta\hbar\omega_i} - 1} \tag{L57}$$

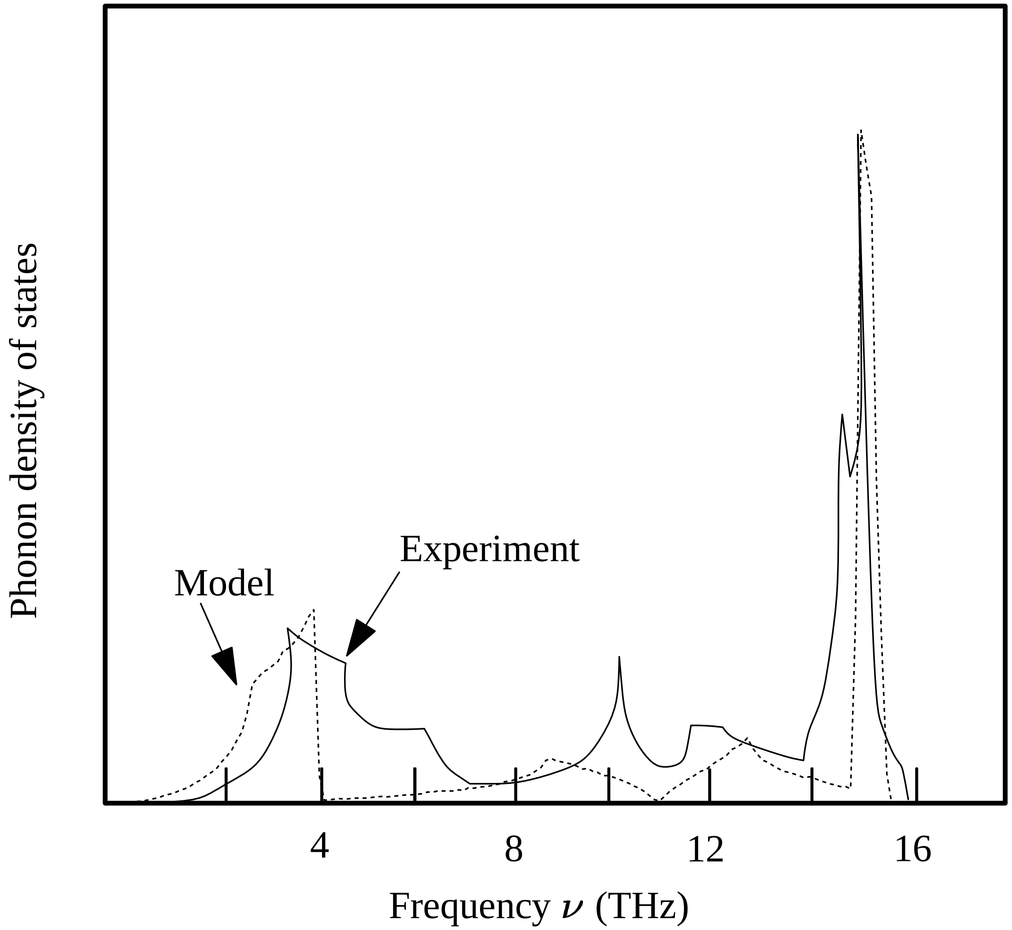
Phonon Specific Heat

$$\Rightarrow C_{\mathcal{V}} = \frac{\partial \mathcal{E}}{\partial T}\Big|_{\mathcal{V}} = \sum_i C_i = \sum_i \hbar\omega_i \frac{\partial n_i}{\partial T}. \tag{L58}$$

$$D(\omega) = \sum_i \delta(\omega - \omega_i) = \sum_{\vec{k}\nu} \delta(\omega - \omega_{\vec{k}\nu}) = \int \frac{d\vec{k}}{(2\pi)^3} \sum_\nu \delta(\omega - \omega_{\vec{k}\nu}), \tag{L59}$$

$$C_{\mathcal{V}} = \mathcal{V} \int_0^\infty d\omega\, D(\omega) \frac{\partial}{\partial T} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}. \tag{L60}$$

Phonon Specific Heat



- Characteristic frequency of 16 THz
- Cusps are van Hove singularities (Section 7.2.1)

Dulong and Petit

$$C_{\mathcal{V}} = Nk_B \tag{L61}$$

$$D(\omega) = \int \frac{d\vec{k}}{(2\pi)^3} \sum_{\nu} \delta(\omega - c_{\nu}(\hat{k})k) \tag{L62}$$

$$= \frac{3\omega^2}{2\pi^2 c^3} \text{ with } \frac{1}{c^3} = \frac{1}{3} \sum_{\nu} \int \frac{d\Sigma}{4\pi} \frac{1}{c_{\nu}^3(\hat{k})} \tag{L63}$$

$$\Rightarrow C_{\mathcal{V}} = \mathcal{V} \frac{\partial}{\partial T} \frac{3(k_B T)^4}{2\pi^2 (c\hbar)^3} \int_0^{\infty} dx \frac{x^3}{e^x - 1} \tag{L64}$$

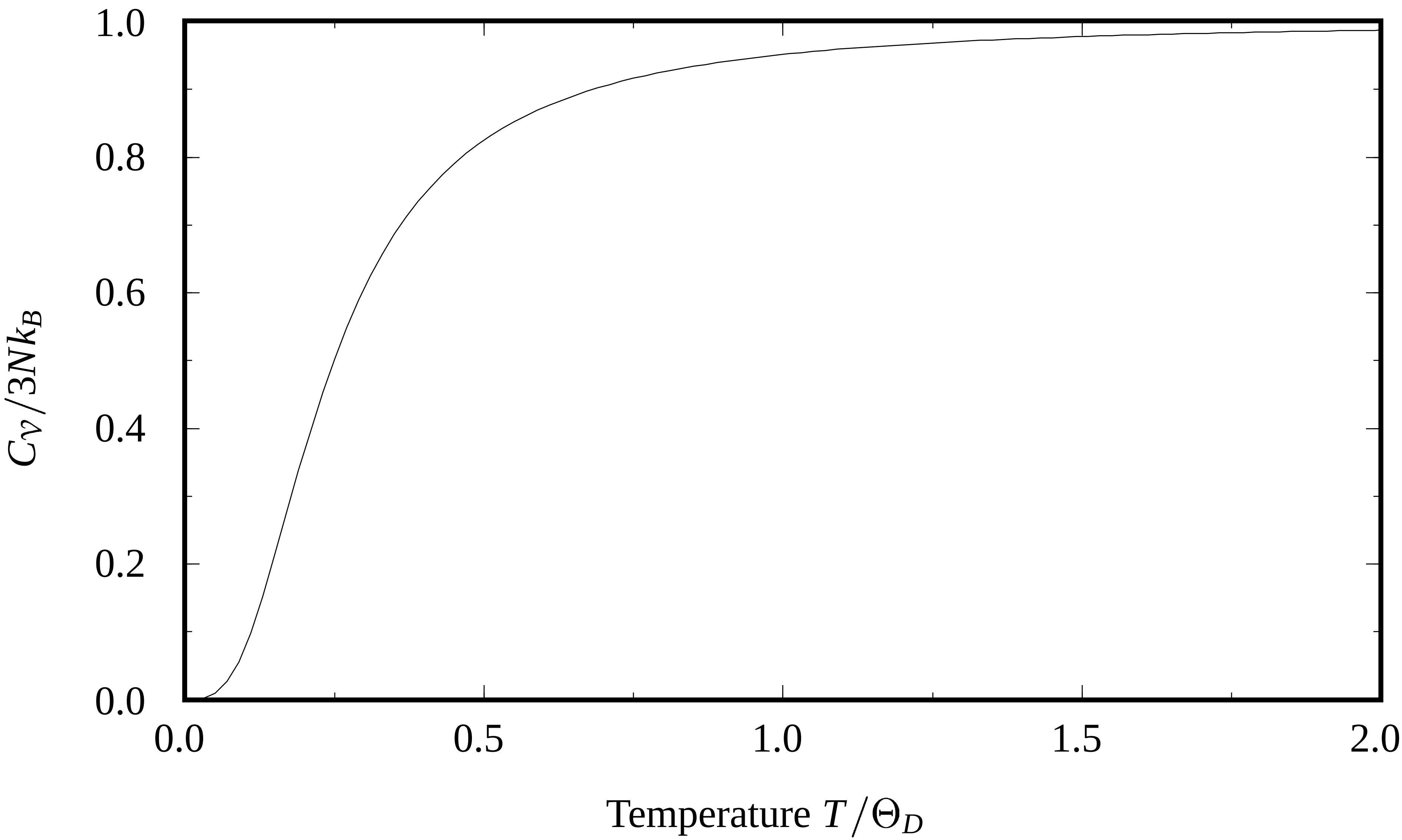
$$= \mathcal{V} \frac{2\pi^2}{5} k_B \left[\frac{k_B T}{\hbar c}\right]^3 . \tag{L65}$$

☞ Einstein Model

$$D(\omega) \quad = \quad \frac{3N}{\mathcal{V}}\delta(\omega-\omega_0), \tag{L66}$$

☞ Debye Model

$$D(\omega) = \frac{3\omega^2}{2\pi^2 c^3}\theta(\omega_D-\omega) \tag{L67}$$



[Data, Dolling and Cowley (1966)]

Total number of modes

$$3N = \mathcal{V}\int_0^\infty d\omega\, D(\omega) \Rightarrow n = \frac{\omega_D^3}{6\pi^2 c^3}. \tag{L68}$$

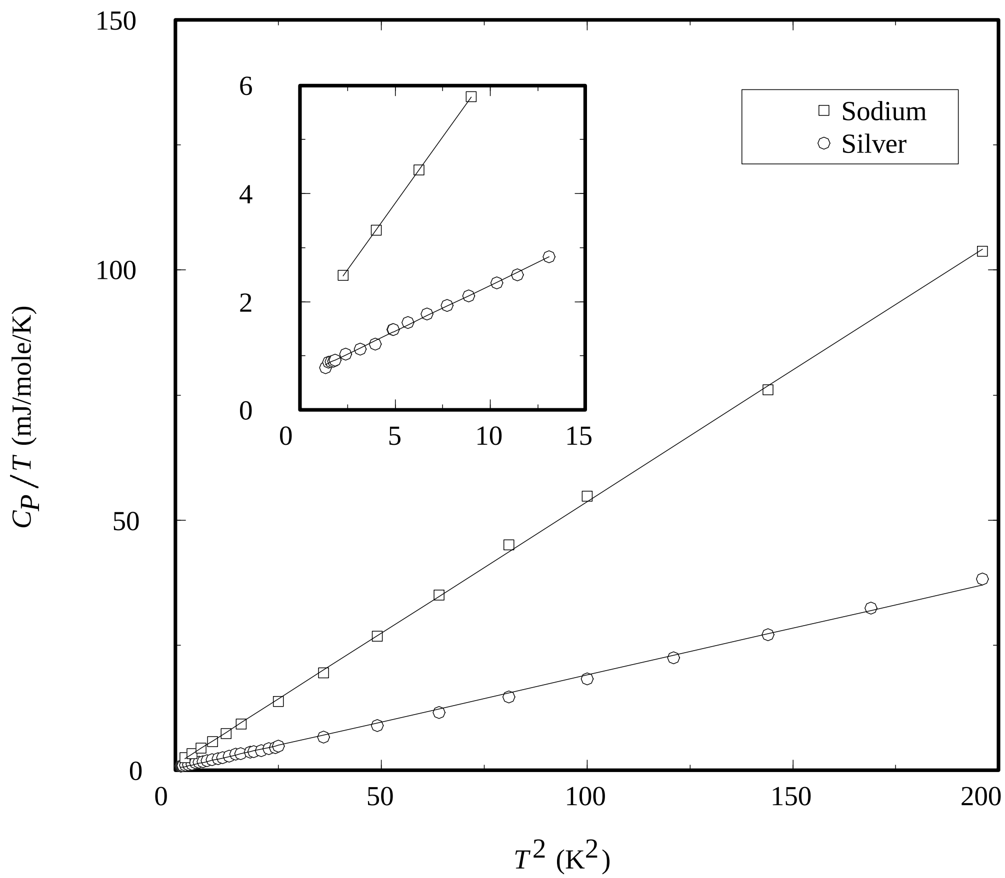
Debye temperature:

$$k_B\Theta_D \equiv \hbar\omega_D \tag{L69}$$

$$C_\mathcal{V} = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{(e^x-1)^2} \tag{L70}$$

Form of specific heat

$$C_P \approx \gamma T + \beta T^3, \tag{L71}$$

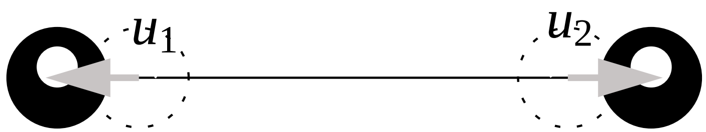


[Data, Touloukian et al (1975)]

Phonon and electron specific heats comparable when $T \approx \Theta_D\sqrt{\Theta_D/T_F}$, 10 K

Debye Temperatures

El.	Θ_D	El.	Θ_D	El.	Θ_D	El.	Θ_D
Am	121	Eu	118	Na	157	Sm	169
Ar	92	Fe	477	Nb	276	Sn	199
Ag	227	Ga	325	Nd	163	Sr	147
Al	433	Ge	373	Ne	74.6	Ta	245
As	282	Gd	182	Ni	477	Tb	176
Au	162	H	122	Np	259	Te	152
Ba	111	He	34-108	Os	467	Th	160
Be	1481	Hf	252	Pa	185	Ti	420
Bi	120	Hg	72	Pb	105	Tl	78.5
B	1480	Ho	190	Pd	271	Tm	200
C(gr)	412	I	109	Pr	152	U	248
C(dia)	2250	In	112	Pt	237	V	399
Ca	229	Ir	420	Pu	206	W	383
Cd	210	K	91.1	Rb	56.5	Xe	64.0
Ce	179	Kr	71.9	Re	416	Y	248
Co	460	La	150	Rh	512	Yb	118
Cr	606	Li	344	Ru	555	Zn	329
Cs	40.5	Lu	183	Sb	220	Zr	290
Cu	347	Mg	403	Sc	346		
Dy	183	Mn	409	Se	153		
Er	188	Mo	423	Si	645		



$$\mathcal{E} = \frac{1}{2}\mathcal{K}x^2. \tag{L72}$$

$$\mathcal{E}(x) = \mathcal{E}_0 + \frac{1}{2}\mathcal{K}x^2 + \dots \tag{L73}$$

$$\bar{x} = \frac{\int dx\, x e^{-\beta\mathcal{E}(x)}}{\int dx e^{-\beta\mathcal{E}(x)}} = \frac{\partial}{\partial A}\left(\ln\int dx e^{Ax-\beta\mathcal{E}(x)}\right)\Big|_{A=0} \tag{L74}$$

$$\approx \frac{\partial}{\partial A}\ln\int dx e^{Ax-\beta\mathcal{E}(x_0)-\beta\mathcal{E}'(x_0)(x-x_0)-\beta\mathcal{E}''(x_0)(x-x_0)^2/2}|_{A=0}. \tag{L75}$$

$$A = \beta\mathcal{E}'(x_0) = \beta\mathcal{K}x_0 \tag{L76}$$

$$\Rightarrow \bar{x} = \frac{\partial}{\partial A}\left[\ln\sqrt{\frac{2\pi}{\beta\mathcal{E}''(x_0)}}e^{Ax_0-\beta\mathcal{E}(x_0)}\right]|_{A=0} \tag{L77}$$

$$= \frac{k_B T}{\mathcal{K}} \frac{\partial}{\partial x_0} \left[\ln \sqrt{\frac{2\pi}{\beta \mathcal{E}''(x_0)}} e^{\beta \mathcal{K} x_0^2/2 - \beta \mathcal{E}_0} \right] |_{x_0=0} \qquad (L78)$$

$$= -\frac{k_B T}{\mathcal{K}\omega} \frac{\partial \omega}{\partial x}|_{x=0}, \text{ with } \mu\omega^2(x) \equiv \mathcal{E}''(x). \qquad (L79)$$

$$\mathcal{V}\beta_T \equiv \frac{\partial \mathcal{V}}{\partial T}|_P = \frac{\partial P/\partial T|_{\mathcal{V}}}{-\partial P/\partial \mathcal{V}|_T} \qquad (L80)$$

$$= -\frac{\mathcal{V}}{B} \frac{\partial^2 \mathcal{F}}{\partial \mathcal{V} \partial T}, \qquad (L81)$$

$$\frac{\partial \mathcal{F}}{\partial \mathcal{V}}|_T = \sum_i (n_i + \tfrac{1}{2}) \frac{\partial \hbar \omega_i}{\partial \mathcal{V}} \qquad (L82)$$

$$\Rightarrow \frac{\partial^2 \mathcal{F}}{\partial \mathcal{V} \partial T} = \sum_i \frac{\partial n_i}{\partial T} \frac{\partial \hbar \omega_i}{\partial \mathcal{V}}. \qquad (L83)$$

Thermal Expansion

Main results

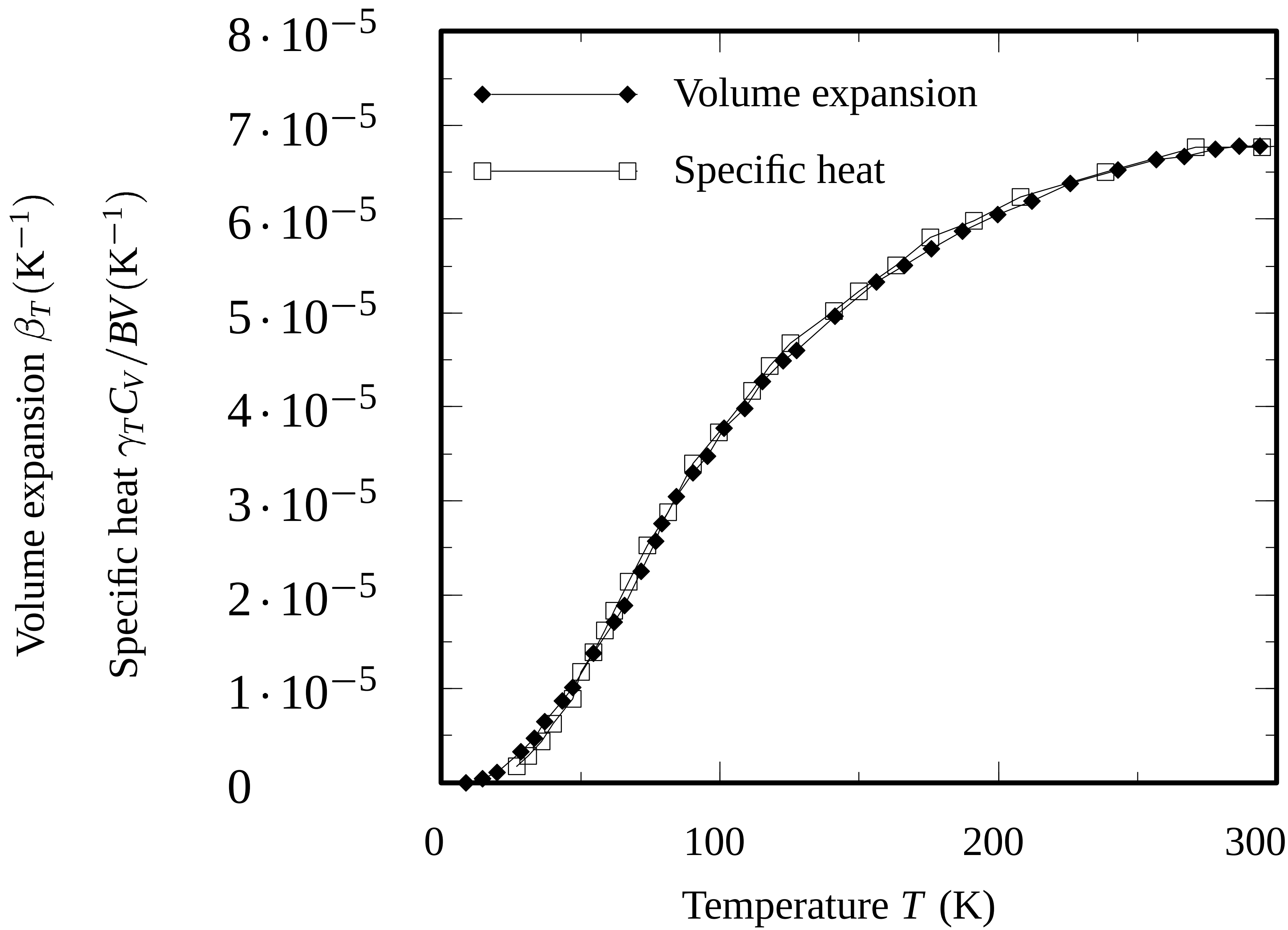
- No thermal expansion until anharmonic effects are taken into account.
- Grüneisen parameter relates thermal volume expansion to specific heat

$$\gamma_T = \frac{\sum_i \frac{\partial n_i}{\partial T}\left(-\mathcal{V}\frac{\partial \hbar\omega_i}{\partial \mathcal{V}}\right)}{\sum_i \hbar\omega_i \frac{\partial n_i}{\partial T}} \tag{L84}$$

$$\Rightarrow -\frac{\partial^2 \mathcal{F}}{\partial \mathcal{V}\partial T} = \frac{\gamma_T C_{\mathcal{V}}}{\mathcal{V}} \tag{L85}$$

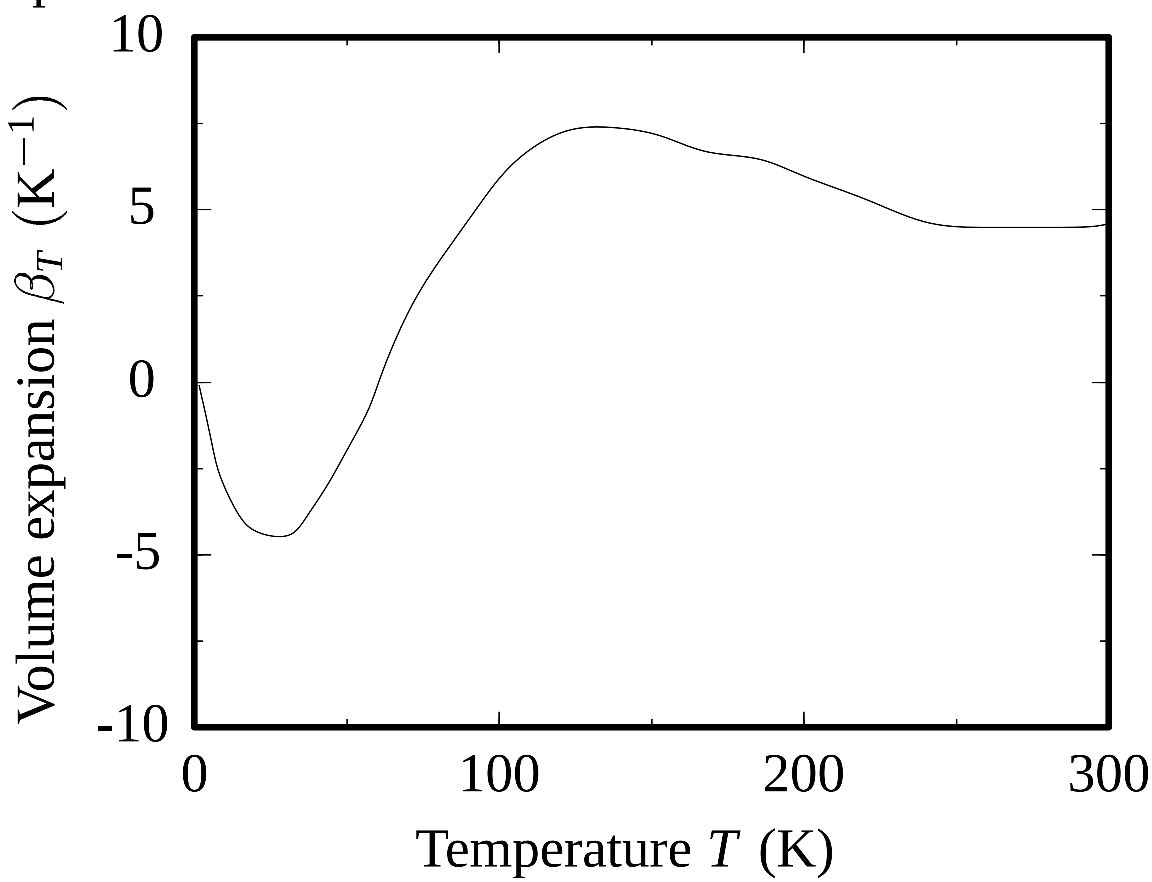
$$\Rightarrow \beta_T = \frac{\gamma_T C_{\mathcal{V}}}{B\mathcal{V}}. \tag{L86}$$

Thermal Expansion



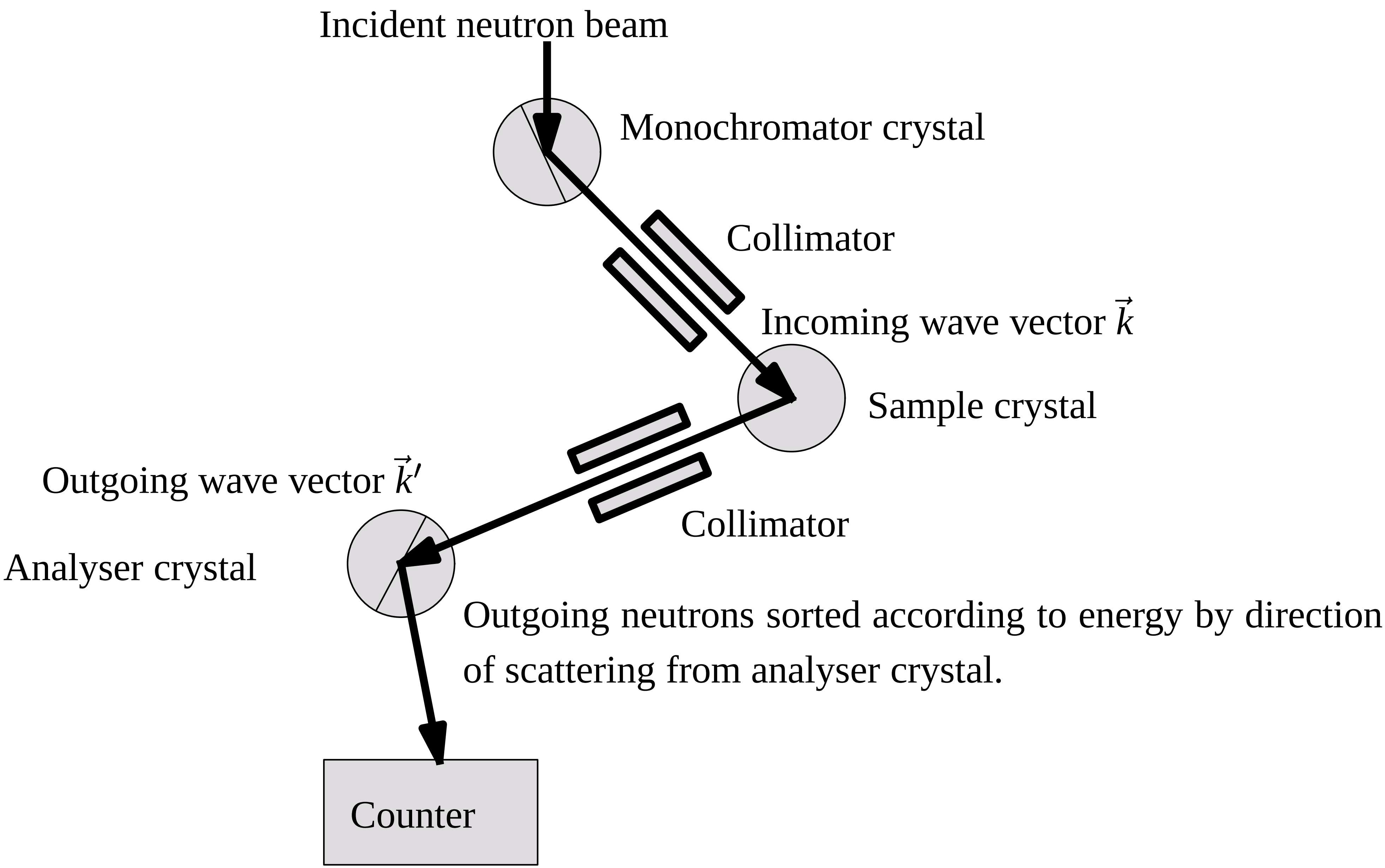
[Data from Touloukian (1970a) and (1975) for aluminum]

Invar, won a Nobel prize!



[Data from Touloukian (1975)]

Inelastic Neutron Scattering



Scattering can be understood from conservation laws

Energy

If neutron creates a phonon, then

$$\frac{\hbar^2 k^2}{2m_{\rm n}} = \frac{\hbar^2 (k')^2}{2m_{\rm n}} + \hbar\omega_{\vec{q}\nu}. \tag{L87a}$$

If, on the other hand, passage of the neutron destroys a phonon and steals its energy, then

$$\frac{\hbar^2 k^2}{2m_{\rm n}} = \frac{\hbar^2 (k')^2}{2m_{\rm n}} - \hbar\omega_{\vec{q}\nu}. \tag{L87b}$$

Momentum

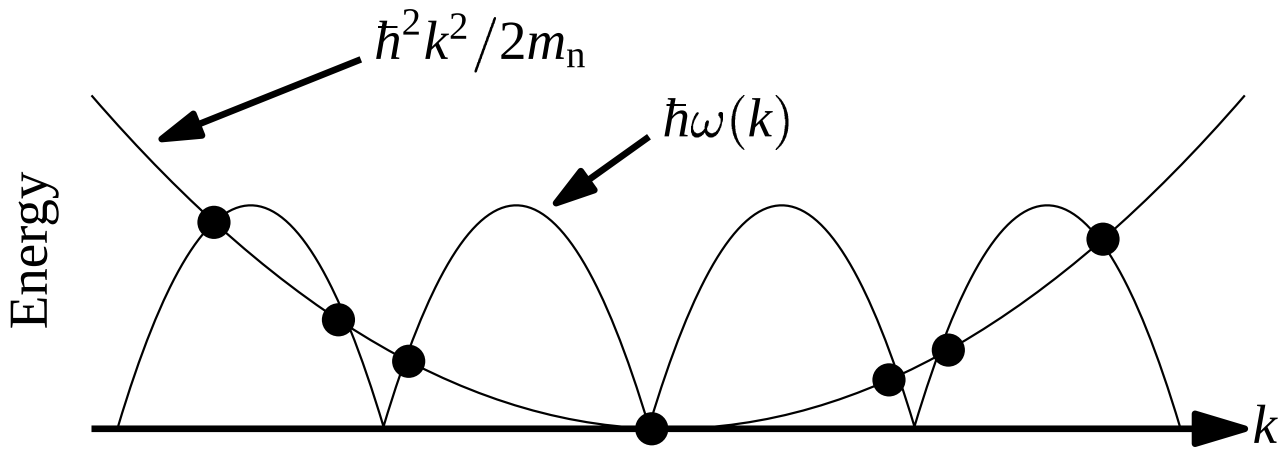
$$\vec{k}' + \vec{q} = \vec{k} + \vec{K} \tag{L88a}$$

for some reciprocal lattice vector $\vec{K}$, and when a phonon is absorbed,

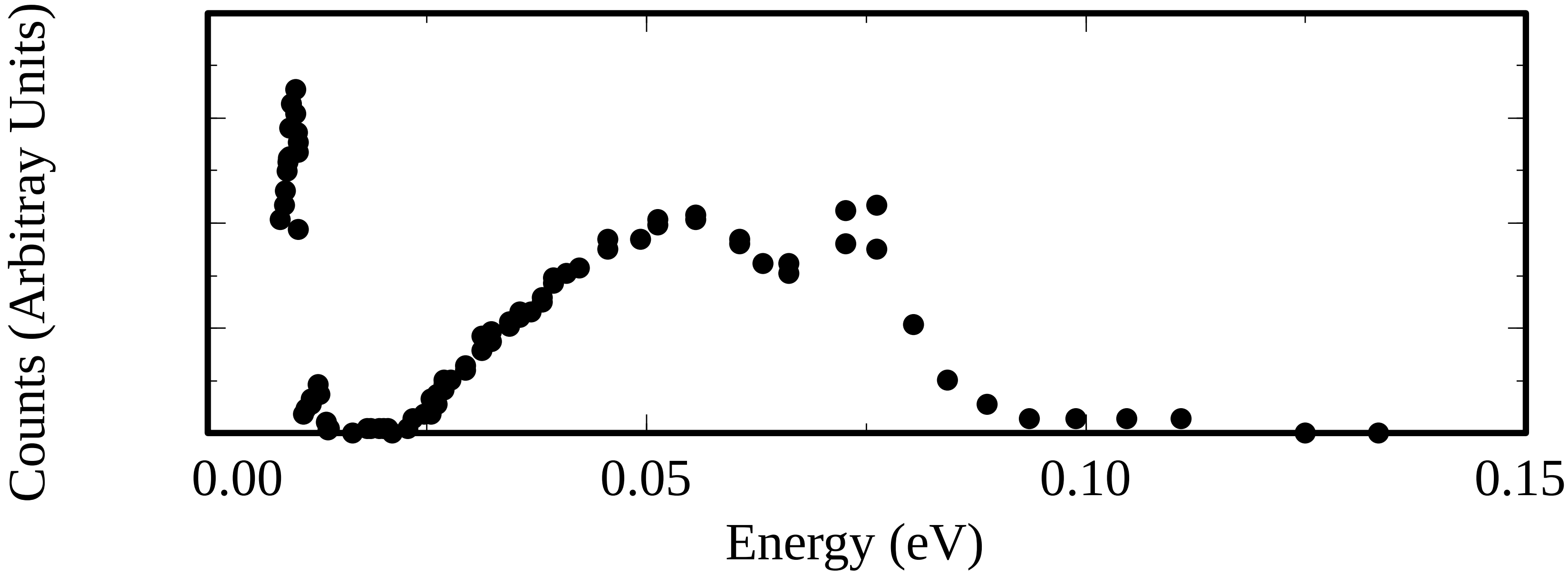
$$\vec{k}' - \vec{q} = \vec{k} + \vec{K}. \tag{L88b}$$

$$\frac{\hbar^2 k^2}{2m_{\mathrm{n}}} \pm \hbar\omega_{(\vec{k}-\vec{k}'),\nu} = \frac{\hbar^2 (k')^2}{2m_{\mathrm{n}}}, \tag{L89}$$

Graphical criterion

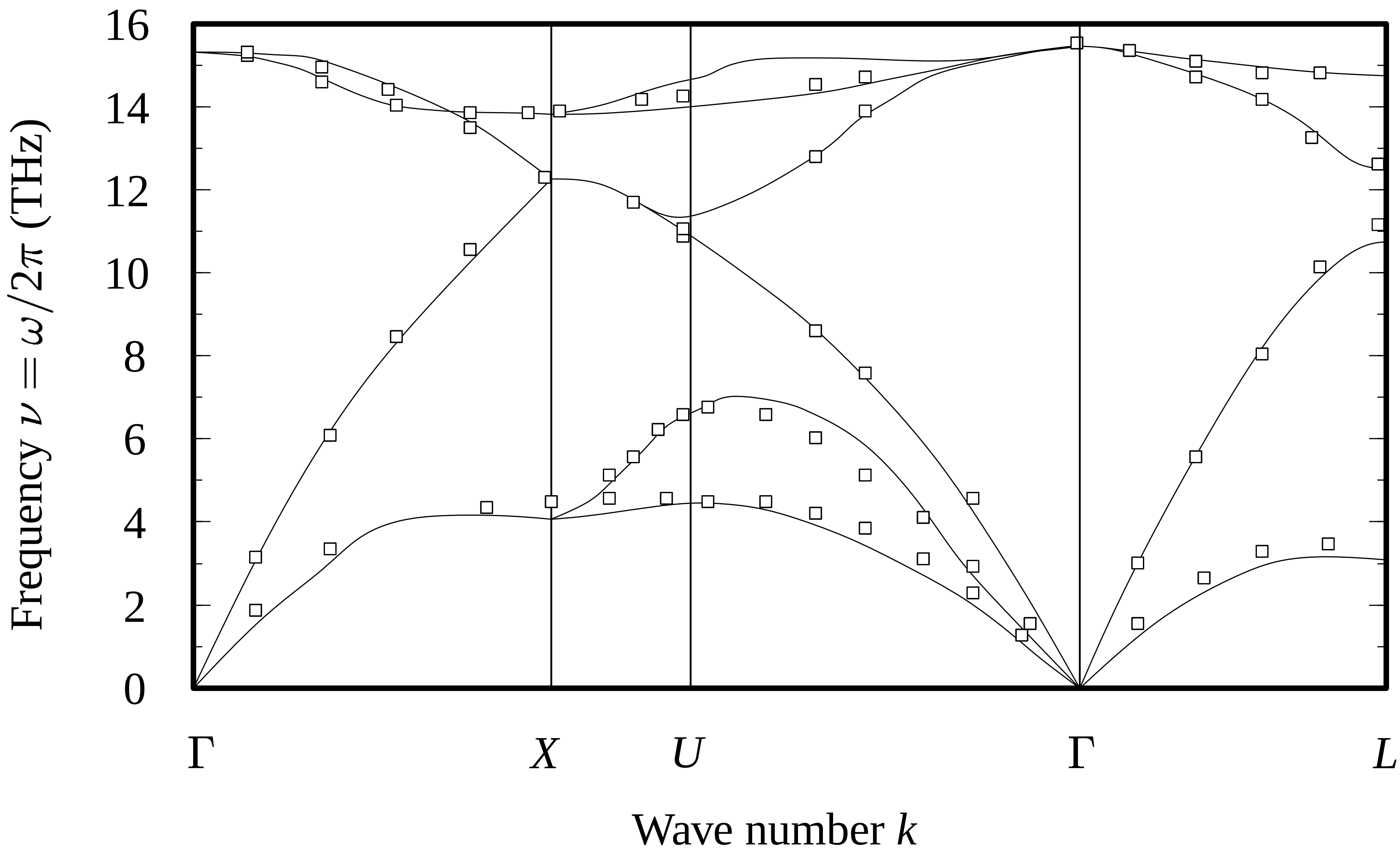


Results



[Data, Mozer et al (1965)]

Results



[Data Dolling and Cowley (1972), Nilsson and Nelin (1972), density functional computations We and Chou (1994)]

Nuclear scale is 10^{-13} cm

$$\hat{U} \quad = \quad \frac{2\pi\hbar^2 a}{m_\mathrm{n}} \sum_l \delta(\hat{R}_\mathrm{n} - \vec{R}^l - \hat{u}^l). \tag{L90}$$

$$\frac{\mathcal{P}\mathcal{V}d\vec{k}'}{(2\pi)^3} \tag{L91}$$

$$\frac{\mathcal{P}\mathcal{V}m_\mathrm{n}\hbar k' d\mathcal{E}_\mathrm{n} d\Omega}{(2\pi\hbar)^3}. \tag{L92}$$

$I = \hbar k/\mathcal{V}m_\mathrm{n}$

$$\frac{d\sigma}{d\Omega d\mathcal{E}_\mathrm{n}} = \frac{k'}{k}\frac{(\mathcal{V}m_\mathrm{n})^2}{(2\pi\hbar)^3}\mathcal{P}(\vec{k} \to \vec{k}'). \tag{L93}$$

$$\mathcal{P}(\vec{k} \to \vec{k}') = \sum_{\text{final states f}} \frac{2\pi}{\hbar}\delta(\mathcal{E}^\mathrm{f} - \mathcal{E}^\mathrm{i})|\langle\Psi^\mathrm{f}|\hat{U}|\Psi^\mathrm{i}\rangle|^2. \tag{L94}$$

$$\langle\Psi^{\rm f}|\hat{U}|\Psi^{\rm i}\rangle = \int d\vec{r}\langle\vec{k}'|\vec{r}\rangle\langle\vec{r}|\langle\Phi^{\rm f}|\sum_l \frac{2\pi\hbar^2 a}{m_{\rm n}}\delta(\hat{R}-\vec{R}^l-\vec{u}^l)|\vec{k}\rangle|\Phi^{\rm i}\rangle \quad \text{(L95)}$$

$$= \int \frac{d\vec{r}}{\mathcal{V}} e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}\langle\Phi^{\rm f}|\frac{2\pi\hbar^2 a}{m_{\rm n}}\sum_l \delta(\vec{r}-\vec{R}^l-\vec{u}^l)|\Phi^{\rm i}\rangle \quad \text{(L96)}$$

$$= \frac{1}{\mathcal{V}}\frac{2\pi\hbar^2 a}{m_{\rm n}}\sum_l \langle\Phi^{\rm f}|e^{i(\vec{k}-\vec{k}')\cdot(\hat{u}^l+\vec{R}^l)}|\Phi^{\rm i}\rangle. \quad \text{(L97)}$$

$$\hbar\omega_{\rm n} = \frac{\hbar^2 k^2}{2m_{\rm n}} - \frac{\hbar^2 k'^2}{2m_{\rm n}} \quad \text{(L98)}$$

$$\mathcal{P}(\vec{k}\to\vec{k}') = \frac{(2\pi\hbar)^3}{(m_{\rm n}\mathcal{V})^2}a^2\sum_{\rm f}\delta(\mathcal{E}^{\rm f}_{\rm ph}-\mathcal{E}^{\rm i}_{\rm ph}+\hbar\omega_{\rm n})\Big|\sum_l\langle\Phi^{\rm f}|e^{i(\vec{k}-\vec{k}')\cdot(\hat{u}^l+\vec{R}^l)}|\Phi^{\rm i}\rangle\Big|^2. \quad \text{(L99)}$$

$$\frac{d\sigma}{d\Omega d\mathcal{E}_{\rm n}} = \frac{k'}{k}\frac{Na^2}{\hbar}S^{\rm i}(\vec{k}-\vec{k}',\omega_n), \quad \text{(L100)}$$

$$S^{\mathrm{i}}(\vec{q},\omega) = \frac{1}{N}\sum_{\mathrm{f}} \delta([\mathcal{E}^{\mathrm{f}}_{\mathrm{ph}} - \mathcal{E}^{\mathrm{i}}_{\mathrm{ph}}]/\hbar + \omega)\left|\sum_{l}\langle\Phi^{\mathrm{f}}|e^{i\vec{q}\cdot(\hat{u}^{l}+\vec{R}^{l})}|\Phi^{\mathrm{i}}\rangle\right|^{2}. \qquad \text{(L101)}$$

$$S^{\mathrm{i}} = \frac{1}{N}\sum_{\mathrm{f}}\int\frac{dt}{2\pi}e^{it\left([\mathcal{E}^{\mathrm{f}}_{\mathrm{ph}}-\mathcal{E}^{\mathrm{i}}_{\mathrm{ph}}]/\hbar+\omega\right)}\sum_{ll'}e^{i\vec{q}\cdot(\vec{R}^{l}-\vec{R}^{l'})}\,[\langle\Phi^{\mathrm{i}}|e^{-i\vec{q}\cdot\hat{u}^{l'}}|\Phi^{\mathrm{f}}\rangle \times\langle\Phi^{\mathrm{f}}|e^{i\vec{q}\cdot\hat{u}^{l}}|\Phi^{\mathrm{i}}\rangle] \qquad \text{(L102)}$$

$$= \frac{1}{N}\sum_{\mathrm{f}}\int\frac{dt}{2\pi}e^{it\omega}\sum_{ll'}e^{i\vec{q}\cdot(\vec{R}^{l}-\vec{R}^{l'})}\,[\langle\Phi^{\mathrm{i}}|e^{-i\vec{q}\cdot\hat{u}^{l'}}|\Phi^{\mathrm{f}}\rangle \times\langle\Phi^{\mathrm{f}}|e^{i\hat{\mathcal{H}}_{\mathrm{ph}}t/\hbar}e^{i\vec{q}\cdot\hat{u}^{l}}e^{-i\hat{\mathcal{H}}_{\mathrm{ph}}t/\hbar}|\Phi^{\mathrm{i}}\rangle] \qquad \text{(L103)}$$

$$= \frac{1}{N}\sum_{\mathrm{f}}\int\frac{dt}{2\pi}e^{it\omega}\sum_{ll'}e^{i\vec{q}\cdot(\vec{R}^{l}-\vec{R}^{l'})}\langle\Phi^{\mathrm{i}}|e^{-i\vec{q}\cdot\hat{u}^{l'}}|\Phi^{\mathrm{f}}\rangle\langle\Phi^{\mathrm{f}}|e^{i\vec{q}\cdot\hat{u}^{l}(t)}|\Phi^{\mathrm{i}}\rangle \qquad \text{(L104)}$$

$$= \frac{1}{N}\int\frac{dt}{2\pi}e^{it\omega}\sum_{ll'}e^{i\vec{q}\cdot(\vec{R}^{l}-\vec{R}^{l'})}\langle\Phi^{\mathrm{i}}|e^{-i\vec{q}\cdot\hat{u}^{l'}}e^{i\vec{q}\cdot\hat{u}^{l}(t)}|\Phi^{\mathrm{i}}\rangle. \qquad \text{(L105)}$$

$$\langle\hat{A}\rangle = \frac{\sum_{\mathrm{i}}\langle\Phi^{\mathrm{i}}|e^{-\beta\hat{\mathcal{H}}}\hat{A}|\Phi^{\mathrm{i}}\rangle}{\sum_{\mathrm{i}}\langle\Phi^{\mathrm{i}}|e^{-\beta\hat{\mathcal{H}}}|\Phi^{\mathrm{i}}\rangle}. \qquad \text{(L106)}$$

$$S(\vec{q},\omega) = \frac{1}{N}\sum_{ll'} e^{i\vec{q}\cdot(\vec{R}^l - \vec{R}^{l'})} \int \frac{dt}{2\pi} e^{i\omega t} \langle e^{-i\vec{q}\cdot\hat{u}^{l'}} e^{i\vec{q}\cdot\hat{u}^l(t)} \rangle \quad \text{(L107)}$$

$$= \frac{1}{N}\int d\vec{r}d\vec{r}'\frac{dt}{2\pi} e^{i\vec{q}\cdot(\vec{r}-\vec{r}')} e^{i\omega t} \sum_{ll'} \langle \delta(\vec{r}-\vec{R}^l - \hat{u}^l)\delta(\vec{r}'-\vec{R}^{l'} - \hat{u}^{l'}(t))\rangle. \quad \text{(L108)}$$

$$\mathcal{S} \equiv \langle e^{\hat{A}} \rangle \tag{L109}$$

$$\mathcal{S} = \langle 1 + \hat{A} + \frac{1}{2}\hat{A}^2 + \ldots \rangle. \tag{L110}$$

$$\mathcal{S} = 1 + \frac{1}{2}\langle \hat{A}\hat{A} \rangle + \frac{1}{4!}\langle \hat{A}\hat{A}\hat{A}\hat{A} \rangle + \ldots. \tag{L111}$$

Wick's theorem

$$\begin{aligned} \mathcal{S} &= 1 + \frac{1}{2}\langle \hat{A}\hat{A} \rangle + \frac{1}{2!}\frac{1}{2^2}\langle \hat{A}\hat{A} \rangle^2 + \ldots + \frac{1}{2^l}\frac{1}{l!}\langle \hat{A}\hat{A} \rangle^l \ldots. & \text{(L112)} \\ &= \exp[\frac{1}{2}\langle \hat{A}^2 \rangle]. & \text{(L113)} \end{aligned}$$

$$\langle e^{\hat{A}} e^{\hat{B}} \rangle = e^{\frac{1}{2}\langle \hat{A}^2 + 2\hat{A}\hat{B} + \hat{B}^2 \rangle}. \tag{L114}$$

$$\mathfrak{M} \equiv \langle e^{-i\vec{q}\cdot\hat{u}^{l'}} e^{i\vec{q}\cdot\hat{u}^{l}(t)} \rangle. \tag{L115}$$

Quantitative account of how thermal fluctuations degrade scattering peaks

$$\mathfrak{M} = \exp[-\langle(\vec{q}\cdot\hat{u}^l)^2\rangle]\exp[\langle(\vec{q}\cdot\hat{u}^{l'})(\vec{q}\cdot\hat{u}^l(t))\rangle]. \quad \text{(L116)}$$

$$\begin{aligned} 2W &\equiv \langle(\vec{q}\cdot\hat{u}^l)^2\rangle \\ &= \frac{1}{N}\sum_{\substack{\vec{k}\vec{k}' \\ \nu\nu'}}\langle(\vec{q}\cdot[\hat{u}_{\vec{k}\nu}e^{i\vec{k}\cdot\vec{R}^l}+\hat{u}^\dagger_{\vec{k}\nu}e^{-i\vec{k}\cdot\vec{R}^l}])(\vec{q}\cdot[\hat{u}_{\vec{k}'\nu'}e^{i\vec{k}'\cdot\vec{R}^l}+\hat{u}^\dagger_{\vec{k}'\nu'}e^{-i\vec{k}'\cdot\vec{R}^l}])\rangle. \quad \text{(L117)} \end{aligned}$$

$$\begin{aligned} 2W &= \sum_{\vec{k}\nu}\frac{1}{N}\frac{\hbar^2|\vec{\epsilon}_{\vec{k}\nu}\cdot\vec{q}|^2}{2M\hbar\omega_{\vec{k}\nu}}\langle\hat{a}^\dagger_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}+\hat{a}_{\vec{k}\nu}\hat{a}^\dagger_{\vec{k}\nu}\rangle \quad \text{(L118)} \\ &= \sum_{\vec{k}\nu}\frac{1}{N}\frac{\hbar^2|\vec{\epsilon}_{\vec{k}\nu}\cdot\vec{q}|^2}{2M\hbar\omega_{\vec{k}\nu}}\left(2n_{\vec{k}\nu}+1\right). \quad \text{(L119)} \end{aligned}$$

Low temperature

$$2W = \sum_{\vec{k}\nu} \frac{1}{N} \frac{\hbar^2 (\vec{\epsilon}_{\vec{k}\nu} \cdot \vec{q})^2}{2M\hbar\omega_{\vec{k}\nu}}. \quad \text{(L120)}$$

In Debye approximation

$$2W = \frac{3}{4} \frac{q^2 \hbar^2}{M\hbar c k_D}. \quad \text{(L121)}$$

Evaluation of Structure Factor

$$S(\vec{q},\omega) = \sum_{ll'} \frac{1}{N} e^{i\vec{q}\cdot(\vec{R}^l - \vec{R}^{l'})} \int \frac{dt}{2\pi} e^{i\omega t} e^{-2W} e^{\langle \vec{q}\cdot\hat{u}^{l'} \vec{q}\cdot\hat{u}^l(t)\rangle}. \tag{L122}$$

$$\begin{aligned} S^{(0)}(\vec{q},\omega) &= \sum_{l} e^{i\vec{q}\cdot\vec{R}^l} \int \frac{dt}{2\pi} e^{i\omega t} e^{-2W} && \text{(L123)} \\ &= \delta(\omega) N e^{-2W} \sum_{\vec{K}} \delta_{\vec{q}\vec{K}}. && \text{(L124)} \end{aligned}$$

$$S^{(1)}(\vec{q},\omega) = \sum_{ll'} \frac{1}{N} e^{i\vec{q}\cdot(\vec{R}^l - \vec{R}^{l'})} \int \frac{dt}{2\pi} e^{i\omega t} e^{-2W} \langle \left(\vec{q}\cdot\hat{u}^{l'}\right)\left(\vec{q}\cdot\hat{u}^l(t)\right)\rangle. \tag{L125}$$

$$\begin{aligned} \mathfrak{M}' &= \langle \left(\vec{q}\cdot\hat{u}^{l'}\right)\left(\vec{q}\cdot\hat{u}^l(t)\right)\rangle \\ &= \frac{1}{N} \sum_{\substack{\vec{k}\vec{k}' \\ \nu\nu'}} \begin{array}{l} \langle(\vec{q}\cdot[\hat{u}_{\vec{k}\nu} e^{i\vec{k}\cdot\vec{R}^{l'}} + \hat{u}^\dagger_{\vec{k}\nu} e^{-i\vec{k}\cdot\vec{R}^{l'}}]) \\ \times(\vec{q}\cdot[\hat{u}_{\vec{k}'\nu'} e^{i\vec{k}'\cdot\vec{R}^l - i\omega_{\vec{k}'\nu'}t} + \hat{u}^\dagger_{\vec{k}'\nu'} e^{-i\vec{k}'\cdot\vec{R}^l + i\omega_{\vec{k}'\nu'}t}])\rangle \end{array} && \text{(L126)} \end{aligned}$$

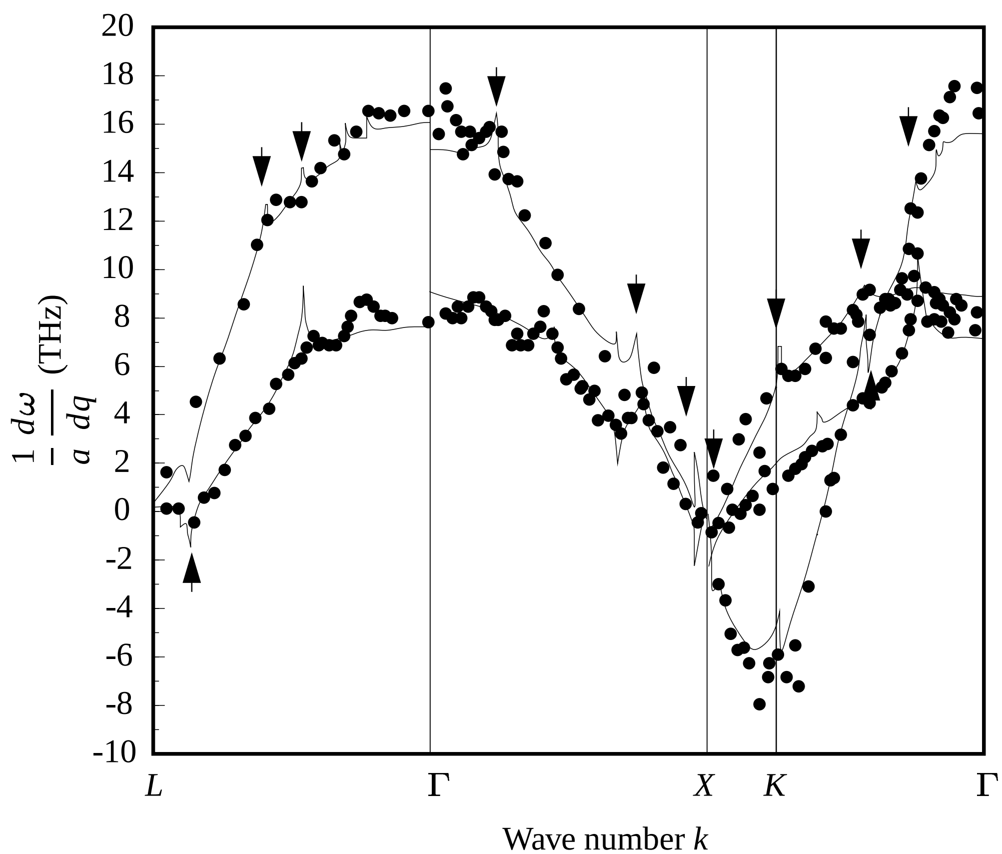
$$= \sum_{\vec{k}\nu} \frac{1}{N} \frac{\hbar^2(\vec{\epsilon}_{\vec{k}\nu}\cdot\vec{q})^2}{2M\hbar\omega_{\vec{k}\nu}} \langle \hat{a}^\dagger_{\vec{k}\nu}\hat{a}_{\vec{k}\nu}e^{-i\omega_{\vec{k}\nu}t} + \hat{a}_{\vec{k}\nu}\hat{a}^\dagger_{\vec{k}\nu}e^{i\omega_{\vec{k}\nu}t}\rangle e^{i\vec{k}\cdot(\vec{R}^{l'}-\vec{R}^{l})} \quad \text{(L127)}$$

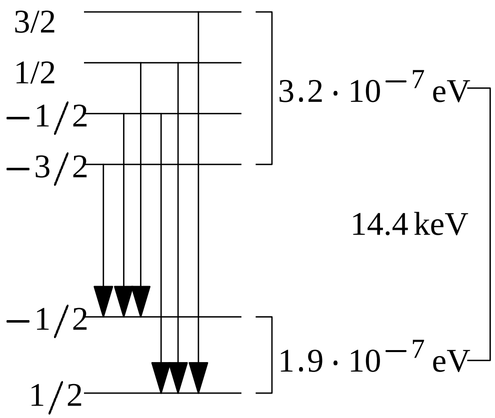
$$= \sum_{\vec{k}\nu} \frac{1}{N} \frac{\hbar^2(\vec{\epsilon}_{\vec{k}\nu}\cdot\vec{q})^2}{2M\hbar\omega_{\vec{k}\nu}} \left([n_{\vec{k}\nu}+1]e^{i\omega_{\vec{k}\nu}t} + n_{\vec{k}\nu}e^{-i\omega_{\vec{k}\nu}t}\right) e^{i\vec{k}\cdot(\vec{R}^{l'}-\vec{R}^{l})}, \quad \text{(L128)}$$

$$S^{(1)}(\vec{q},\omega) = e^{-2W}\sum_{\nu}\frac{\hbar^2[\vec{q}\cdot\vec{\epsilon}_{\vec{q}\nu}]^2}{2M\hbar\omega_{\vec{q}\nu}}[(1+n_{\vec{q}\nu})\,\delta(\omega+\omega_{\vec{q}\nu})+n_{\vec{q}\nu}\delta(\omega-\omega_{\vec{q}\nu})]. \quad \text{(L129)}$$

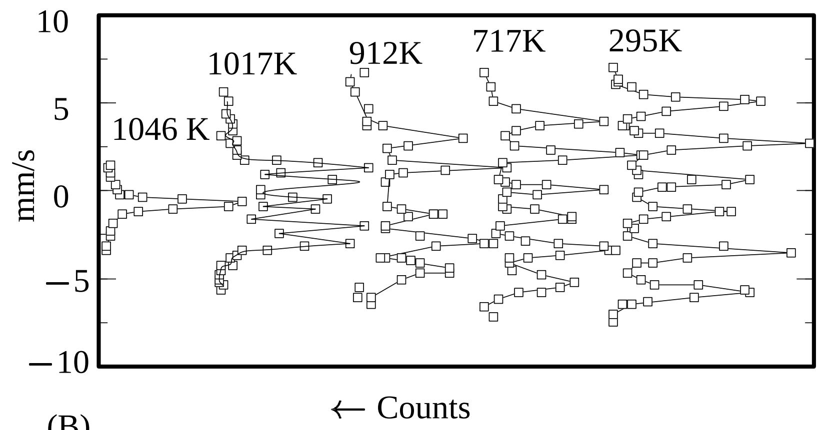
Kohn Anomalies

$q = 2k_F$





(A)



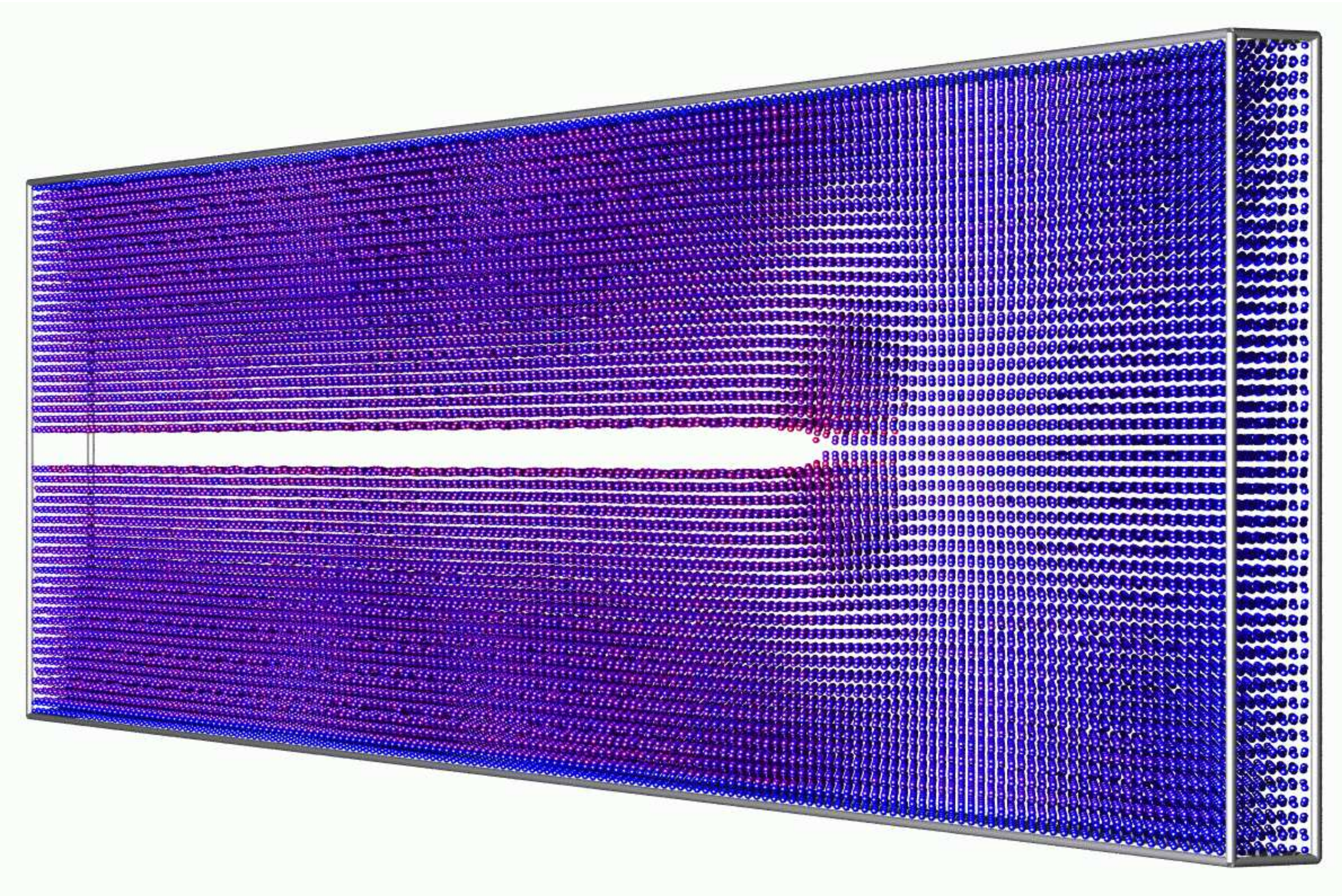
(B)

$$S(\vec{q}) = \frac{1}{N}\sum_{ll'} e^{i\vec{q}\cdot(\vec{R}^l-\vec{R}^{l'})}\int_0^\infty \frac{dt}{2\pi}\left[e^{i(\Delta\mathcal{E}/\hbar+i\Gamma)t}+e^{-i(\Delta\mathcal{E}/\hbar-i\Gamma)t}\right]\langle e^{-i\vec{q}\cdot\hat{u}^{l'}}e^{i\vec{q}\cdot\hat{u}^{l}(t)}\rangle. \quad \text{(L130)}$$

$$\frac{2\Gamma}{(\Delta\mathcal{E}/\hbar)^2+\Gamma^2} \quad \text{(L131)}$$

$$f = \exp\left[-\frac{3}{4}\frac{q^2\hbar^2}{M\hbar c k_D}\right]. \quad \text{(L132)}$$

Dislocations and Cracks



Definitions

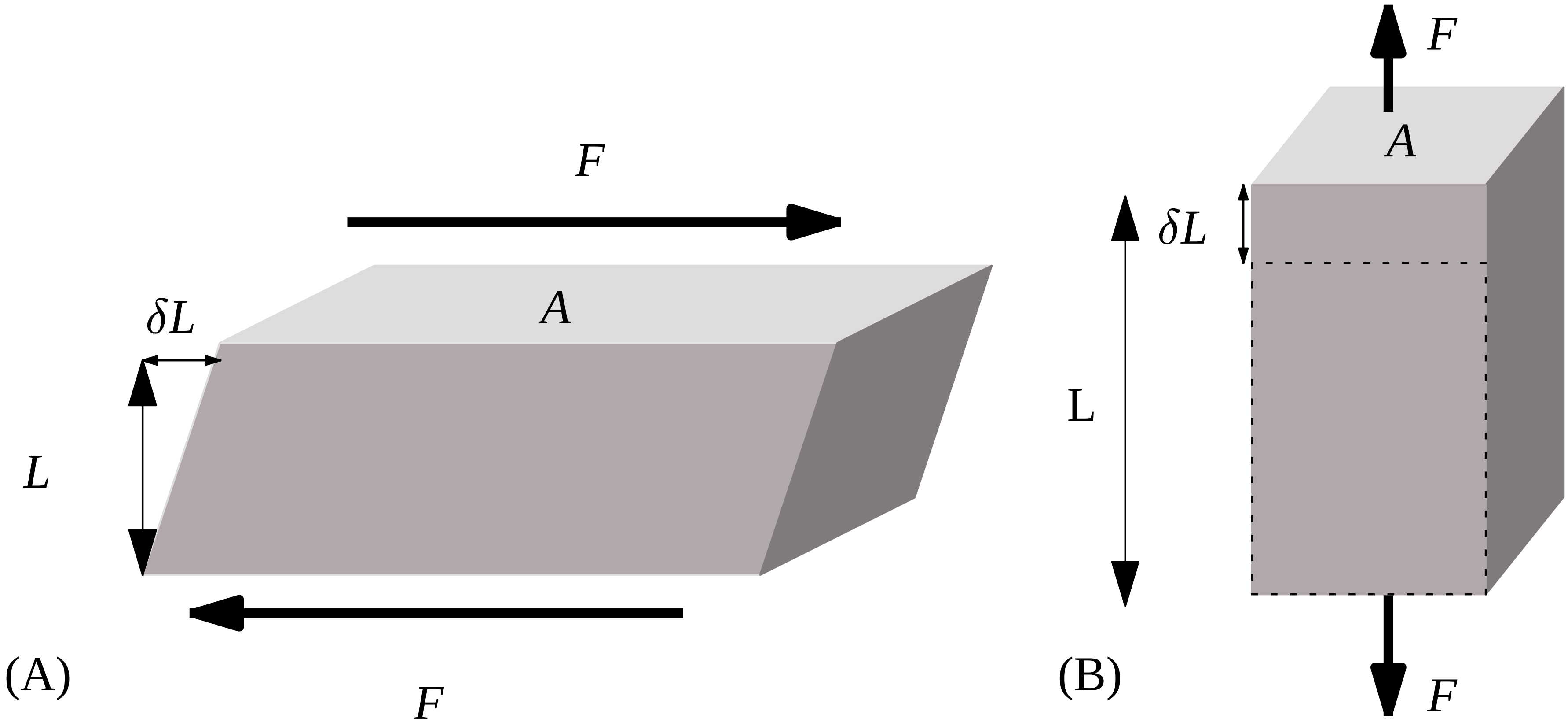
- Brittle
- Ductile
- Dislocation
- Burgers Vector
- Glide Plane
- Frenkel–Kontorova Model
- Hexatic Phases
- Orientational Order, Mermin–Wagner Theorem
- Kosterlitz–Thouless–Berezinkskii Transition
- Cracks
- Conformal Mapping
- Stress Intensity Factor

Definitions

Given surface energy of $\Gamma = 1$ J/m^2, height h at which it pays to split object in two is

$$h = \sqrt{\frac{4\Gamma}{\rho g}} \approx 1.4 \text{ cm.} \tag{L1}$$

Failure in Shear



$$G\frac{\delta L}{L} = \frac{F}{A}, \qquad \text{(L2)}$$

Failure in Shear

$$\mathcal{S} = \frac{F}{A} = \begin{cases} \dfrac{G}{5} & \text{shear} \\[2ex] \dfrac{Y}{5} & \text{tension.} \end{cases} \tag{L3}$$

Material	Shear modulus $G/5$ (10^{11} ergs cm^{-3})	Yield strength (10^{11} ergs cm^{-3})
Iron	1.0–1.6	0.02–1
Copper	1.0	0.005
Titanium	1.0	0.08

Failure in Tension

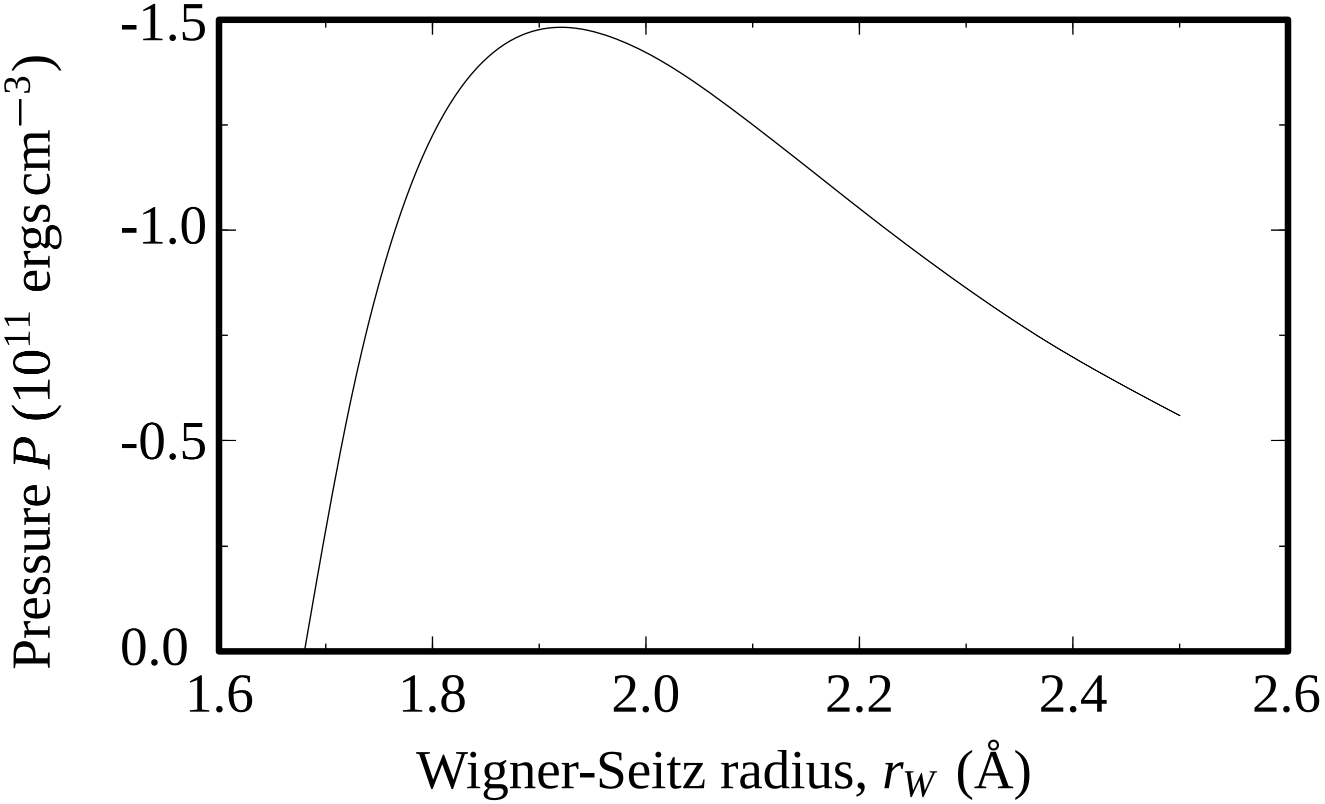
$$\mathcal{S} = \frac{F}{A} = \begin{cases} \dfrac{G}{5} & \text{shear} \\ \dfrac{Y}{5} & \text{tension.} \end{cases} \tag{L4}$$

$$Y\frac{\delta L}{L} = \frac{F}{A}. \tag{L5}$$

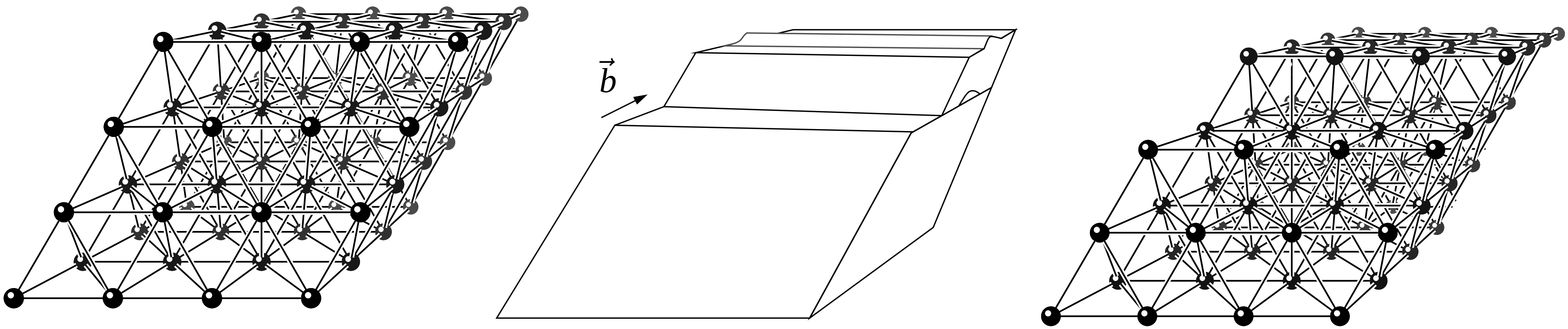
Material	Young's Modulus $Y/5$ (10^{11} ergs cm^{-3})	Theoretical Strength (10^{11} ergs cm^{-3})	Practical Strength (10^{11} ergs cm^{-3})	Ratio
Iron	4.0	4	0.03	0.008
Titanium	2.2	3.1	0.03	0.009
Silicon	3.2	1.5	0.07	0.05
Glass	1.4	4	0.04	0.01

Complete Cohesive Energy Curve

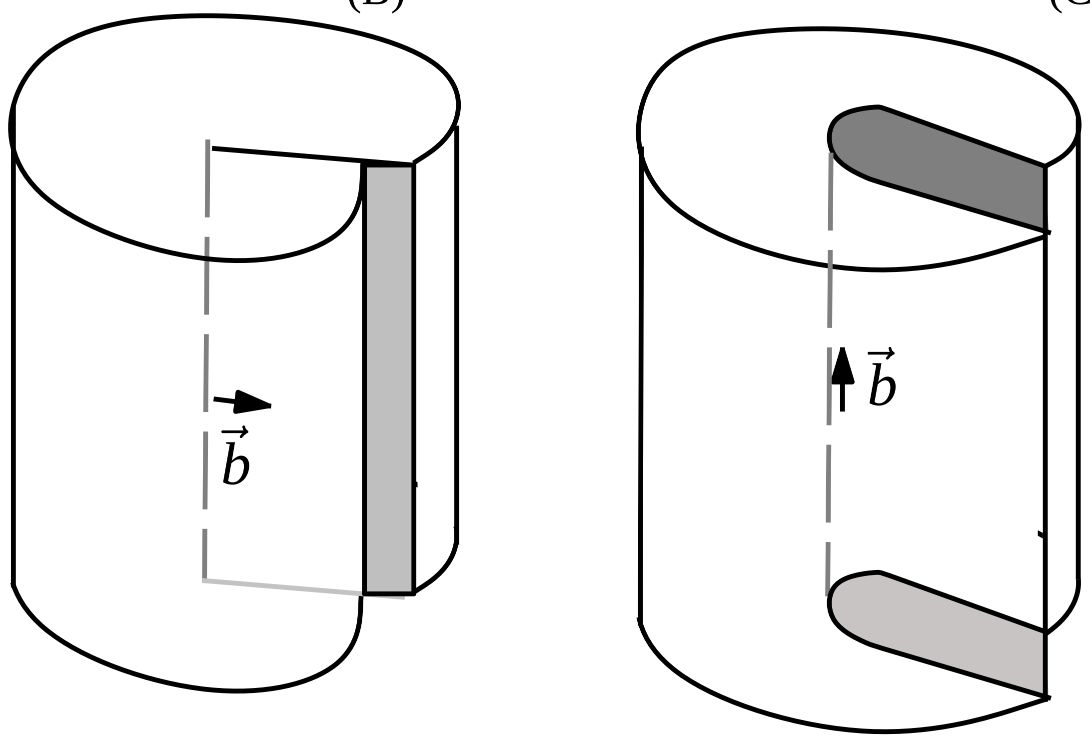
$$-P = \frac{1}{4\pi r_W^2} \frac{\partial \mathcal{E}(r_W)}{\partial r_W}. \tag{L6}$$



Dislocations

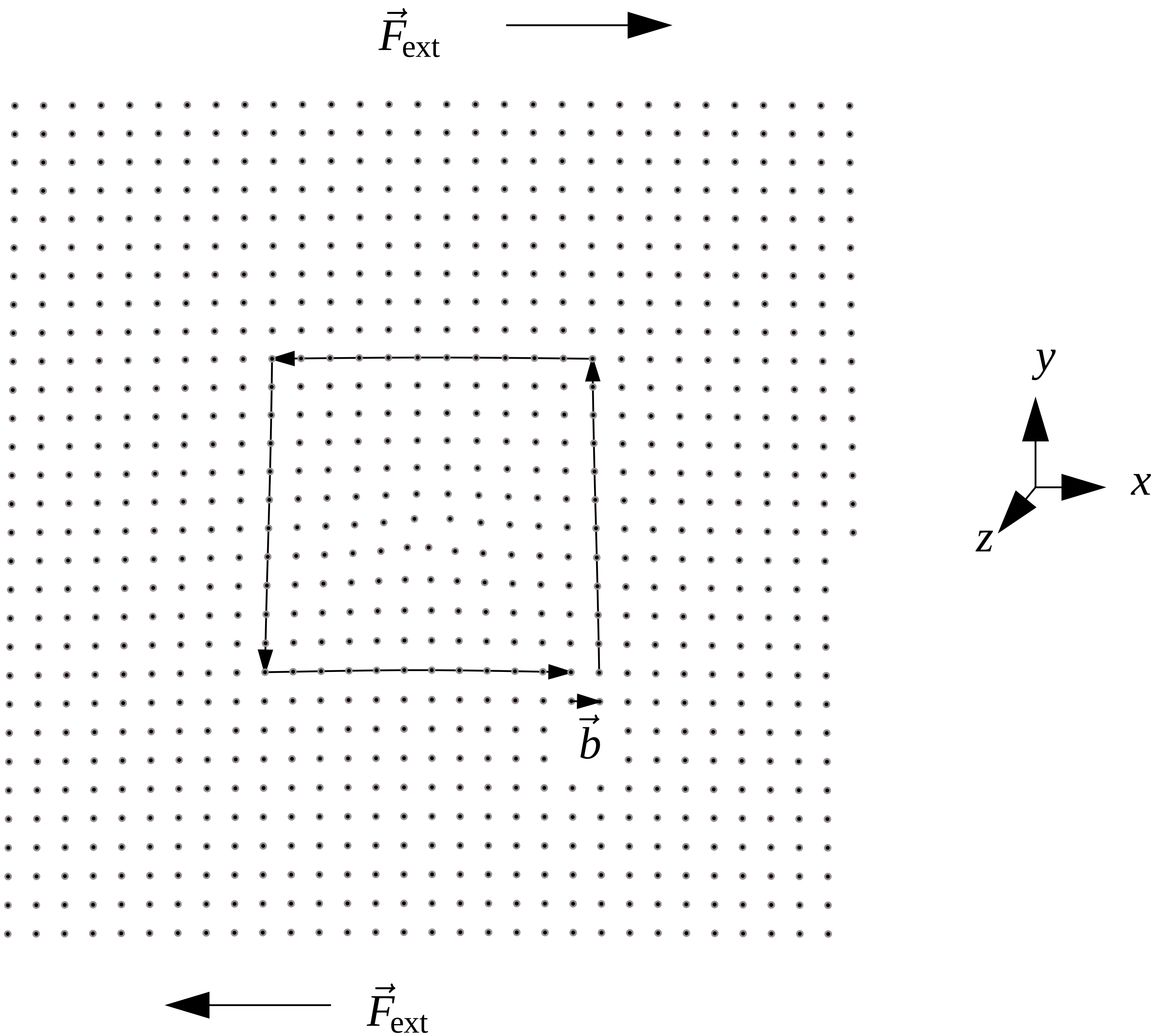


(A) (B) (C)

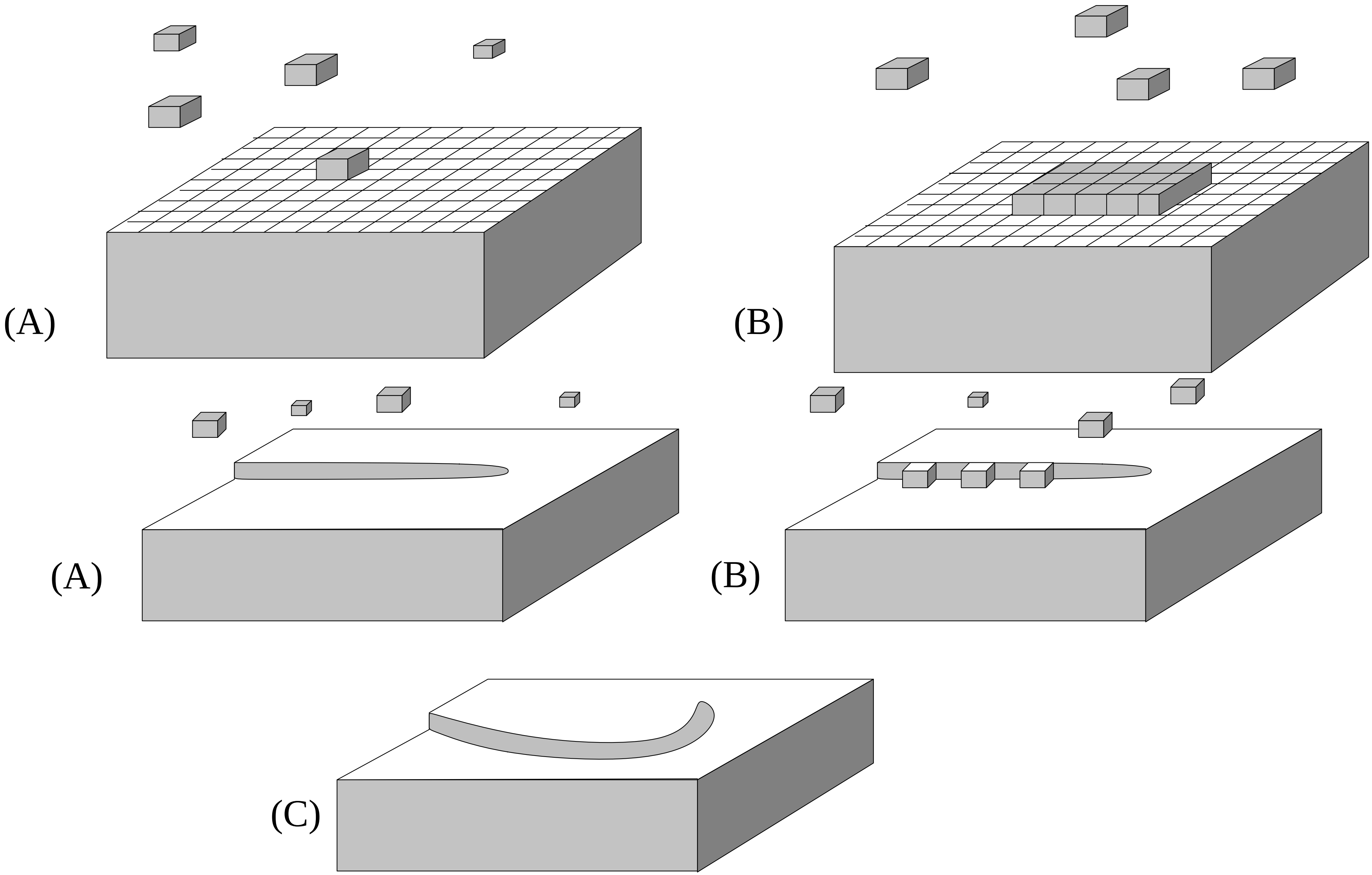


(A) Edge (B) Screw

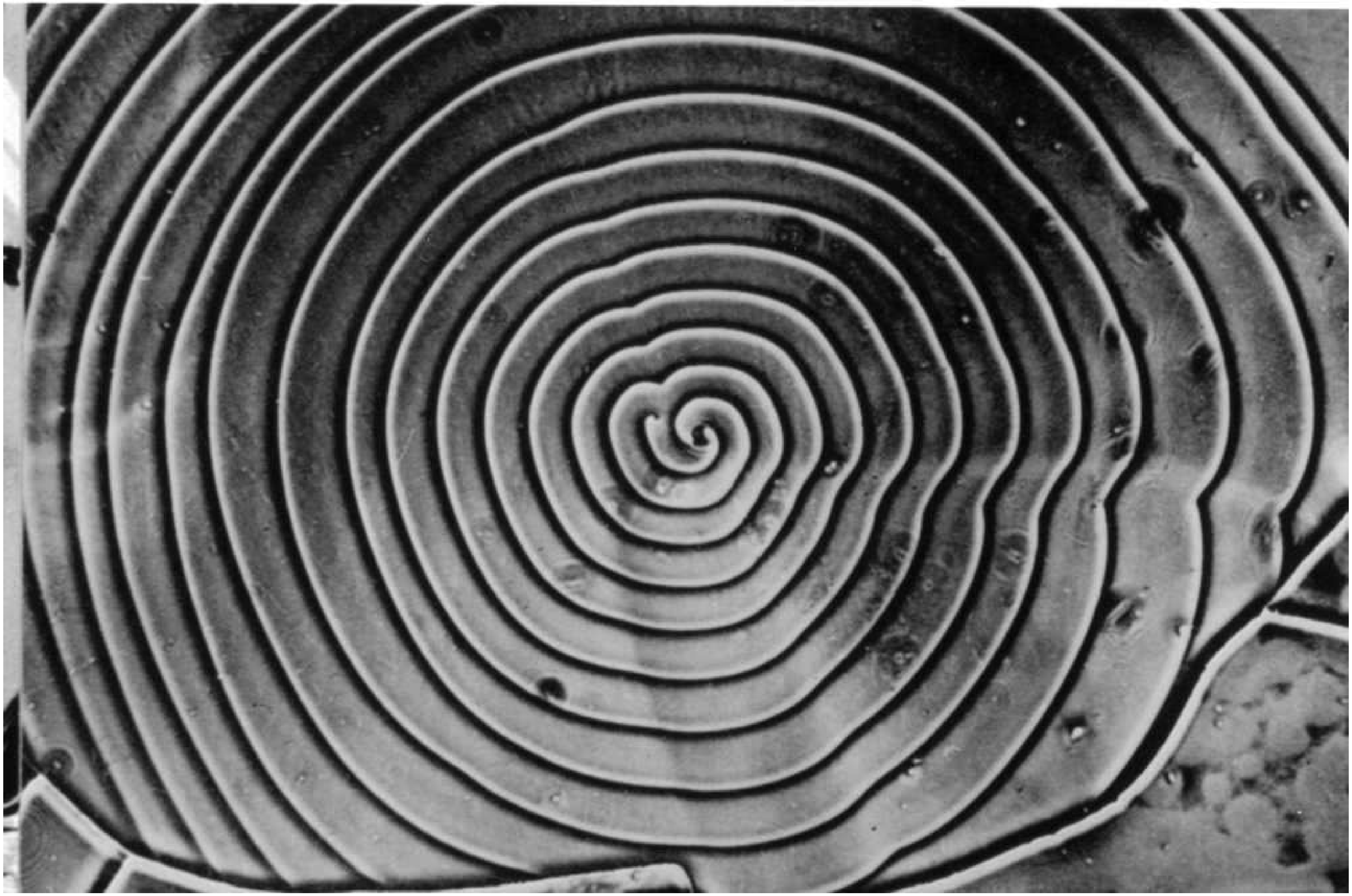
Burgers Vector



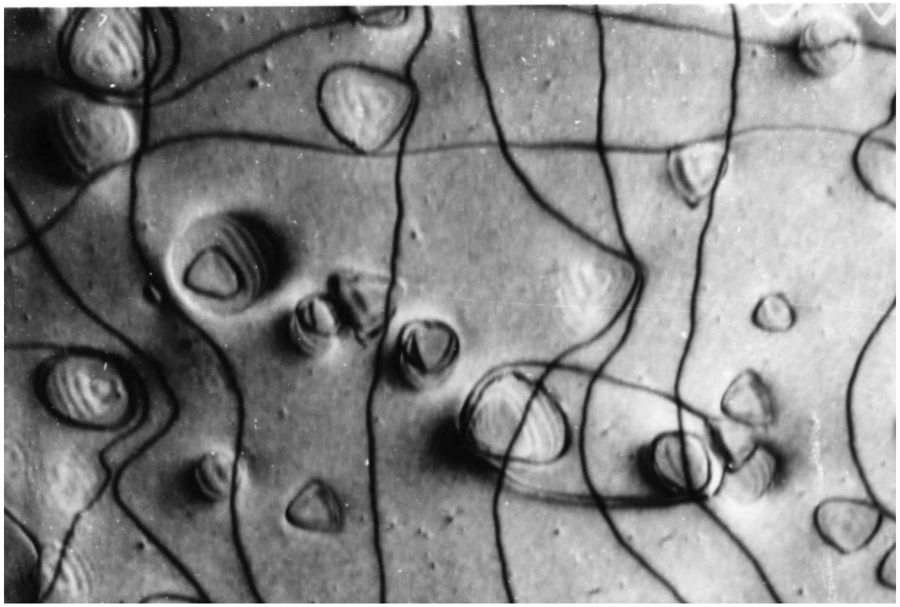
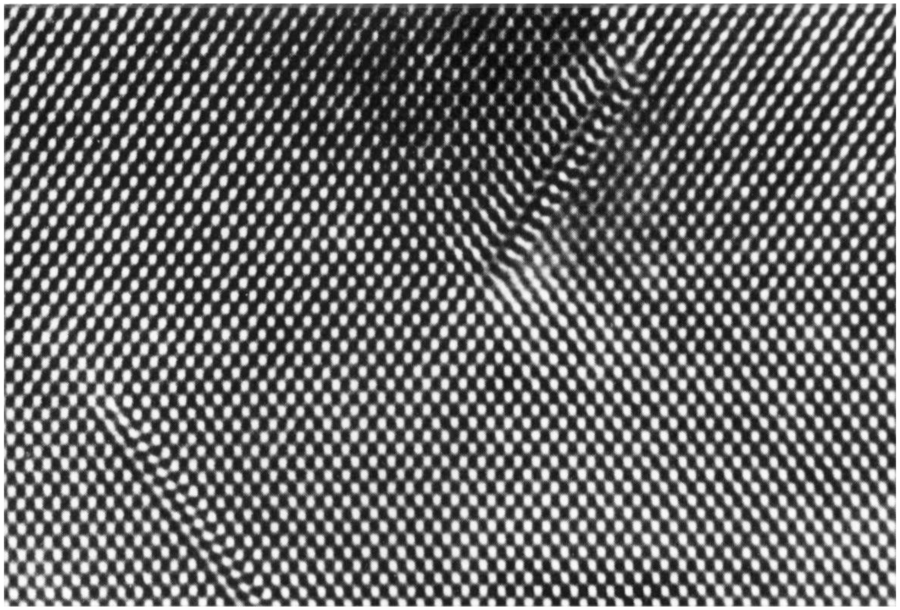
Experimental Observations of Dislocations



Experimental Observations of Dislocations



[Source: Amelinckx (1964)]

(A)  (B) 

(A) Courtesy of J. Humphreys, Manchester University.)

[(B) Cullis et al. (1985)]

Force to Move a Dislocation

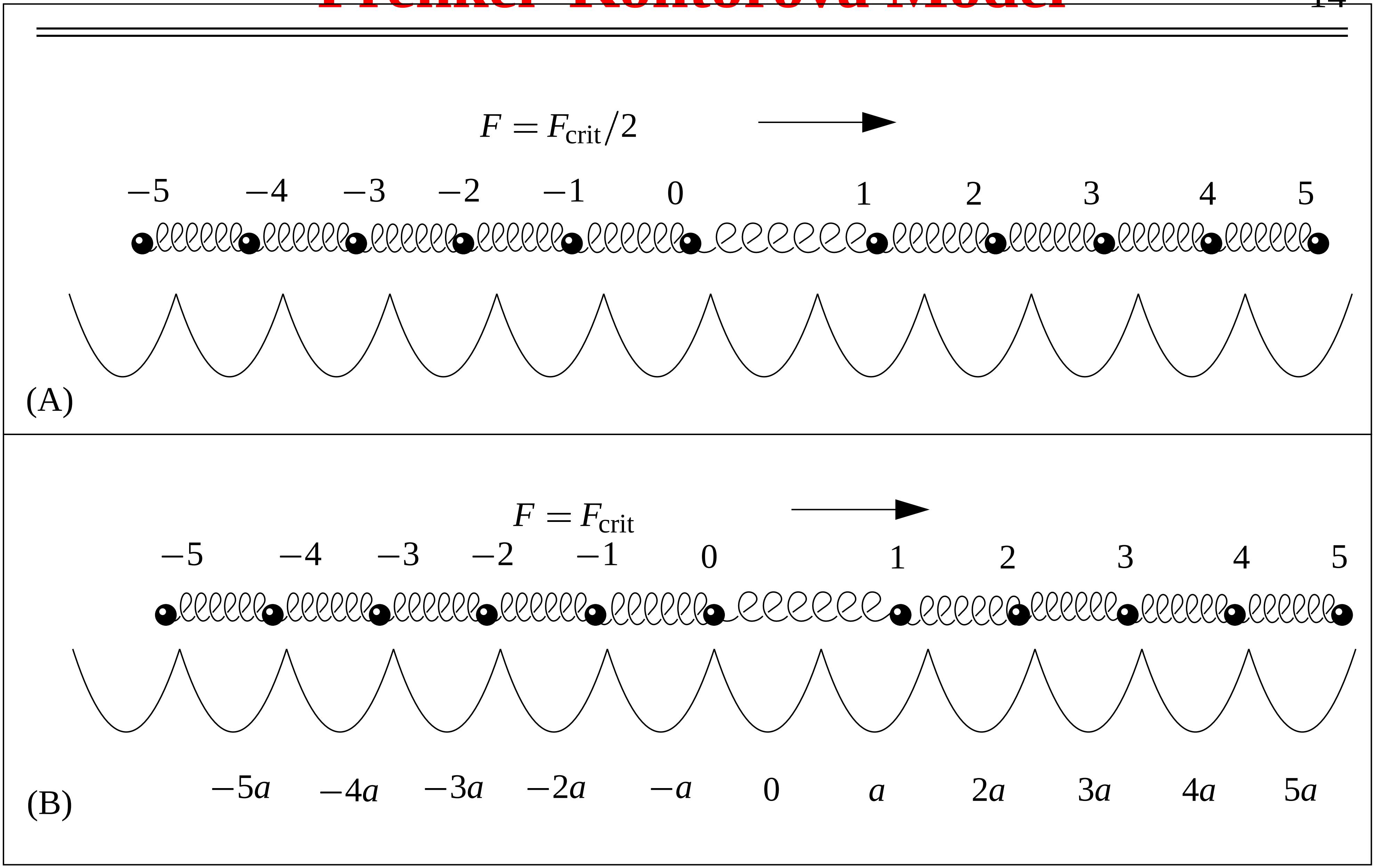
$$f_x = \sigma_{xy} b_x, \tag{L7}$$

$$\sigma_{xy} = \frac{F_{\rm ext}}{Na^2} \tag{L8}$$

$$\vec{f} = (\sigma \cdot \vec{b}) \times \hat{L}. \tag{L9}$$

Peach–Kohler force

One-Dimensional Dislocations: Frenkel–Kontorova Model



Find force needed to move dislocation in simple one–dimensional model.

One-Dimensional Dislocations: Frenkel–Kontorova Model

$$U(x) = \frac{1}{2}\mathcal{K}[x - a\,\mathrm{int}(x/a + \tfrac{1}{2})]^2 - fx, \quad \text{(L10)}$$

$$f_n = k[x_{n+1} - x_n - a] + k[x_{n-1} - x_n + a] - \frac{\partial U}{\partial x}. \quad \text{(L11)}$$

$$f_n = \begin{cases} k[x_{n+1} - x_n - a] + k[x_{n-1} - x_n + a] + f - \mathcal{K}[x_n - (n-1)a] & \text{for} \quad n \le 0 \\ k[x_{n+1} - x_n - a] + k[x_{n-1} - x_n + a] + f - \mathcal{K}[x_n - na] & \text{for} \quad n > 0. \end{cases} \quad \text{(L12)}$$

$$x_n = f/\mathcal{K} + a(n-1) + A_l e^{qn}, \quad \text{(L13)}$$

$$k(e^q - 2 + e^{-q}) - \mathcal{K} = 0 \quad \text{(L14)}$$

$$x_n = f/\mathcal{K} + an + A_r e^{-qn}. \quad \text{(L15)}$$

One-Dimensional Dislocations: Frenkel–Kontorova Model

$$
\begin{aligned}
-a+A_l &= A_r && \text{(L16a)}\\
A_l e^q &= a+A_r e^{-q}, && \text{(L16b)}
\end{aligned}
$$

$$
\begin{aligned}
A_l &= \frac{a}{e^q+1} && \text{(L17a)}\\
A_r &= \frac{-a}{e^{-q}+1}. && \text{(L17b)}
\end{aligned}
$$

$$x_0 = -\frac{a}{2} = \frac{f_c}{\mathcal{K}} - a + A_l \tag{L18}$$

$$\Rightarrow f_c = \frac{a\mathcal{K}}{2}\tanh\frac{q}{2}. \tag{L19}$$

$$q \approx \sqrt{\frac{\mathcal{K}}{k}} \tag{L20}$$

One-Dimensional Dislocations: Frenkel–Kontorova Model

$$f_c \approx \frac{a\mathcal{K}}{4}\sqrt{\frac{\mathcal{K}}{k}}. \tag{L21}$$

Impossibility of Crystalline Order in Two Dimensions

Peierls and Landau showed that two–dimensional crystals are destroyed by thermal fluctuations.

$$U = \int d^2r\,\tfrac{1}{2}C\sum_{\alpha\beta}\frac{\partial u_\alpha}{\partial r_\beta}\frac{\partial u_\alpha}{\partial r_\beta}. \tag{L22}$$

$$u_\alpha(\vec{r}) = \sum_{\vec{k}} e^{i\vec{r}\cdot\vec{k}}u_\alpha(\vec{k}). \tag{L23}$$

$$\vec{u}(\vec{k}) = 0 \text{ for } k > 1/\mathcal{D}. \tag{L24}$$

$$U = \int d^2r\,\tfrac{1}{2}C\sum_{\beta\alpha\vec{k}\vec{k}'} k_\beta k'_\beta e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}u_\alpha(\vec{k})u^*_\alpha(\vec{k}') \tag{L25}$$

$$= \frac{\mathcal{V}C}{2}\sum_{\alpha\vec{k}} k^2|u_\alpha(\vec{k})|^2 \tag{L26}$$

$$\langle u^2 \rangle = \langle \int \frac{d^2 r}{\mathcal{V}} \sum_{\beta} u_\beta(\vec{r}) u_\beta(\vec{r}) \rangle \tag{L27}$$

$$= \sum_{\beta \vec{k}} \langle |u_\beta(\vec{k})|^2 \rangle \tag{L28}$$

$$\vec{u}(\vec{k}) = \vec{u}^*(-\vec{k}) \tag{L29}$$

$$\langle |u_\beta(\vec{k})|^2 \rangle$$

$$= \frac{\int \prod_{\alpha \vec{k}'} du_\alpha(\vec{k}') |u_\beta(\vec{k})|^2 e^{-\beta \frac{\mathcal{V}C}{2} \sum_{\alpha \vec{k}'} k'^2 |u_\alpha(\vec{k}')|^2}}{\int \prod_{\alpha \vec{k}'} du_\alpha(\vec{k}') e^{-\beta \frac{\mathcal{V}C}{2} \sum_{\alpha \vec{k}'} k'^2 |u_\alpha(\vec{k}')|^2}} \tag{L30}$$

$$= \frac{\int du_\beta(\vec{k}) |u_\beta(\vec{k})|^2 e^{-\beta \mathcal{V} C k^2 |u_\beta(\vec{k})|^2}}{\int du_\beta(\vec{k}) e^{-\beta \mathcal{V} C k^2 |u_\beta(\vec{k})|^2}} \tag{L31}$$

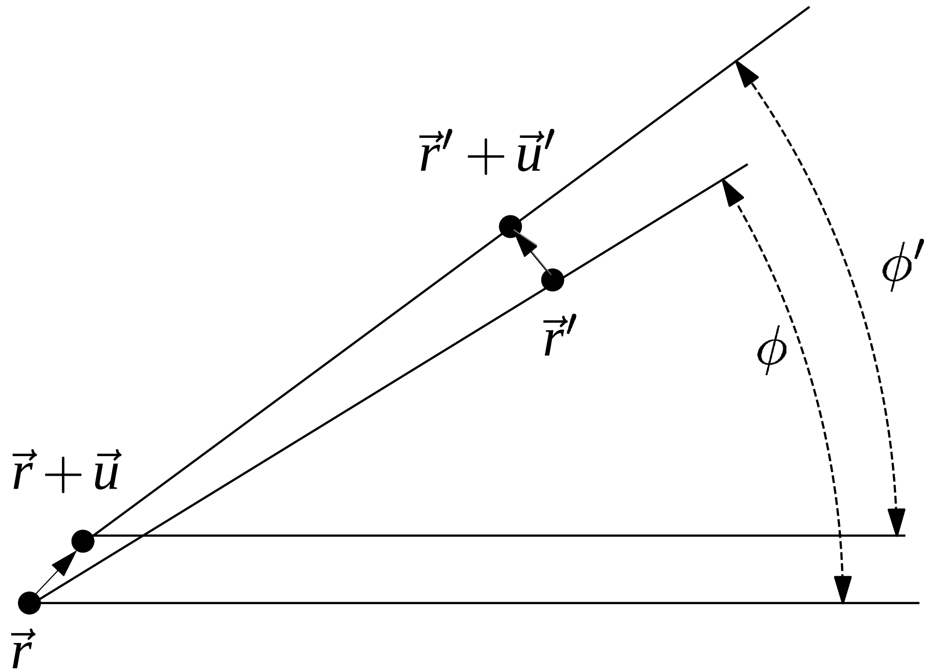
$$= \frac{\int du^r du^i [(u^r)^2 + (u^i)^2] e^{-\beta \mathcal{V} C k^2 [(u^r)^2 + (u^i)^2]}}{\int du^r du^i e^{-\beta \mathcal{V} C k^2 [(u^r)^2 + (u^i)^2]}} \tag{L32}$$

$$= \frac{k_B T}{\mathcal{V} C k^2}. \tag{L33}$$

$$\langle u^2 \rangle = \sum_{\alpha \vec{k}} \frac{k_B T}{\mathcal{V} C k^2} \tag{L34}$$

$$= 2 \int \frac{d^2 k}{(2\pi)^2} \frac{k_B T}{C k^2} \tag{L35}$$

$$= 2 \int_0^{1/\mathcal{D}} \frac{dk}{2\pi k} \frac{k_B T}{C} \to \infty. \tag{L36}$$



$$(dx, dy) = \vec{r}' - \vec{r}. \tag{L37}$$

$$\phi = \tan^{-1}(dy/dx). \tag{L38}$$

$$\vec{r} + \vec{u}(\vec{r}) \quad \text{and} \quad \vec{r}' + \vec{u}(\vec{r}'). \tag{L39}$$

$$\phi' = \tan^{-1}\left(\frac{dy + \partial u_y/\partial x\, dx + \partial u_y/\partial y\, dy}{dx + \partial u_x/\partial x\, dx + \partial u_x/\partial y\, dy}\right) \tag{L40}$$

$$\approx \phi + \frac{dx\, dy}{dx^2 + dy^2}\left[\left(\frac{\partial u_y}{\partial y} - \frac{\partial u_x}{\partial x}\right) + \frac{dx}{dy}\frac{\partial u_y}{\partial x} - \frac{dy}{dx}\frac{\partial u_x}{\partial y}\right] \tag{L41}$$

$$\Rightarrow \phi' - \phi = \cos\phi \sin\phi \left(\frac{\partial u_y}{\partial y} - \frac{\partial u_x}{\partial x}\right) + \cos^2\phi \frac{\partial u_y}{\partial x} - \sin^2\phi \frac{\partial u_x}{\partial y}. \tag{L42}$$

$$\delta\phi(\vec{r}) = \frac{1}{2}\left(\frac{\partial u_y}{\partial x} - \frac{\partial u_x}{\partial y}\right). \tag{L43}$$

$$\delta\phi(\vec{r}) = \frac{1}{2}\sum_{\vec{k}} (ik_x u_y(\vec{k}) - ik_y u_x(\vec{k}))e^{i\vec{k}\cdot\vec{r}}. \tag{L44}$$

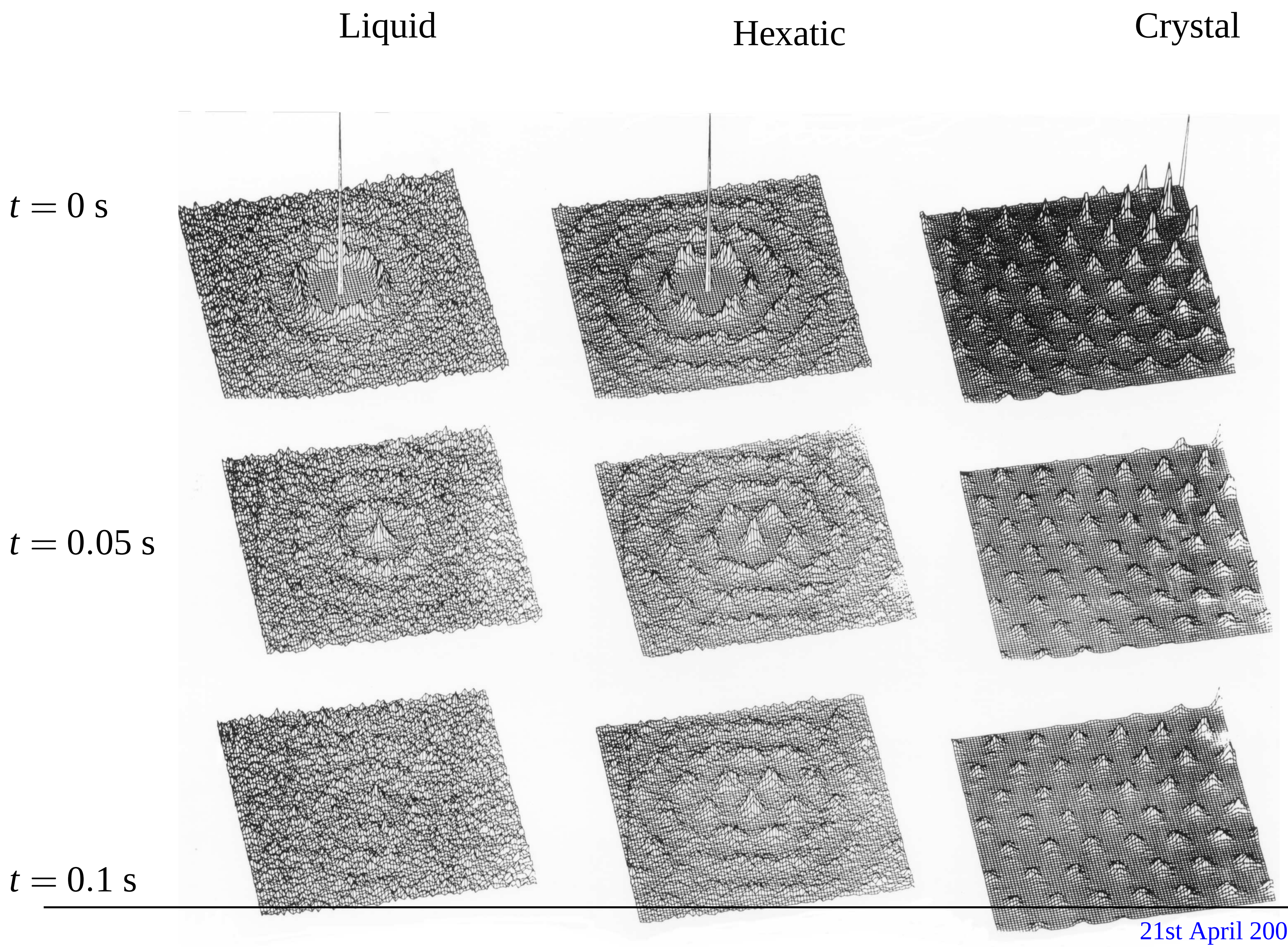
$$\int \frac{d^2r}{\mathcal{V}} \langle \delta\phi(\vec{r})\delta\phi(\vec{r})\rangle \tag{L45}$$

$$= \tfrac{1}{4}\sum_{\vec{k}} k_x^2 \langle |u_x(\vec{k})|^2\rangle + k_y^2\langle |u_y(\vec{k})|^2\rangle - k_x k_y \langle (u_x(\vec{k})u_y^*(\vec{k}) + u_y(\vec{k})u_x^*(\vec{k}))\rangle \tag{L46}$$

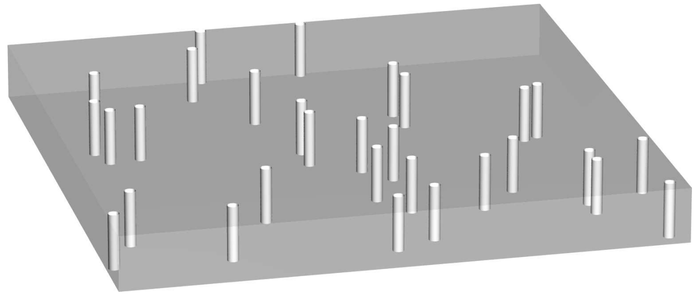
$$= \quad \tfrac{1}{4}\sum_{\vec{k}} \frac{k_B T}{C\mathcal{V}k^2}(k_x^2+k_y^2) \tag{L47}$$

$$= \quad \frac{k_B T}{4C}\int_0^{2\pi} d\theta \int_0^{1/\mathfrak{D}} \frac{dk\,k}{(2\pi)^2} = \frac{k_B T}{16\pi\mathfrak{D}^2 C}. \tag{L48}$$

Kosterlitz–Thouless–Berezinskii Transition



[Murray and Grier (1996)]



$$u_x = 0, \quad u_y = 0, \quad u(x,y) = u_z(x,y). \tag{L49}$$

$$U = \frac{a\mu}{2} \int d^2r \, (\nabla u)^2 \tag{L50}$$

$$\nabla^2 u = 0. \tag{L51}$$

$$u(x,y) = \frac{a}{2\pi} \mathrm{Im} \ln[x + iy]. \tag{L52}$$

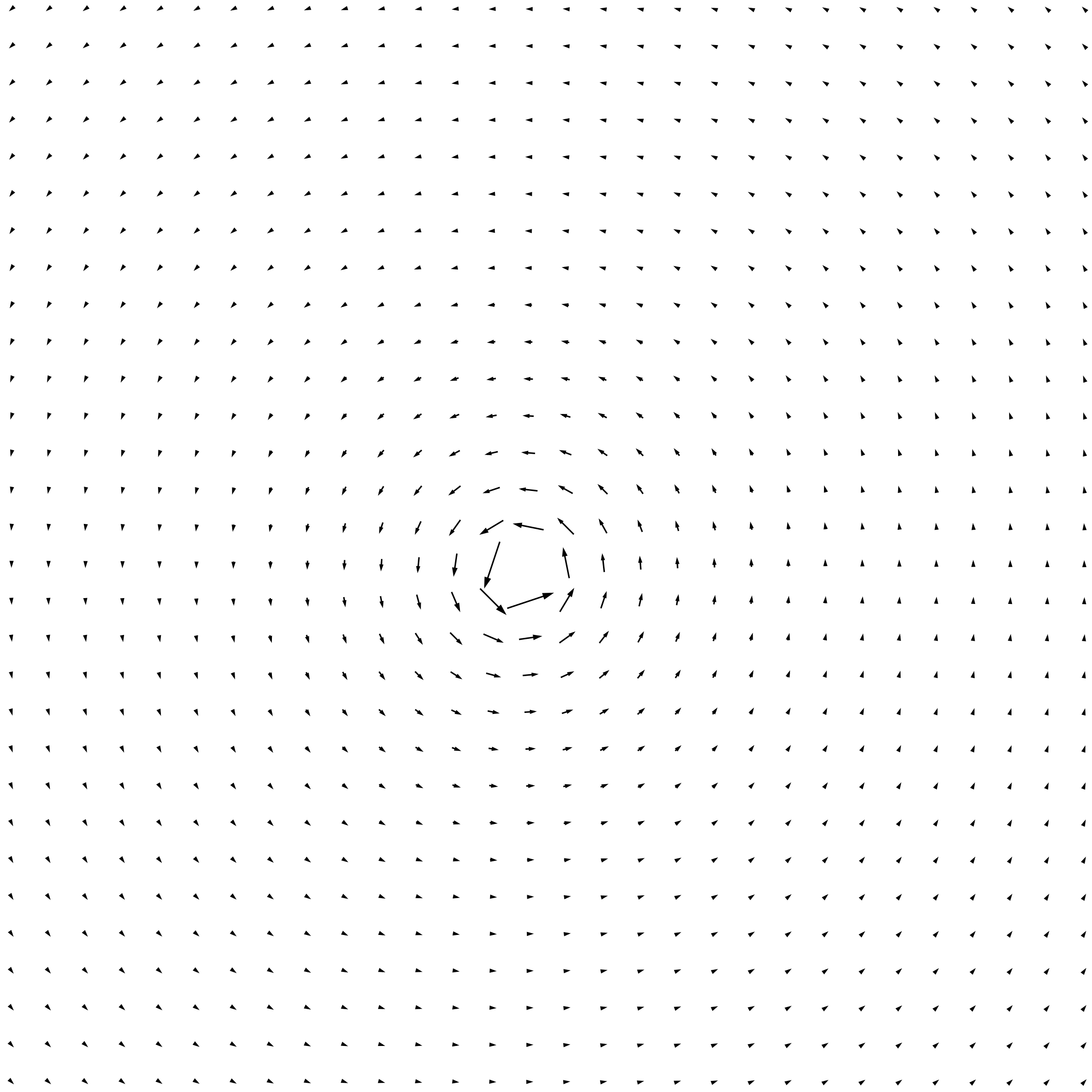
$$U = \frac{a\mu}{2} \left(\frac{a}{2\pi}\right)^2 \int d^2r \left[\frac{-y}{x^2+y^2}\right]^2 + \left[\frac{x}{x^2+y^2}\right]^2 \tag{L53}$$

$$= \quad \frac{a\mu}{2}\left(\frac{a}{2\pi}\right)^2 \int_a^R dr\, 2\pi r \frac{1}{r^2} \tag{L54}$$

$$\rightarrow \quad \frac{1}{4\pi}(a^3\mu)\ln\left(\frac{R}{a}\right) + w. \tag{L55}$$

$$u(x,y) = \frac{a}{2\pi}\mathrm{Im}\left\{\ln[x+iy] - \ln[x-x_0+iy]\right\}. \tag{L56}$$

$$2q^2\ln\left(\frac{x_0}{a}\right) + 2w \quad \text{with } q^2 = \frac{a^3\mu}{4\pi}. \tag{L57}$$



$$S = 2k_B \ln(L/a), \tag{L58}$$

$$\mathcal{E} = q^2 \ln(L/a). \tag{L59}$$

$$k_B T_c = \frac{q^2}{2}. \tag{L60}$$

$$\mathcal{H} = \frac{1}{2} \sum_{i \neq j} U(|\vec{r}_i - \vec{r}_j|) + 2w \quad \text{with} \quad U(r) = 2q^2 \ln(r/a) \tag{L61}$$

$$\langle r^2 \rangle = \frac{\int_a^\infty dr\, 2\pi r\, r^2 e^{-\beta U(r)}}{\int_a^\infty dr\, 2\pi r e^{-\beta U(r)}} \tag{L62}$$

$$= a^2 \left[\frac{\beta q^2 - 1}{\beta q^2 - 2} \right]. \tag{L63}$$

$$Z_{\mathrm{gr}} = 1 + \sum_{\vec{r}_1 \vec{r}_2} e^{-\beta U(|\vec{r}_1 - \vec{r}_2|) - 2\beta w} + \ldots. \tag{L64}$$

$$n(r)dr = \frac{dr}{R^2}\langle\delta_{r,|\vec{r}_1-\vec{r}_2|}\rangle = \frac{dr}{R^2}\sum_{\vec{r}_1\vec{r}_2} e^{-\beta U(|\vec{r}_1-\vec{r}_2|)-2\beta w}\delta_{r,|\vec{r}_1-\vec{r}_2|} + \dots \quad \text{(L65)}$$

$$\approx \frac{1}{a^2}\frac{2\pi r^2 dr}{a^2}e^{-\beta U(r)-2\beta w}. \quad \text{(L66)}$$

$$\vec{p} = \alpha\vec{E} = rq\langle(\cos\theta,\sin\theta)\rangle \quad \text{(L67)}$$

$$= \int\frac{d\theta}{2\pi}e^{-\beta U(r)-2\beta w+\beta Eqr\cos\theta}rq(\cos\theta,\sin\theta) \quad \text{(L68)}$$

$$= \frac{1}{2}\beta q^2 r^2 \vec{E}. \quad \text{(L69)}$$

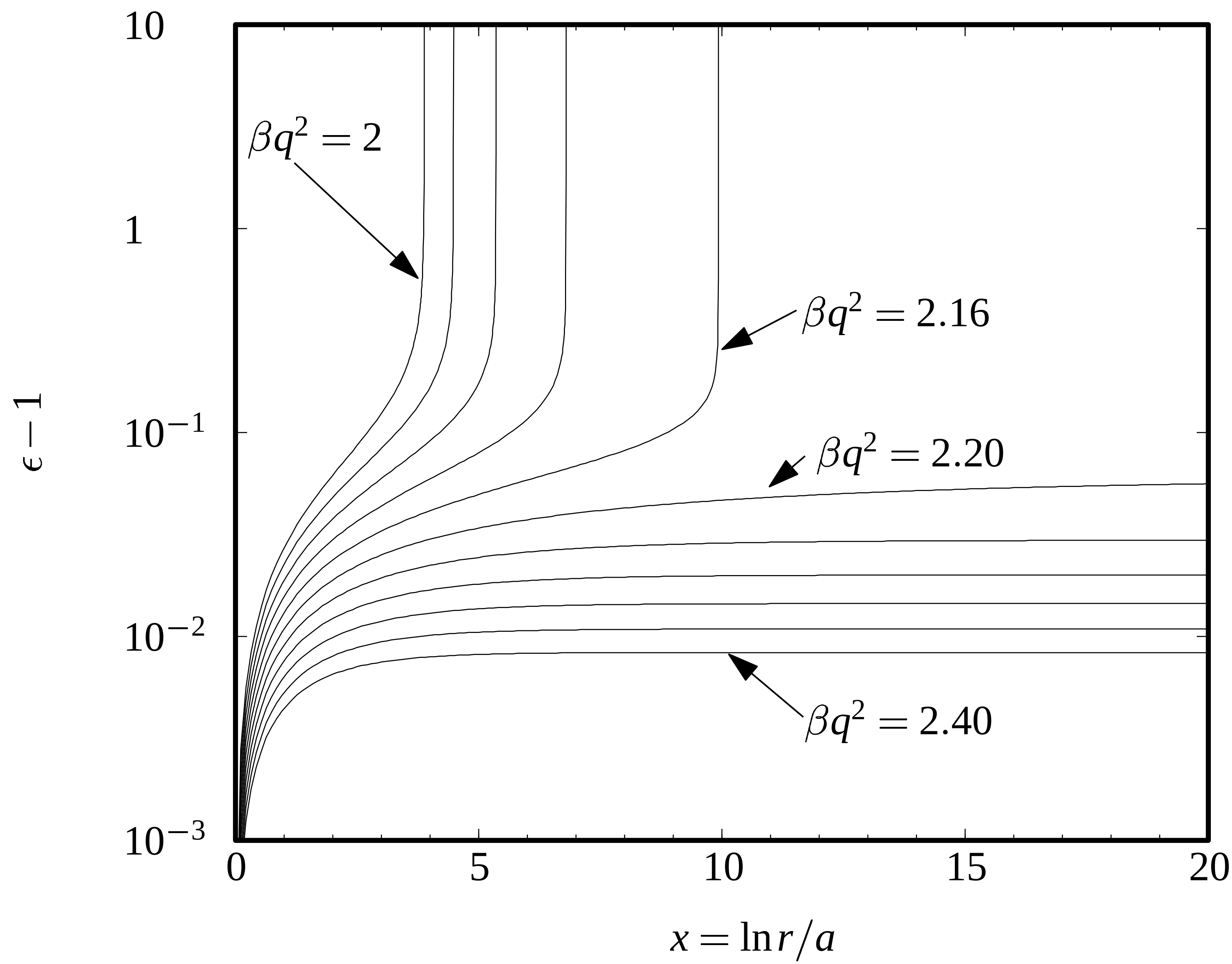
$$d\chi(r) = n(r)\,dr\,\alpha(r) = \frac{1}{2}\beta q^2\left(\frac{r}{a}\right)^2\frac{2\pi r\,dr}{a^2}e^{-\beta U/\epsilon(r)-2\beta w}. \quad \text{(L70)}$$

$$\epsilon(r) = 1+4\pi\int^r d\chi = 1+4\pi\int_a^r dr'\,n(r')\alpha(r') \quad \text{(L71)}$$

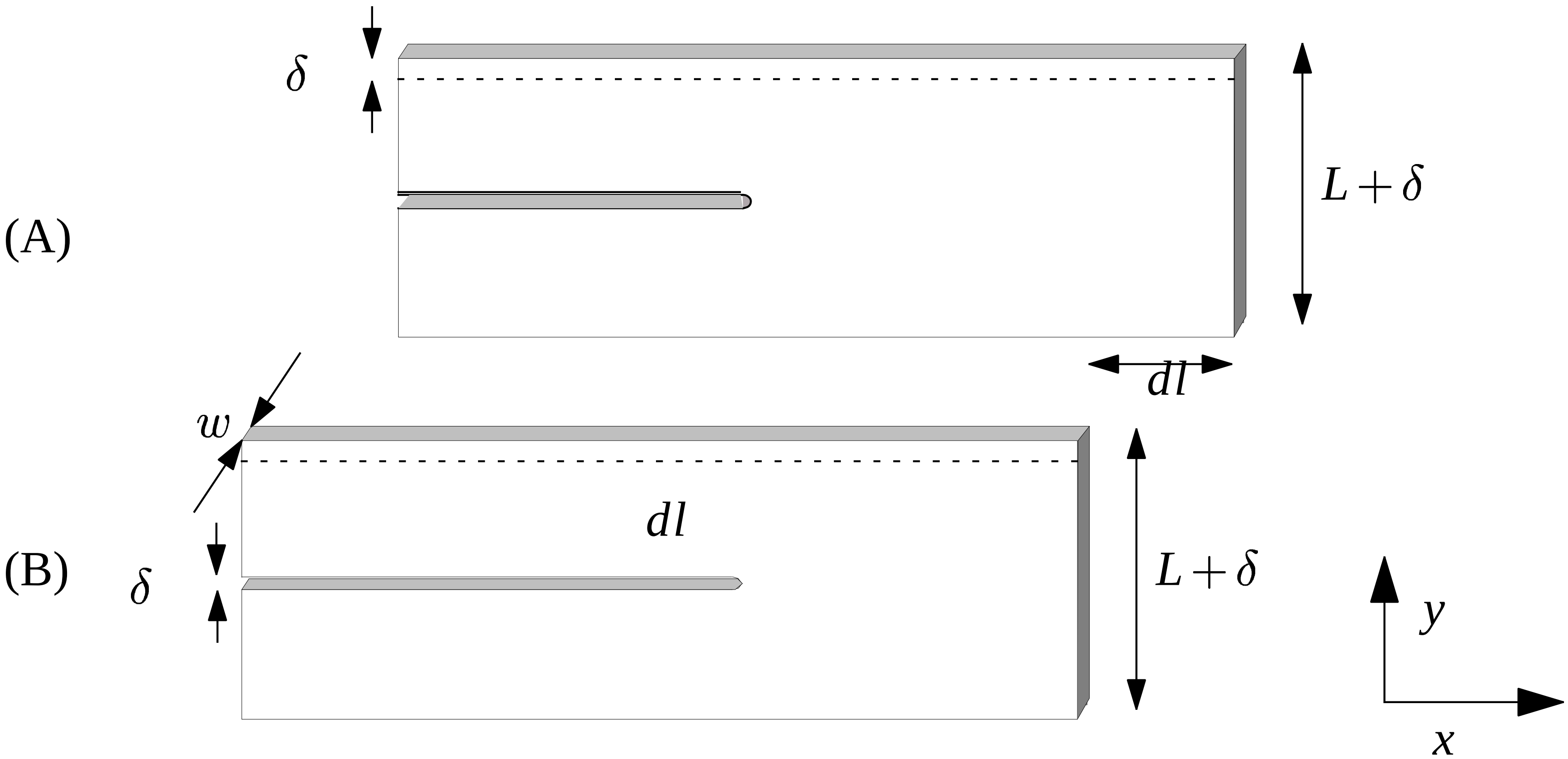
$$\Rightarrow \frac{d\epsilon(r)}{dr} = 4\pi^2\beta q^2 \frac{r^3}{a^4} e^{-\beta U(r)/\epsilon(r)-2\beta w} \quad \text{(L72)}$$

$$\Rightarrow \frac{d\epsilon(x)}{dx} = 4\pi^2\beta q^2 x^{3-2\beta q^2/\epsilon(x)} e^{-2\beta w}. \quad \text{(L73)}$$

Kosterlitz–Thouless–Berezinskii Transition



Fracture of a Strip



$$U = \frac{1}{2}\delta^2 w \frac{Y}{L}, \tag{L74}$$

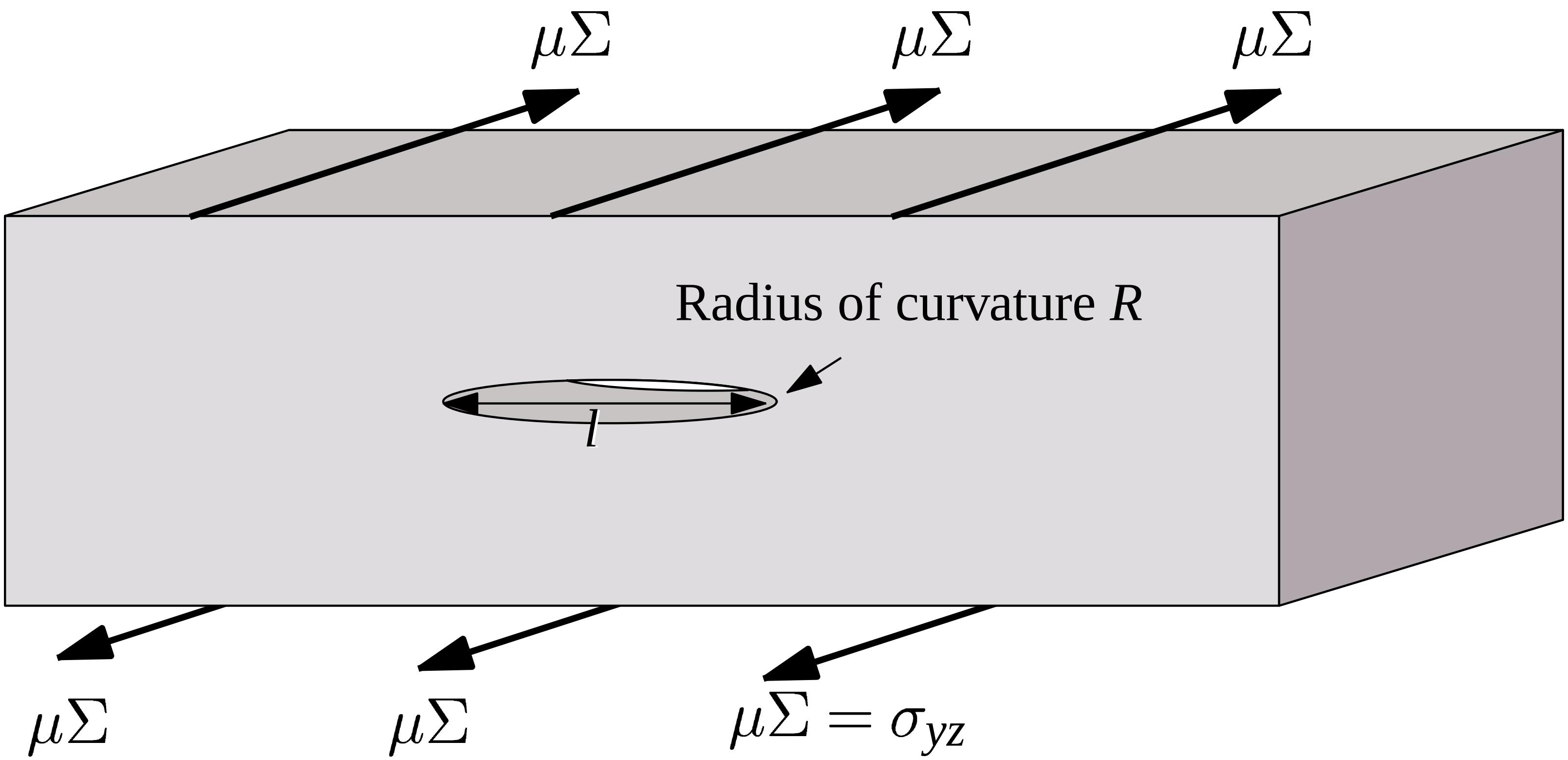
$$dU = dl \frac{1}{2}\delta^2 w \frac{Y}{L}. \tag{L75}$$

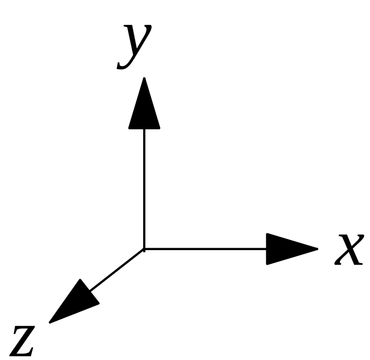
Fracture of a Strip

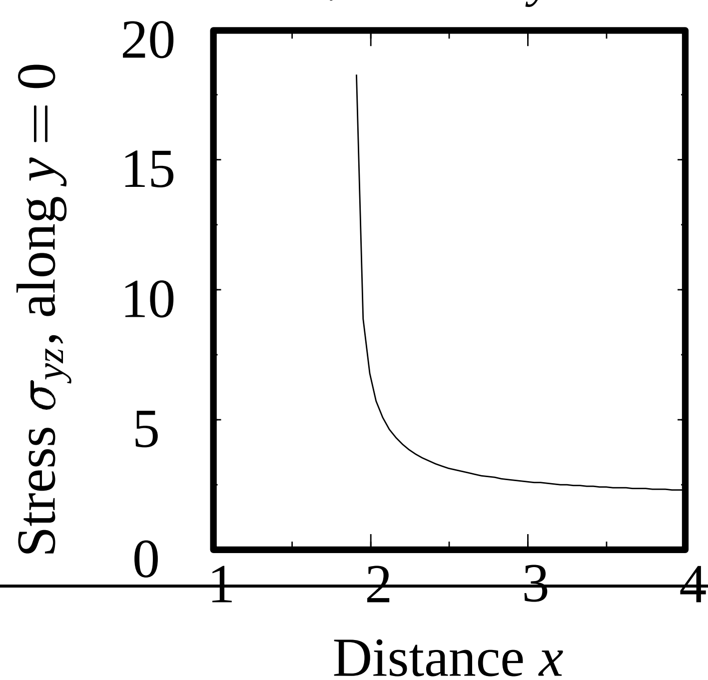
$$\Gamma w\, dl = dl \frac{1}{2} \delta^2 w \frac{Y}{L} \tag{L76}$$

$$\Rightarrow \quad \delta = \sqrt{\frac{2\Gamma L}{Y}} \quad \text{and} \quad \sigma_{yy} = Y \frac{\delta}{L} = \sqrt{\frac{2\Gamma Y}{L}}. \tag{L77}$$

Fracture of a Strip







Fracture of a Strip

$$\frac{\text{Maximum stress}}{\text{applied stress}} \propto \sqrt{\frac{l}{R}}, \qquad \text{(L78)}$$

$$\nabla^2 u = 0. \tag{L79}$$

$$u = \frac{\phi(\zeta) + \overline{\phi(\zeta)}}{2}, \tag{L80}$$

$$\sigma_{yz} = \mu \frac{\partial u}{\partial y} = \frac{\mu}{2}[i\phi'(x+iy) - i\overline{\phi'(x+iy)}] \tag{L81}$$

$$\Rightarrow \quad \phi'(\zeta) \to -i\Sigma \text{ for } \zeta \to \infty. \tag{L82}$$

$$(x(t), y(t)) \tag{L83}$$

$$\vec{T} = \left(\frac{\partial x}{\partial t}, \frac{\partial y}{\partial t}\right) \quad \text{and} \quad \vec{N} = \left(-\frac{\partial y}{\partial t}, \frac{\partial x}{\partial t}\right) \tag{L84}$$

$$(\sigma_{xz}, \sigma_{yz}) \cdot \vec{N} = 0 \tag{L85}$$

$$\Rightarrow \quad \mu\left(\frac{\partial u}{\partial x},\frac{\partial u}{\partial y}\right)\cdot\left(-\frac{\partial y}{\partial t},\frac{\partial x}{\partial t}\right)=0\Rightarrow\frac{\partial u}{\partial y}\frac{\partial x}{\partial t}-\frac{\partial u}{\partial x}\frac{\partial y}{\partial t}=0 \tag{L86}$$

$$\Rightarrow \quad \left(-\frac{\partial \phi}{\partial ix}+\frac{\partial \overline{\phi}}{\partial ix}\right)\frac{\partial x}{\partial t}=\left(\frac{\partial \phi}{\partial iy}-\frac{\partial \overline{\phi}}{\partial iy}\right)\frac{\partial y}{\partial t} \tag{L87}$$

$$\Rightarrow \quad \frac{\partial \phi}{\partial t}=\frac{\partial \overline{\phi}}{\partial t} \tag{L88}$$

$$\Rightarrow \quad \phi(\zeta)=\overline{\phi(\zeta)} \tag{L89}$$

$$\zeta=\omega+\frac{p}{\omega}, \tag{L90}$$

$$\omega=e^{i\theta}, \tag{L91}$$

$$\phi(\omega)=\overline{\phi(\omega)}=\bar{\phi}\left(\frac{1}{\omega}\right), \tag{L92}$$

$$\omega=\frac{\zeta+\sqrt{\zeta^2-4p}}{2}. \tag{L93}$$

$$\phi(\omega) \rightarrow -i\Sigma\omega \quad \text{for } \omega \rightarrow \infty. \tag{L94}$$

$$\bar{\phi}(1/\omega) \rightarrow -i\Sigma\omega \quad \text{for } \omega \rightarrow \infty, \tag{L95}$$

$$\bar{\phi}(\omega) \rightarrow \frac{-i\Sigma}{\omega} \quad \text{for } \omega \rightarrow 0 \tag{L96}$$

$$\phi(\omega) \rightarrow \frac{i\Sigma}{\omega} \quad \text{for } \omega \rightarrow 0. \tag{L97}$$

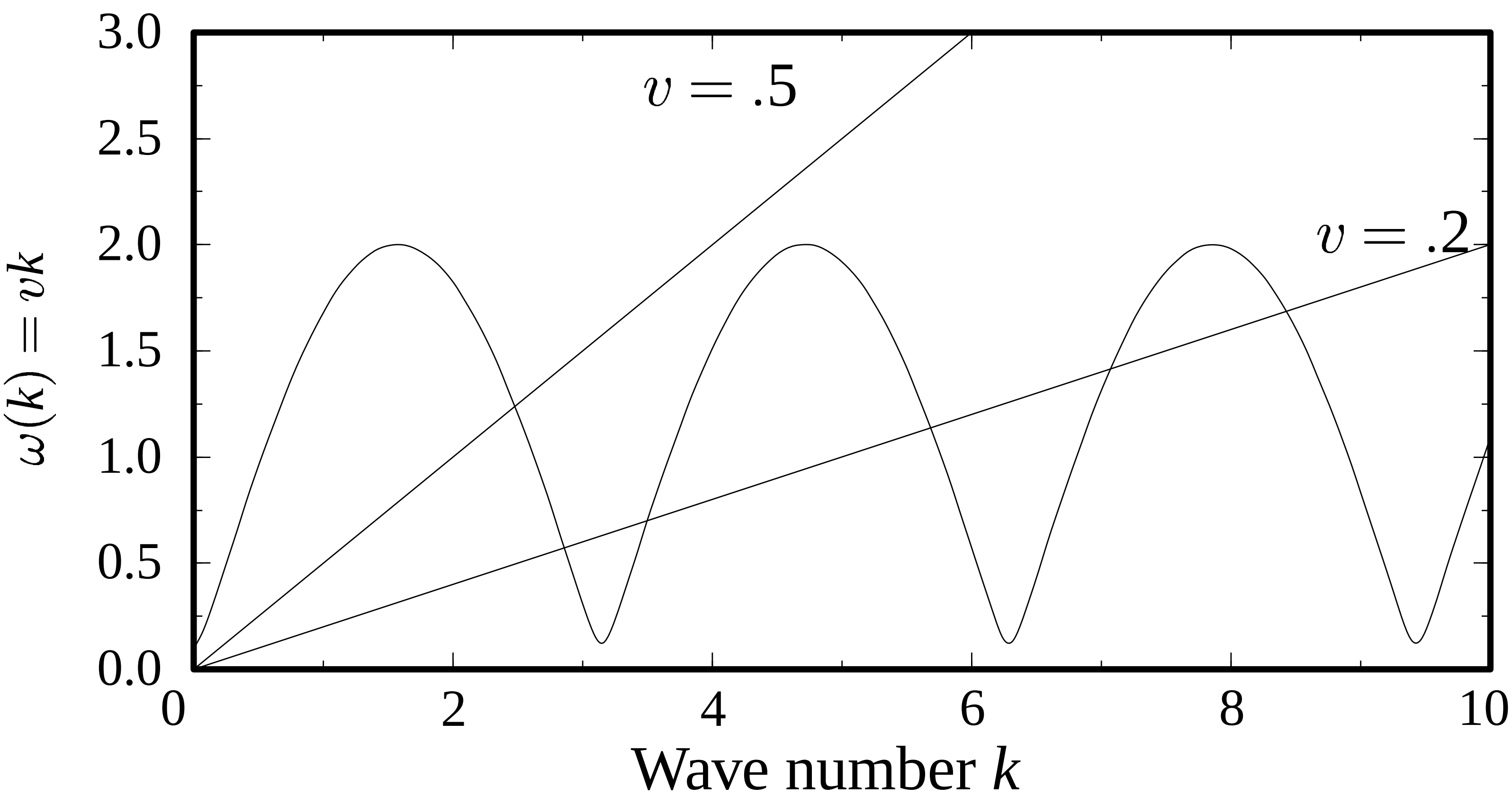
$$\phi(\omega) = -i\Sigma\omega + i\frac{\Sigma}{\omega} \tag{L98}$$

$$\Rightarrow \phi(\zeta) = -i\Sigma\frac{\zeta}{2}(1+\sqrt{1-4p/\zeta^2}) + i\Sigma\frac{\zeta}{2p}(1-\sqrt{1-4p/\zeta^2}). \tag{L99}$$

Stress Intensity Factor

$$\sigma_{yz} = \mu \frac{\partial u}{\partial y} = \frac{\mu \Sigma x}{\sqrt{x-2}\sqrt{x+2}} \rightarrow \frac{\mu \Sigma}{\sqrt{x-2}} \quad \text{as } x \rightarrow 2. \tag{L100}$$

$$K = \lim_{r \rightarrow 0} \sqrt{2\pi r}\,\sigma_{yz}. \tag{L101}$$



$$\vec{r} \rightarrow \vec{r} + \vec{R} \quad \text{(L102a)}$$

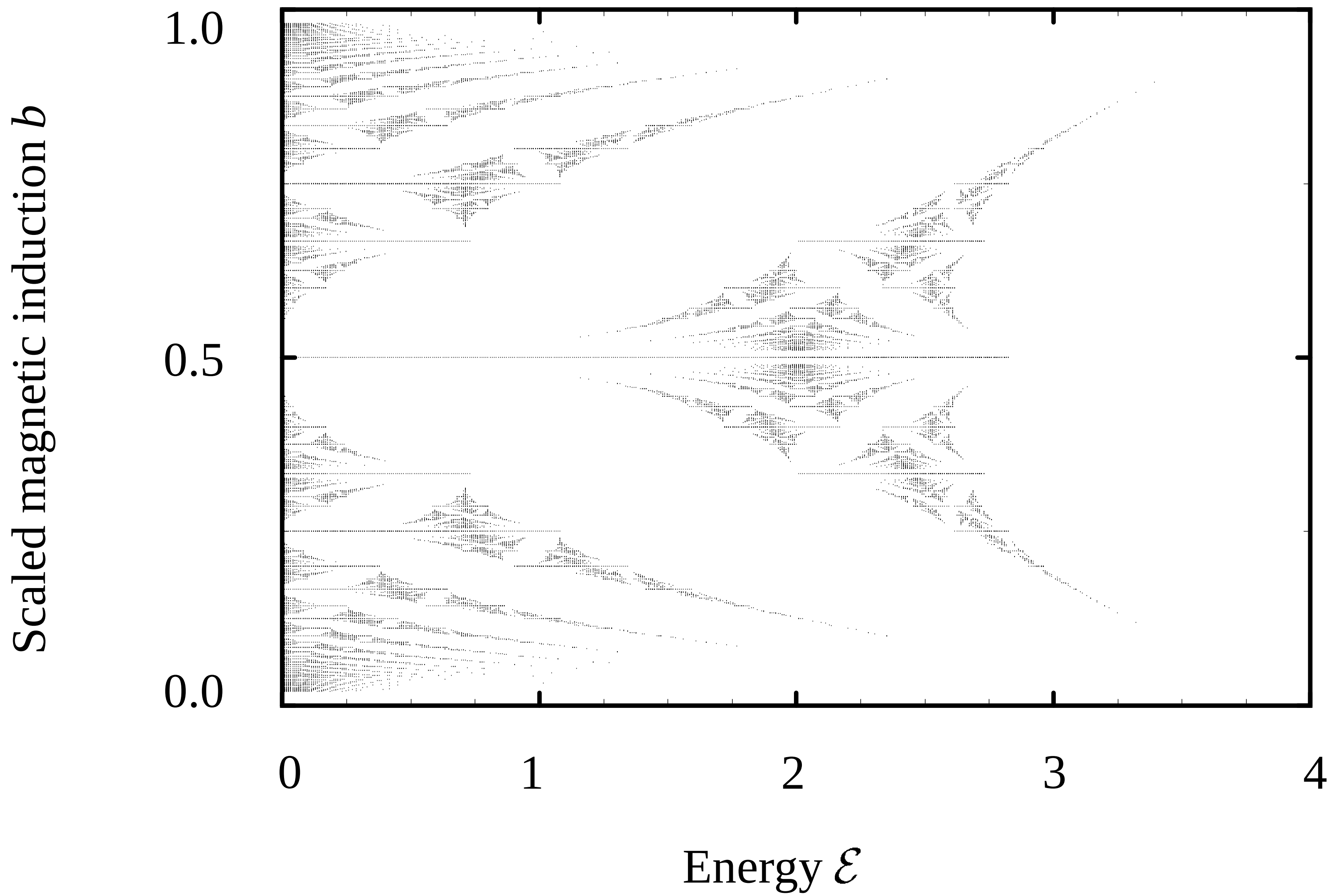
$$t \rightarrow t + a/v. \quad \text{(L102b)}$$

$$e^{i\vec{k}\cdot(\vec{r}+\vec{R})-i\omega(t+a/v)} = e^{i\vec{k}\cdot\vec{r}-i\omega t} \tag{L103}$$

$$\Rightarrow \quad e^{i\vec{k}\cdot\vec{R}-i\omega a/v} = 1 \tag{L104}$$

$$\Rightarrow \quad (\vec{k}+\vec{K})\cdot\vec{v} = \omega(\vec{k}) \tag{L105}$$

$$\Rightarrow \quad \vec{k}\cdot\vec{v} = \omega(\vec{k}). \tag{L106}$$



1.0
0.5
0.0
Scaled magnetic induction b
0
1
2
3
4
Energy $\mathcal{E}$

Definitions

- ☞ Atomic Magnetism
- ☞ Hund's Rules
- ☞ Curie's Law
- ☞ Landau Diamagnetism
- ☞ Aharonov–Bohm Effect
- ☞ Hofstadter Butterfly
- ☞ Integer Quantum Hall Effect
- ☞ Fractional Quantum Hall Effect

$$\hat{\mathcal{H}} = \frac{1}{2m}\sum_l \left[\hat{P}_l + \frac{e}{c}\vec{A}(\hat{R}_l)\right]^2 + 2\mu_B B \hat{S}_l^z, \tag{L1}$$

$$\vec{A}(\hat{R}) = -\frac{1}{2}\hat{R}\times B\hat{z}, \tag{L2}$$

$$\hbar\hat{L} = \sum_j \hat{R}_j \times \hat{P}_j \tag{L3}$$

$$\Rightarrow \hat{P}_j\cdot\vec{A} = -\frac{1}{2}\hat{P}_j\cdot\hat{R}\times\vec{B} = \frac{1}{2}\vec{B}\cdot\hat{R}_j\times\hat{P}_j \tag{L4}$$

$$\Rightarrow \hat{\mathcal{H}} = \frac{1}{2m}\sum_l \hat{P}_l^2 + \mu_B\left(\hat{L}+2\hat{S}\right)\cdot\vec{B} + \frac{e^2}{8mc^2}B^2\sum_j\left(\hat{X}_j^2+\hat{Y}_j^2\right). \tag{L5}$$

$$\Delta\mathcal{E}_l = \mu_B\vec{B}\cdot\langle l|\hat{L}+2\hat{S}|l\rangle + \sum_{l'\neq l}\frac{|\langle l|\mu_B\vec{B}\cdot(\hat{L}+2\hat{S})|l'\rangle|^2}{\mathcal{E}_l-\mathcal{E}_{l'}} + \frac{e^2B^2}{8mc^2}\langle l|\sum_j\left(\hat{X}_j^2+\hat{Y}_j^2\right)|l\rangle. \tag{L6}$$

$$\mu_B B = 5.79\cdot 10^{-5}[B/\text{tesla}]\ \text{eV}. \tag{L7}$$

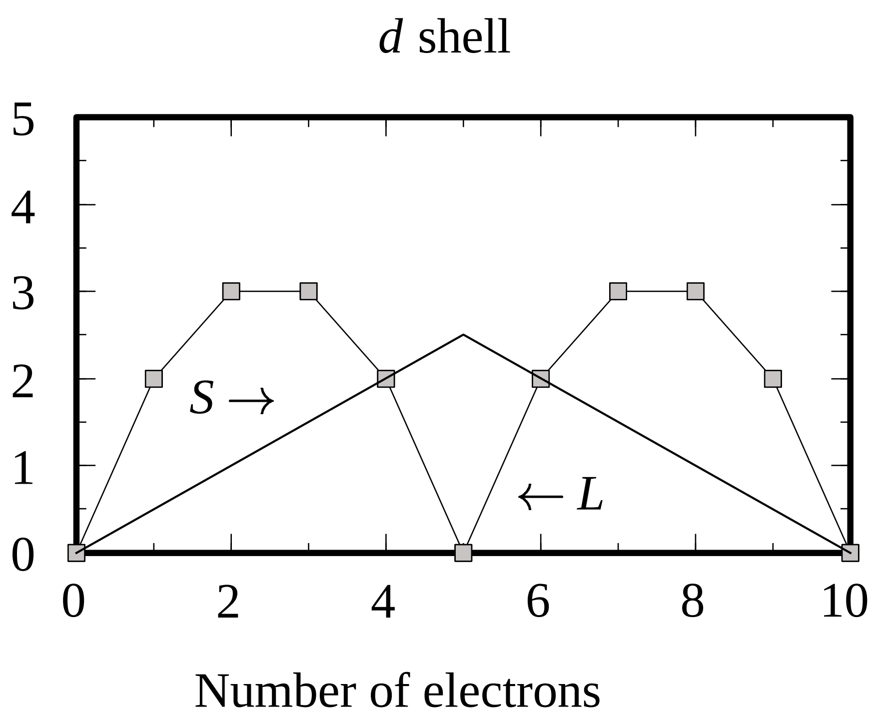
Hund's Rules

1. Maximize S
2. Maximize L, with electrons in different orbitals
3. Less than half full....

$$J = |L - S| \tag{L8a}$$

More than half full....

$$J = L + S \tag{L8b}$$



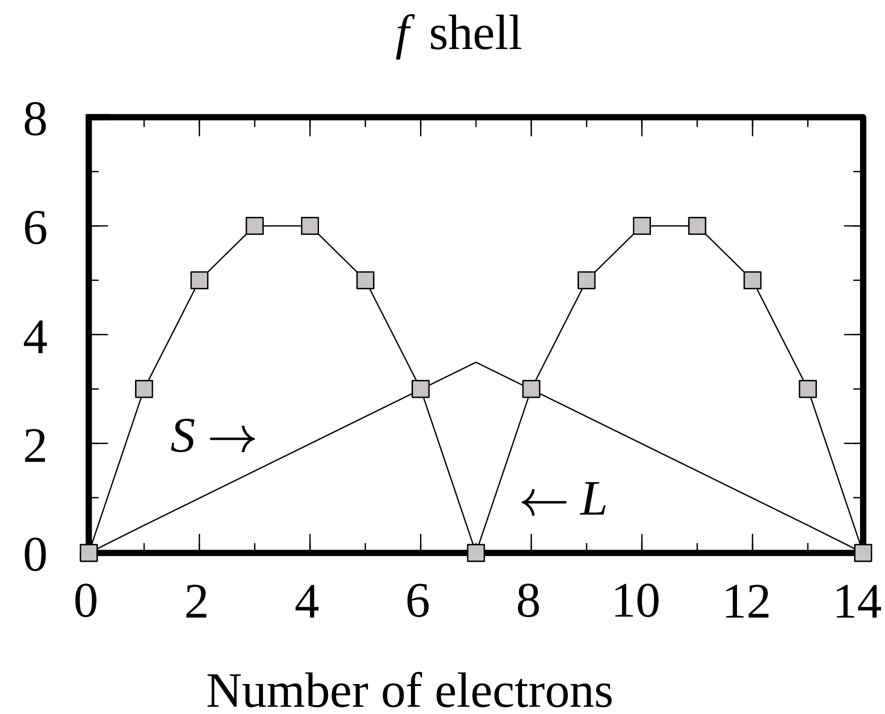


Figure 1: Hund's rules for *d* and *f* shells predict values for spin angular momentum *S* and orbital angular momentum *L* as indicated.

$$\langle l|\hat{L}_z + 2\hat{S}_z|l\rangle. \tag{L9}$$

$$\langle JLSJ_z|\hat{L}_z + 2\hat{S}_z|JLSJ_z'\rangle. \tag{L10}$$

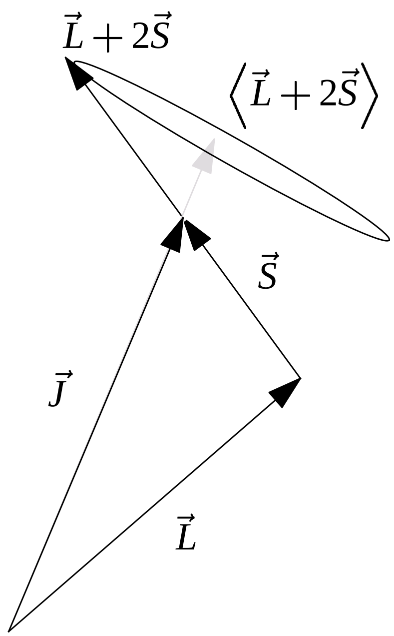


Figure 2: Expectation value of $\vec{L}+\vec{S}$ lies along $\vec{J}$.

$$\langle JLSJ_z|\hat{V}|JLSJ_z'\rangle = g(JLS)\langle JLSJ_z|\hat{J}|JLSJ_z'\rangle, \tag{L11}$$

Finding $g(JLS)$

$$\langle JLSJ_z|\hat{L}_z + 2\hat{S}_z|JLSJ_z'\rangle = g(JLS)\langle JLSJ_z|\hat{J}_z|JLSJ_z'\rangle \quad \text{(L12)}$$

$$= g(JLS)J_z\delta_{J_zJ_z'}. \quad \text{(L13)}$$

$$\langle JLSJ_z|\hat{L} + 2\hat{S}|JLSJ_z'\rangle = g(JLS)\langle JLSJ_z|\hat{J}|JLSJ_z'\rangle \quad \text{(L14)}$$

$$\Rightarrow \langle JLSJ_z|\hat{L} + 2\hat{S}|J'L'S'J_z'\rangle = g(JLS)\langle JLSJ_z|\hat{J}|J'L'S'J_z'\rangle \quad \text{(L15)}$$

$$\Rightarrow \sum_{L'J'S'J_z'} \langle JLSJ_z|\hat{L} + 2\hat{S}|J'L'S'J_z'\rangle \cdot \langle J'L'S'J_z'|\hat{J}|J''L''S''J_z''\rangle$$

$$= g(JLS) \sum_{L'J'S'J_z'} \langle JLSJ_z|\hat{J}|J'L'S'J_z'\rangle \cdot \langle J'L'S'J_z'|\hat{J}|J''L''S''J_z''\rangle. \quad \text{(L16)}$$

$$\langle JLSJ_z|(\hat{L} + 2\hat{S}) \cdot \hat{J}|JLSJ_z'\rangle = g(JLS)\langle JLSJ_z|\hat{J}^2|JLSJ_z'\rangle. \quad \text{(L17)}$$

$$\hat{S}^2 = (\hat{J} - \hat{L})^2 = \hat{J}^2 + \hat{L}^2 - 2\hat{L} \cdot \hat{J} \quad \text{(L18)}$$

$$\hat{L}^2 = (\hat{J} - \hat{S})^2 = \hat{J}^2 + \hat{S}^2 - 2\hat{S}\cdot\hat{J}. \tag{L19}$$

$$g(JLS) = \frac{1}{2}\frac{[3J(J+1) - L(L+1) + S(S+1)]}{J(J+1)}. \tag{L20}$$

Energy level splittings in magnetic field are

$$\frac{\mu_B B}{2}\frac{[3J(J+1) - L(L+1) + S(S+1)]}{J(J+1)}. \tag{L21}$$

$$Z_{\rm ion} = \sum_{J_z=-J}^{J} e^{-\beta g \mu_B B J_z} \quad \text{(L22)}$$

$$= \frac{e^{\beta g \mu_B B(J+1/2)} - e^{-\beta g \mu_B B(J+1/2)}}{e^{\beta g \mu_B B/2} - e^{-\beta g \mu_B B/2}}. \quad \text{(L23)}$$

$$\mathcal{F} = -k_B T \ln Z_{\rm ion} + \frac{1}{8\pi} \int d\vec{r}\, B^2. \quad \text{(L24)}$$

$$H = \frac{4\pi}{\mathcal{V}} \frac{\partial \mathcal{F}}{\partial B} \Rightarrow M = \frac{B}{4\pi} - \frac{1}{\mathcal{V}} \frac{\partial \mathcal{F}}{\partial B} \quad \text{(L25)}$$

$$\Rightarrow M = n k_B T \frac{\partial}{\partial B} \ln Z_{\rm ion} \quad \text{(L26)}$$

$$= n \mu_B g J \mathcal{B}_J(\beta \mu_B g J B), \quad \text{(L27)}$$

where

$$\mathcal{B}_J(x) = ? \qquad ? \quad \text{(L28)}$$

$$\coth x \approx \frac{1}{x} + \frac{x}{3} + \ldots \tag{L29}$$

$$\Rightarrow \mathcal{B}_J = \frac{1}{3}\frac{J+1}{J}\beta\mu_B gJB, \tag{L30}$$

so that

$$M \approx ng^2(\mu_B)^2 \frac{B}{k_BT}\frac{J(J+1)}{3}. \tag{L31}$$

$$\chi = n\frac{1}{3k_BT}\mu_{\rm eff}^2, \tag{L32}$$

$$\mu_{\rm eff} = g(JLS)\sqrt{J(J+1)}.\mu_B \tag{L33}$$

$$\mu_{\rm exp} = \sqrt{\frac{3k_BT\chi}{n}}. \tag{L34}$$

Element	Term	$\mu_{\rm eff}$, Eq. (L33) (μ_B)	$\mu_{\rm exp}$, Eq. (L34) (μ_B)
La^{3+}	$4f^0\ {}^1S$	0	Diamagnetic
Ce^{3+}	$4f^1\ {}^2F_{5/2}$	2.5	2.3
Pr^{3+}	$4f^2\ {}^3H_4$	3.6	3.4
Nd^{3+}	$4f3\ {}^4I_{9/2}$	3.6	3.5
Pm^{3+}	$4f^4\ {}^5I_4$	2.7	Radioactive
Sm^{3+}	$4f^5\ {}^6H_{5/2}$	0.9	1.6
Eu^{3+}	$4f^6\ {}^7F_0$	0	3.4
Gd^{3+}	$4f^7\ {}^8S_{7/2}$	7.9	7.9
Tb^{3+}	$4f^8\ {}^7F_6$	9.7	9.5
Dy^{3+}	$4f^9\ {}^6H_{15/2}$	10.6	10.4
Ho^{3+}	$4f^{10}\ {}^5I_8$	10.6	10.4
Er^{3+}	$4f^{11}\ {}^4I_{15/2}$	9.6	9.4
Tm^{3+}	$4f^{12}\ {}^3H_6$	7.6	7.1
Yb^{3+}	$4f^{13}\ {}^2F_{7/2}$	4.5	4.9
Lu^{3+}	$4f^{14}\ {}^1S$	0	0

Curie's Law

Element	Term	μ_{eff}, Eq. (L33) (μ_B)	μ_{eff}, $J = S$ (μ_B)	μ_{exp}, Eq. (L34) (μ_B)
Ti^{3+}	$3d^1\ {}^2D_{3/2}$	1.6	1.7	1.8
V^{3+}	$3d^2\ {}^3F_2$	1.6	2.8	2.7
Cr^{3+}	$3d^3\ {}^4F_{3/2}$	0.8	3.9	3.8
Mn^{3+}	$3d^4\ {}^5D_0$	0.0	4.9	4.9
Fe^{3+}	$3d^5\ {}^6S_{5/2}$	5.9	5.9	5.9
Fe^{2+}	$3d^6\ {}^5D_4$	6.7	4.9	5.3
Co^{2+}	$3d^7\ {}^4F_{9/2}$	6.5	3.9	4.0
Ni^{2+}	$3d^8\ {}^3F_4$	5.6	2.8	2.9–3.5
Cu^{2+}	$3d^9\ {}^2D_{5/2}$	3.6	1.7	1.7–1.9

$$\chi \approx -n\frac{e^2}{4mc^2}\,6\,\frac{2}{3}r^2. \tag{L35}$$

$$\Delta\mathcal{E} = \frac{e^2}{8mc^2}B^2\langle 0|\sum_j \left(\hat{X}_j^2+\hat{Y}_j^2\right)|0\rangle - \sum_{l'\neq 0}\frac{|\langle l'|\mu_B\vec{B}\cdot(\hat{L}+2\hat{S})|0\rangle|^2}{\mathcal{E}_{l'}-\mathcal{E}_0}. \tag{L36}$$

Element:	He	Ne	Ar	Kr	Xe
$-\chi$, experiment ($10^{-6}\,\mathrm{cm}^3\,\mathrm{mole}^{-1}$):	1.88	7.02	19.18	28.49	43.33
$-\chi$, Eq. (L35)$\times$0.35 ($10^{-6}\,\mathrm{cm}^3\,\mathrm{mole}^{-1}$):	0.99	14.82	20.54	23.74	27.95

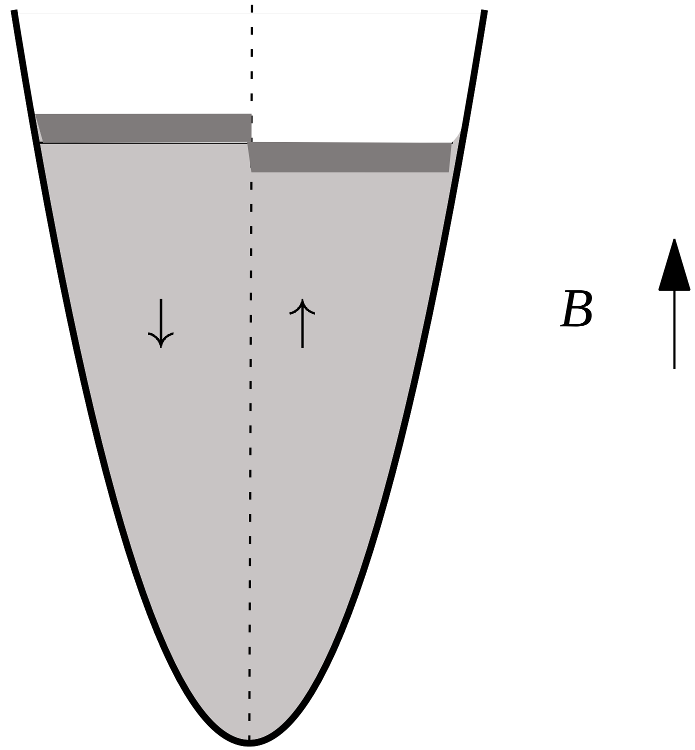


Figure 3: Pauli susceptibility

$$\mathcal{E}_{\vec{k}} = \mathcal{E}^0_{\vec{k}} + \mu_B B. \tag{L37}$$

$$N_{\rm up} = \mathcal{V} \int d\mathcal{E}^0 \, \frac{D\left(\mathcal{E}^0\right)}{2} f(\mathcal{E}^0 + \mu_B B), \tag{L38}$$

Pauli Paramagnetism

$$N_{\mathrm{down}} = \mathcal{V}\int d\mathcal{E}^0 \frac{D\left(\mathcal{E}^0\right)}{2} f(\mathcal{E}^0 - \mu_B B). \tag{L39}$$

$$N_{\mathrm{up}} \approx \frac{N}{2} - \frac{\mu_B B}{2}\frac{\partial N}{\partial \mu}, \tag{L40}$$

$$N_{\mathrm{down}} \approx \frac{N}{2} + \frac{\mu_B B}{2}\frac{\partial N}{\partial \mu}. \tag{L41}$$

$$M = \frac{\mu_B}{\mathcal{V}}(N_{\mathrm{down}} - N_{\mathrm{up}}) = ? \qquad ? \tag{L42}$$

$$\chi = \frac{\partial M}{\partial H} \approx \frac{\partial M}{\partial B} = (\mu_B)^2 \frac{1}{\mathcal{V}}\frac{\partial N}{\partial \mu}, \tag{L43}$$

$$\chi = \mu_B^2 D(\mathcal{E}_F). \tag{L44}$$

$$\chi = \frac{\mu_B^2 k_F m}{\pi^2\hbar^2} = 4.757\cdot 10^{-7}\,(n/[10^{22}\cdot \mathrm{cm}^{-3}])^{1/3}. \tag{L45}$$

$$\omega_c = \frac{eB}{mc}, \tag{L46}$$

$$x_0 = \frac{-\hbar k_y}{m\omega_c}; \tag{L47}$$

$$\mathcal{E}_{\nu,k_z,k_y} = \frac{\hbar^2 k_z^2}{2m} + (\nu + \tfrac{1}{2})\hbar\omega_c. \tag{L48}$$

$$0 < x_0 < L \Rightarrow 0 < ? \qquad ? < L \tag{L49}$$

$$\Rightarrow 0 > l_2 > ? \qquad ?. \tag{L50}$$

$$\Rightarrow N = \frac{BA}{\Phi_0} = \frac{\Phi}{\Phi_0} \tag{L51}$$

$$\Phi_0 \equiv \frac{hc}{e} = 4.14 \cdot 10^{-7}\,\mathrm{G\,cm}^2; \tag{L52}$$

$$D(k_z,\nu) = 2\frac{m\omega_c}{2\pi\hbar}\frac{1}{2\pi}. \tag{L53}$$

$$D(\mathcal{E},\nu) = \frac{2}{(2\pi)^2}\frac{\hbar\omega_c}{2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[\mathcal{E}-\left(\nu+\tfrac{1}{2}\right)\hbar\omega_c\right]^{-1/2} \tag{L54}$$

$$\equiv \hbar\omega_c G\left[\mathcal{E}-\left(\nu+\tfrac{1}{2}\right)\hbar\omega_c\right], \tag{L55}$$

with

$$G(x) = \frac{1}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}x^{-1/2}. \tag{L56}$$

$$\Pi = -k_BT\mathcal{V}\int d\mathcal{E}\sum_{\nu}D(\mathcal{E},\nu)\ln[1+e^{\beta(\mu-\mathcal{E})}] \tag{L57}$$

$$= -k_BT\hbar\omega_c\mathcal{V}\int d\mathcal{E}\sum_{\nu=0}^{\infty}G(\mathcal{E})\ln[1+e^{\beta[\mu-(\mathcal{E}+(\nu+1/2)\hbar\omega_c)]}]. \tag{L58}$$

$$\sum_{\nu=0}^{\infty} F\left(\nu + \frac{1}{2}\right) \approx \int_0^{\infty} F(x)dx + \frac{1}{24} F'(0). \tag{L59}$$

$$\begin{aligned}
\Pi = & -\mathcal{V} \int d\mathcal{E}\, k_B T\, \hbar\omega_c\, G(\mathcal{E}) \int d\nu \ln[1 + e^{\beta\mu - \beta(\mathcal{E} + \nu\hbar\omega_c)}] \\
& + \frac{\mathcal{V}}{24} \int d\mathcal{E}\, (\hbar\omega_c)^2 G(\mathcal{E}) \frac{1}{e^{\beta\mathcal{E} - \beta\mu} + 1} && \text{(L60)} \\
= & \quad \Pi_0 + \frac{\mathcal{V}}{24} (\hbar\omega_c)^2 \int d\mathcal{E}\, G(\mathcal{E}) f(\mathcal{E}), && \text{(L61)}
\end{aligned}$$

with

$$\Pi_0 = -\mathcal{V} \int d\mathcal{E} \int_0^{\infty} dx\, k_B T G(\mathcal{E}) \ln\left[1 + e^{\beta(\mu - \mathcal{E} - x)}\right]. \tag{L62}$$

$$\mathcal{V} \int d\mathcal{E}\, G(\mathcal{E}) f(\mathcal{E}) = -\frac{\partial^2 \Pi_0}{\partial \mu^2}. \tag{L63}$$

$$\Pi = \Pi_0 - \frac{1}{6}(B\mu_B)^2 \frac{\partial^2 \Pi_0}{\partial \mu^2} \tag{L64}$$

$$\Rightarrow M = -\frac{\partial \Pi}{\partial H}\Big|_\mu \approx -\frac{\partial \Pi}{\partial B}\Big|_\mu = -\frac{1}{3} B\mu_B^2 \frac{\partial N}{\partial \mu} \tag{L65}$$

$$\Rightarrow \chi = -\frac{1}{3}\mu_B^2 \frac{\partial N}{\partial \mu}. \tag{L66}$$

$$\chi = \frac{2}{3}\mu_B^2 \frac{\partial N}{\partial \mu} \tag{L67}$$

$$= \frac{2}{3}\frac{\mu_B^2 k_F m}{\pi^2 \hbar^2}. \tag{L68}$$

Landau Diamagnetism

Metal	Z	χ [Eq. (L68)] ($10^{-6}\,cm^3\,mole^{-1}$)		χ (Experimental) ($10^{-6}\,cm^3\,mole^{-1}$)
Li	1	6.90	p	25.00
Na	1	10.26	p	14.00
K	1	15.83	p	18.00
Au	1	5.84	d	−28.00
Be	2	4.50	d	−9.00
Mg	2	9.08	p	6.00
Ba	2	17.78	p	20.00
Zn	2	6.86	d	−9.15
Cd	2	8.66	d	−20.23
Hg	2	5.96	d	−17.10
Al	3	8.32	p	16.40
Ga	3	9.29	d	−21.68
Sn	4	12.65	d	−29.68
Bi	5	16.40	d	−271.67

$$\Phi = \int d^2r\, B_z = \int d\vec{l}\cdot\vec{A}, \tag{L69}$$

$$A_\phi = \frac{\Phi}{2\pi r}. \tag{L70}$$

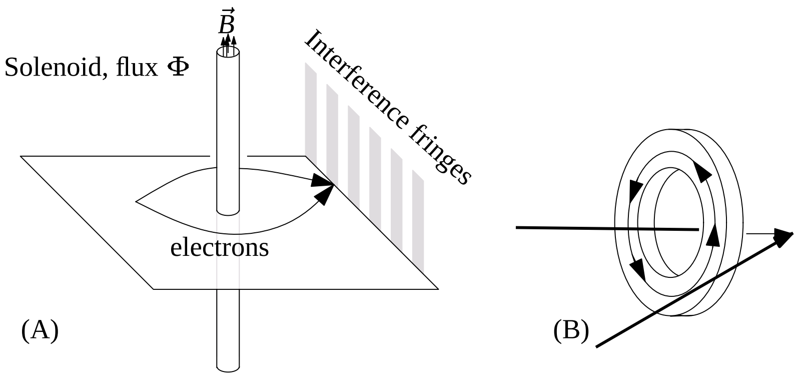
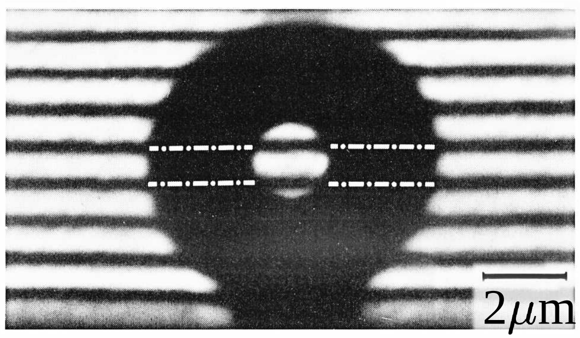


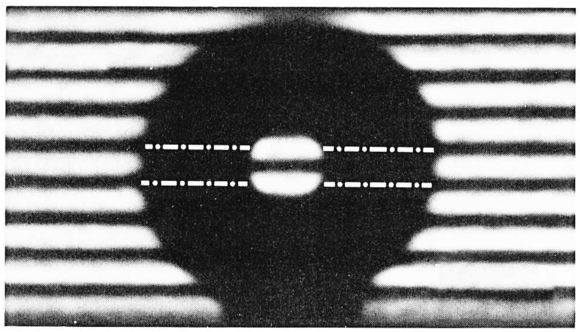
Figure 4: (A) Electrons traveling around a flux tube (B)Small toroidal magnet with no flux leakage

$$\frac{1}{2m}\left[\frac{\hbar}{i}\vec{\nabla}+\frac{e}{c}\vec{A}\right]^2\psi = \mathcal{E}\psi \tag{L71}$$

$$\Rightarrow \psi \quad \propto \quad \exp\left[i\vec{k}\cdot\vec{r} - i\frac{e}{\hbar c}\int^{\vec{r}} d\vec{r}\,' \cdot \vec{A}(\vec{r}\,') \right]. \qquad \text{(L72)}$$



(A)



(B)

Figure 5: Interference fringes of electrons passing through small toroidal magnet. In (A) the phase change is 0, while in (B) the phase change is π. [Source: Tonomura (1993), p. 67.]

$$\hat{P} - \frac{e}{c}\vec{A} = e^{ie\vec{A}\cdot\hat{R}/\hbar c}\hat{P}e^{-ie\vec{A}\cdot\hat{R}/\hbar c} \tag{L73}$$

$$\hat{\mathcal{H}} \rightarrow e^{ie\vec{A}\cdot\hat{R}/\hbar c}\hat{\mathcal{H}}e^{-ie\vec{A}\cdot\hat{R}/\hbar c}. \tag{L74}$$

$$\sum_{\vec{R}\vec{\delta}} e^{-ie\vec{A}\cdot\vec{\delta}/\hbar c}|\vec{R}\rangle \mathfrak{t}\langle\vec{R}+\vec{\delta}| + \sum_{\vec{R}} |\vec{R}\rangle U\langle\vec{R}|. \tag{L75}$$

$$2\psi_l \cos(2\pi lb - \kappa) + \psi_{l+1} + \psi_{l-1} = \mathcal{E}\psi_l, \tag{L76}$$

$$b = \frac{Ba^2}{\Phi_0} \tag{L77}$$

$$\kappa = ak_x. \tag{L78}$$

$$\psi_{l+q} = e^{ikq}\psi_l. \tag{L79}$$

$$\begin{pmatrix} \psi_{l+1} \\ \psi_l \end{pmatrix} = \begin{pmatrix} \mathcal{E} - 2\cos(2\pi lb - \kappa) & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \psi_l \\ \psi_{l-1} \end{pmatrix}. \tag{L80}$$

$$e^{iqk} \begin{pmatrix} \psi_1 \\ \psi_0 \end{pmatrix} = \begin{pmatrix} \psi_{q+1} \\ \psi_q \end{pmatrix} = \mathbf{Q}(\mathcal{E}, \kappa) \begin{pmatrix} \psi_1 \\ \psi_0 \end{pmatrix} \tag{L81}$$

$$\mathbf{Q} = \prod_{l=1}^{q} \begin{pmatrix} \mathcal{E} - 2\cos(2\pi lb - \kappa) & -1 \\ 1 & 0 \end{pmatrix} \tag{L82}$$

$$\Rightarrow \mathrm{Det} \left| \mathbf{Q}(\mathcal{E}, \kappa) - e^{iqk} \right| = 0. \tag{L83}$$

$$\mathrm{Det}\{\mathbf{Q}(\mathcal{E}, \kappa)\} + e^{2iqk} - \mathrm{Tr}\{\mathbf{Q}(\mathcal{E}, \kappa)\} e^{iqk} = 0. \tag{L84}$$

$$\mathrm{Tr}\{\mathbf{Q}(\mathcal{E}, \kappa)\} = 2\cos qk, \tag{L85}$$

$$\mathrm{Tr}\{\mathbf{Q}(\mathcal{E}, \kappa)\} = \mathrm{Tr}\{\mathbf{Q}(\mathcal{E}, \kappa')\} \tag{L86}$$

$$\mathrm{Tr}\left\{\mathbf{Q}(\mathcal{E},\kappa)\right\} = \sum_{l=-\infty}^{\infty} F_l e^{iq\kappa l}. \tag{L87}$$

$$\mathrm{Tr}\left\{\mathbf{Q}(\mathcal{E},\kappa)\right\} = F_0(\mathcal{E}) + F_1(\mathcal{E})e^{iq\kappa} + F_1^*(\mathcal{E})e^{-iq\kappa}. \tag{L88}$$

$$\prod_{l=1}^{q}(-)\left[e^{i(2\pi lb-\kappa)} + e^{-i(2\pi lb-\kappa)}\right] \tag{L89}$$

$$F_1(\mathcal{E}) = (-1)^q \prod_{l=1}^{q} e^{-2\pi ilb} \tag{L90}$$

$$= (-1)^q e^{-2\pi biq(q+1)/2}. \tag{L91}$$

$$F_0(\mathcal{E}) = \mathrm{Tr}\left\{\mathbf{Q}(\mathcal{E},\kappa_0)\right\}. \tag{L92}$$

$$(-1)^q 2\cos\left[2\pi b\left(q^2+q\right)/2 - q\kappa\right]. \tag{L93}$$

$$\pi p(q+1) - q\kappa, \tag{L94}$$

$$\kappa_0 = \frac{\pi}{2q}. \tag{L95}$$

$$\mathrm{Tr}\{\mathbf{Q}(\mathcal{E},\kappa)\} = 2\cos qk = \mathrm{Tr}\{\mathbf{Q}(\mathcal{E},\pi/2q)\} + 2\cos\left[\pi b(q^2+q) + \pi q - q\kappa\right]. \tag{L96}$$

$$\left|\mathrm{Tr}\{\mathbf{Q}(\mathcal{E},\pi/2q)\}\right| \leq 4. \tag{L97}$$

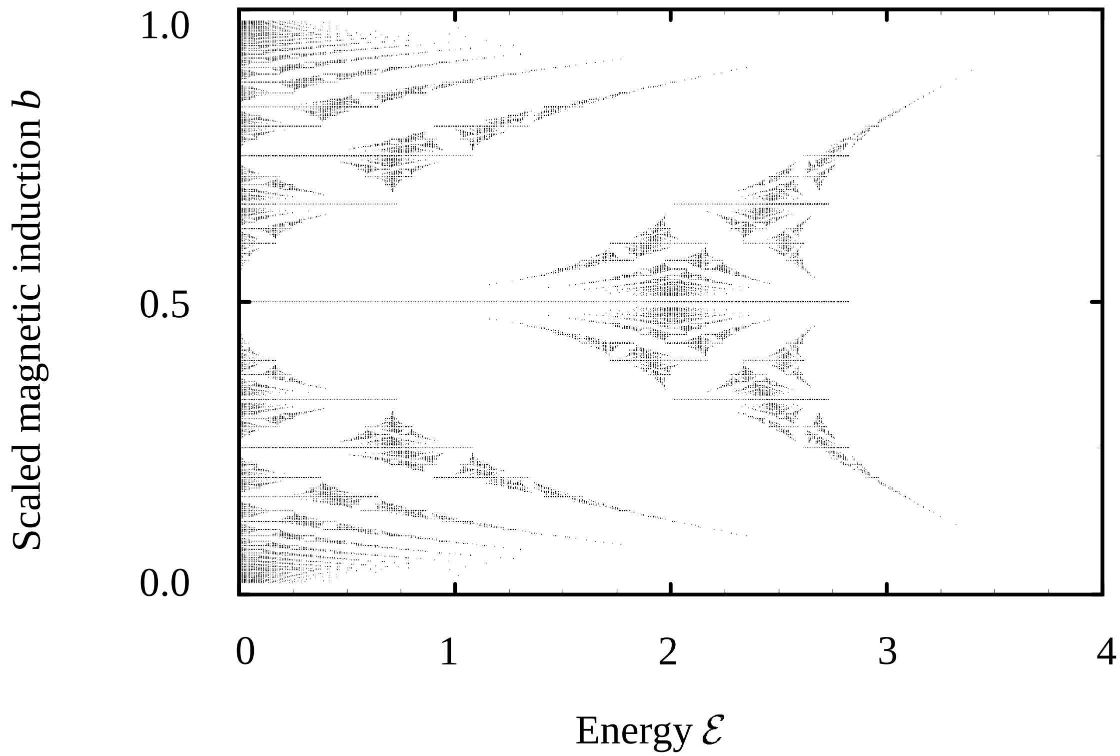


Figure 6: The Hofstadter Butterfly

$$\sigma_{xy} = \frac{\nu}{R_H}, \tag{L98}$$

$$R_H = \frac{h}{e^2} = 25\,813\,\Omega. \tag{L99}$$

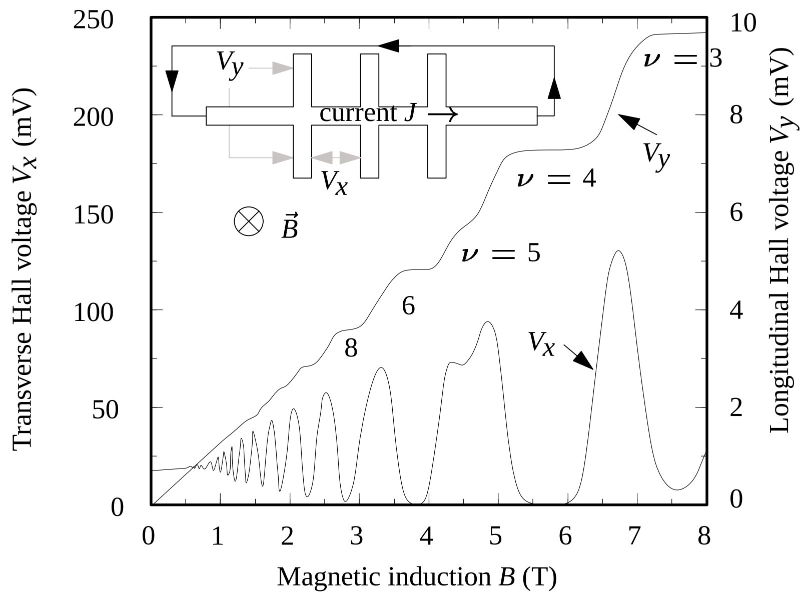


Figure 7: Integer quantum Hall effect. [Source: Cage (1987), p. 44.]

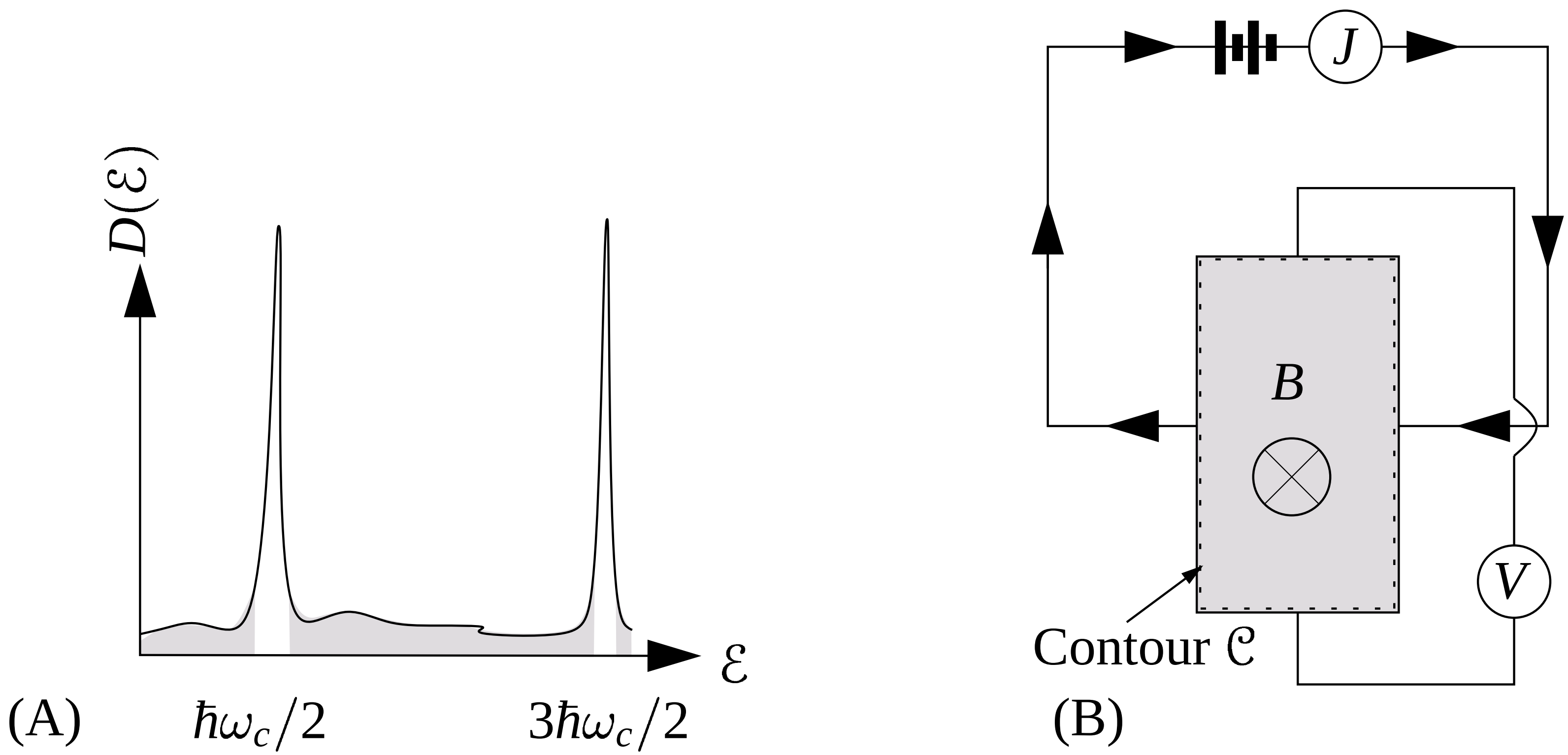


Figure 8: (A) States at energies $\hbar\omega_c(\nu+1/2)$,and localized states (shaded). (B) Schematic circuit for quantum Hall effect

Streda argument

$$\oint_{\mathcal{C}} d\vec{l}\cdot\vec{E} = \frac{-1}{c}\frac{\partial\Phi}{\partial t}. \qquad \text{(L100)}$$

$$j_\perp = \sigma_{xy}E_{||}, \qquad \text{(L101)}$$

$$\frac{1}{\sigma_{xy}}\oint_{\mathcal{C}} dl\, j_\perp = \frac{-1}{c}\frac{\partial\Phi}{\partial t} \qquad \text{(L102)}$$

$$\Rightarrow \frac{\partial Q}{\partial t} = -\frac{\sigma_{xy}}{c}\frac{\partial\Phi}{\partial t} \qquad \text{(L103)}$$

$$\Rightarrow \sigma_{xy} = -c\frac{\partial Q}{\partial\Phi}. \qquad \text{(L104)}$$

$$Q = -e\nu\frac{\Phi}{\Phi_0} \qquad \text{(L105)}$$

$$\Rightarrow \sigma_{xy} = \frac{ec\nu}{\Phi_0} = \frac{\nu e^2}{h} = \frac{\nu}{R_H}. \qquad \text{(L106)}$$

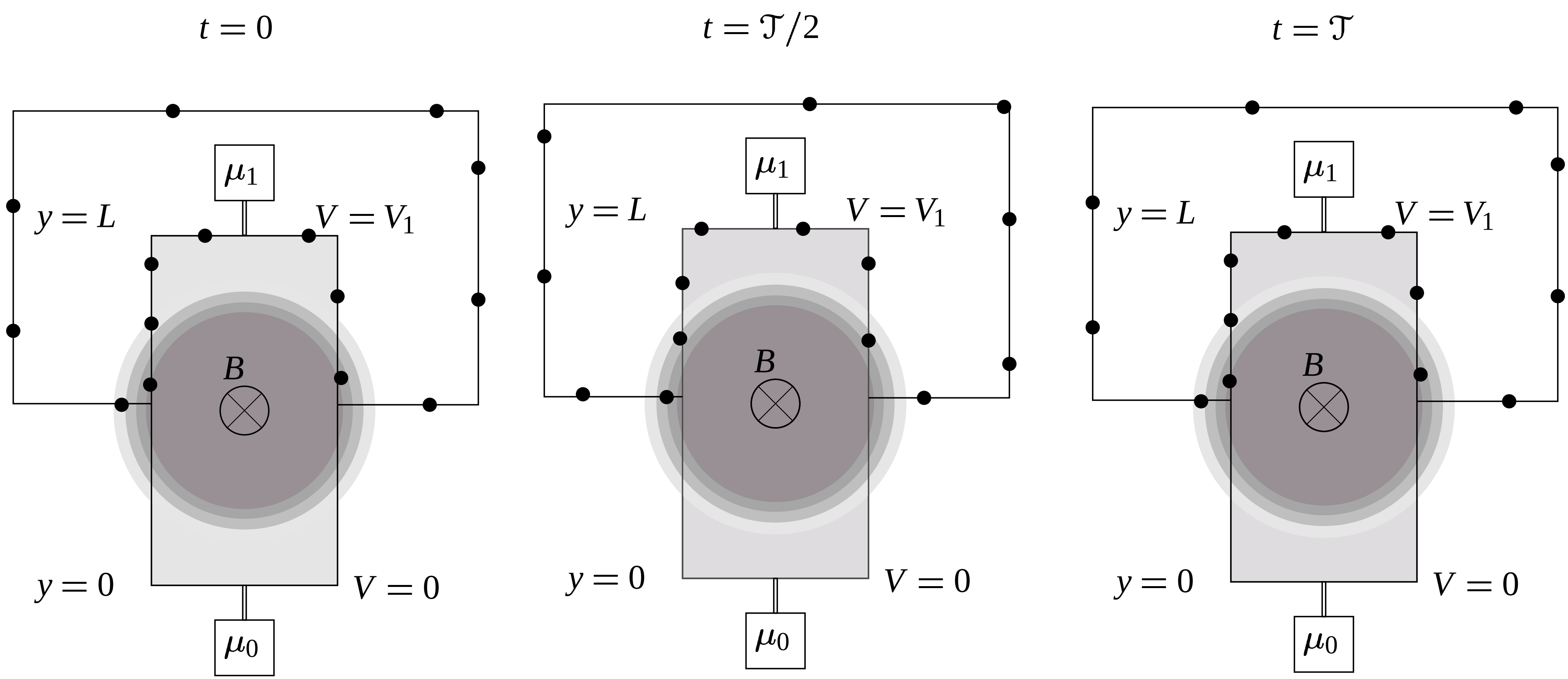


Figure 9: Gauge invariance for integer Hall effect

$$\vec{A} = \hat{y}xB, \tag{L107}$$

Laughlin's Argument

$$\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial y}+\frac{exB}{c}\right)^2+U(\vec{r})-\mathcal{E}\right]\psi(\vec{r})=0. \qquad \text{(L108)}$$

$$\mathcal{B}[\psi(x,L)]=0, \qquad \text{(L109)}$$

$$\mathcal{B}[\psi^{\gamma}(x,L)e^{i\gamma}]=0. \qquad \text{(L110)}$$

$$\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial y}+\frac{exB}{c}+eE_y(\vec{r})t\right)^2+U(\vec{r})-\mathcal{E}\right]\psi(\vec{r})=0. \qquad \text{(L111)}$$

$$\psi=e^{ieVt/\hbar}\tilde{\psi}, \qquad \text{(L112)}$$

$$\vec{E}=-\vec{\nabla}V. \qquad \text{(L113)}$$

Laughlin's Argument

$$\mathcal{B}[e^{-ietV_1/\hbar}\tilde{\psi}(x,L)] = 0. \tag{L114}$$

$$\gamma = -\frac{eV_1 t}{\hbar}. \tag{L115}$$

$$\frac{eV_1 t}{\hbar} = 2\pi. \tag{L116}$$

$$\mathcal{T} = \frac{h}{eV_1}. \tag{L117}$$

$$J_x = \frac{\nu e}{\mathcal{T}} = \frac{\nu e^2 V_1}{h}, \tag{L118}$$

$$\sigma_{xy} = \nu \frac{e^2}{h} = \frac{\nu}{R_H}. \tag{L119}$$

Fractional Quantum Hall Effect

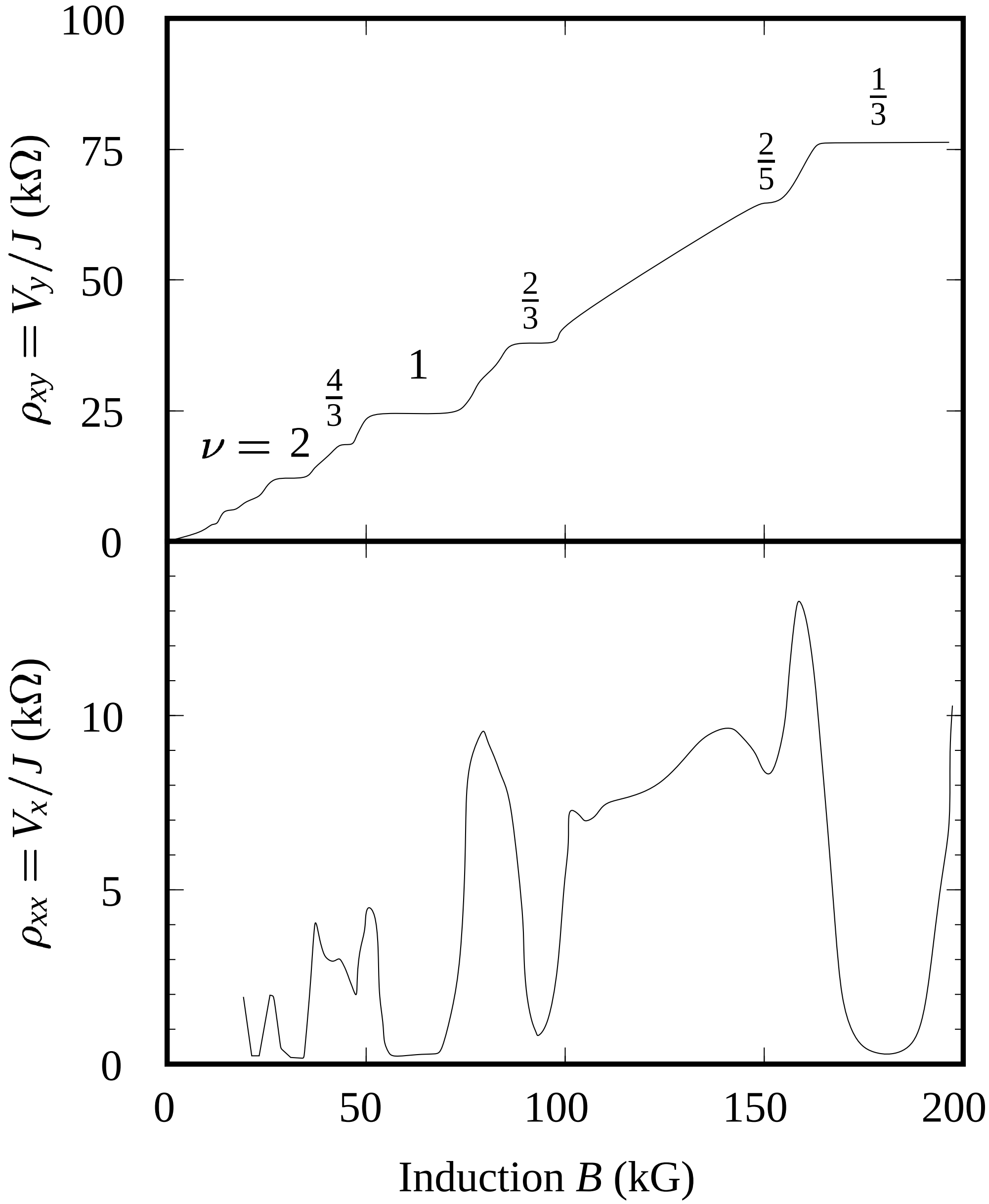


Figure 10: Fractional quantum Hall effect. Data of Boebinger, Chang, Störmer, and Tsui.

Laughlin's Wave Function

$$\frac{p}{q}\frac{e^2}{h}, \tag{L120}$$

$$\frac{e^2\sqrt{n}}{\epsilon^0\hbar\omega_c} = \frac{m^\star c e^2}{\epsilon^0\hbar\sqrt{eBhc}} = \frac{m^\star}{\epsilon^0 m}1.93\cdot 10^2/\sqrt{B/\mathrm{T}}. \tag{L121}$$

$$\left[\frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial y} - \frac{exB}{2c}\right)^2 + \frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x} + \frac{eyB}{2c}\right)^2 - \mathcal{E}\right]\psi(\vec{r}) = 0. \tag{L122}$$

$$l_B = \sqrt{\frac{2\hbar c}{eB}}, \text{ and define variables } \tilde{y} = \frac{y}{l_B} \text{ and } \tilde{x} = \frac{x}{l_B}. \tag{L123}$$

$$\frac{\hbar\omega_c}{4}\left[\left(\frac{1}{i}\frac{\partial}{\partial\tilde{y}} - \tilde{x}\right)^2 + \left(\frac{1}{i}\frac{\partial}{\partial\tilde{x}} + \tilde{y}\right)^2\right]\psi = \psi\mathcal{E}. \tag{L124}$$

$$z = \tilde{x} + i\tilde{y}, \text{ and define } \psi = e^{-|z|^2/2}\phi(z,\bar{z}). \tag{L125}$$

$$\hbar\omega_c\left\{\frac{\partial\phi}{\partial\bar z}\bar z - \frac{\partial^2\phi}{\partial z\partial\bar z} + \tfrac{1}{2}\phi\right\} = \mathcal{E}\phi. \tag{L126}$$

$$\phi(z,\bar z) = f(z) \Rightarrow \psi(z,\bar z) = f(z)e^{-|z|^2/2}, \tag{L127}$$

$$\Psi = f(z_0\ldots z_{N-1})e^{-\sum_{l=0}^{N-1}|z_l|^2/2}, \tag{L128}$$

$$\Psi = \prod_{l<l'} f_2(z_l - z_{l'})e^{-\sum_{l=0}^{N-1}|z_l|^2/2}. \tag{L129}$$

$$\hat L_l = -i\frac{\partial}{\partial\theta_l} = \left[z_l\frac{\partial}{\partial z_l} - \bar z_l\frac{\partial}{\partial\bar z_l}\right], \tag{L130}$$

$$z\frac{\partial f_2(z)}{\partial z} = q f_2(z) \Rightarrow f_2(z) = z^q. \tag{L131}$$

$$\Psi = \prod_{l<l'}(z_l - z_{l'})^q e^{-\sum_{l=0}^{N-1}|z_l|^2/2}. \tag{L132}$$

Laughlin's Wave Function

$$\Psi = \begin{vmatrix} 1 & 1 & \dots & 1 \\ z_0 & z_1 & \dots & z_{N-1} \\ . & . & \dots & . \\ . & . & \dots & . \\ . & . & \dots & . \\ z_0^{N-1} & z_1^{N-1} & \dots & z_{N-1}^{N-1} \end{vmatrix} e^{-\sum_{l=0}^{N-1} |z_l|^2/2}. \tag{L133}$$

$$z_2^m - z_1^m = (z_2 - z_1) \sum_{l=0}^{m-1} z_2^l z_1^{m-l-1}. \tag{L134}$$

$$e^{-|z|^2/2}, ze^{-|z|^2/2}, z^2 e^{-|z|^2/2} \dots z^{N-1} e^{-|z|^2/2} \tag{L135}$$

$$A = \pi N l_B^2 = \frac{2\pi N\hbar c}{eB} \Rightarrow N = \frac{BA}{\Phi_0}. \tag{L136}$$

$$|z_0|^2 = q(N-1) \Rightarrow N = \frac{BA}{q\Phi_0}. \tag{L137}$$

Fractional Charge

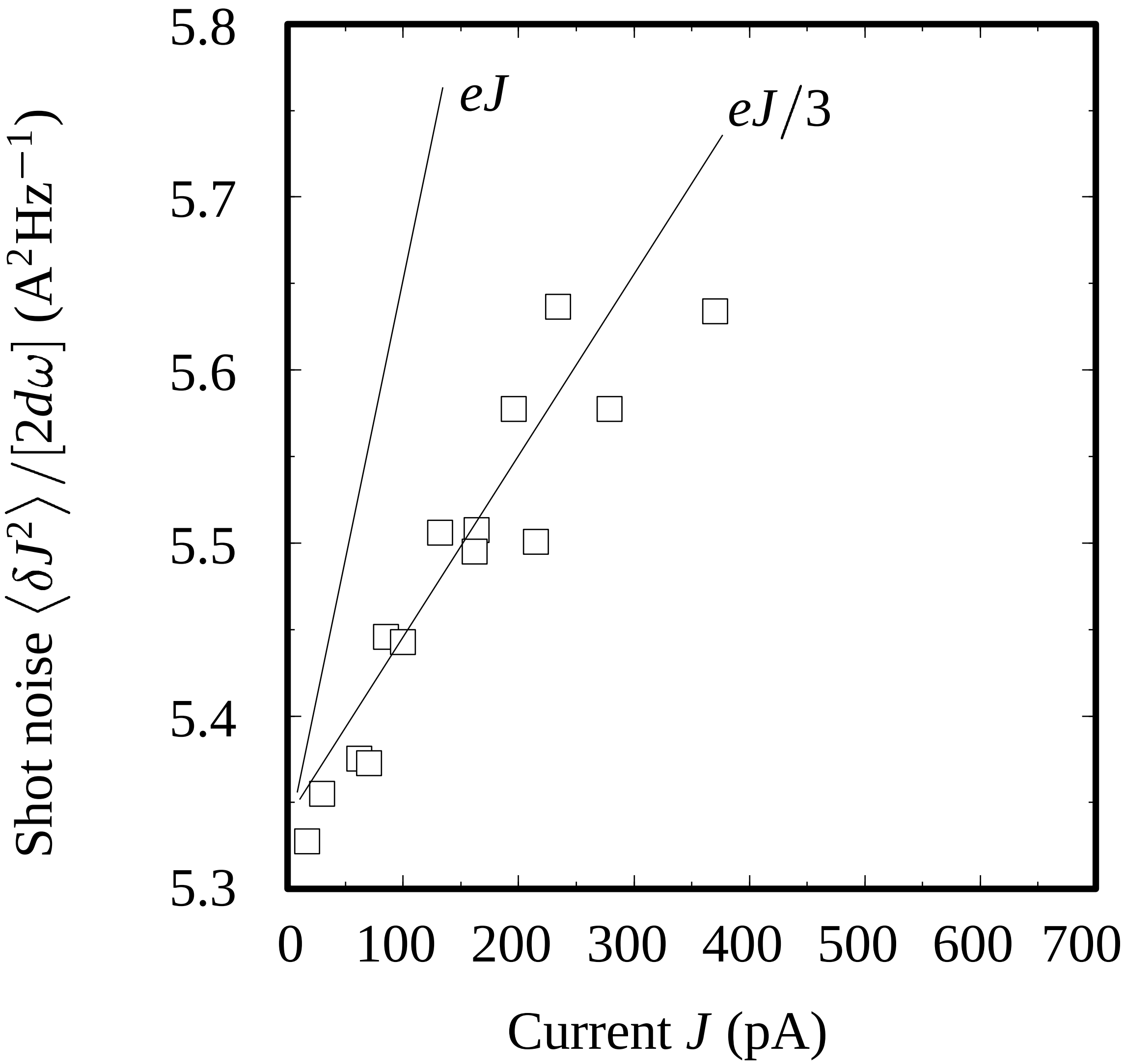
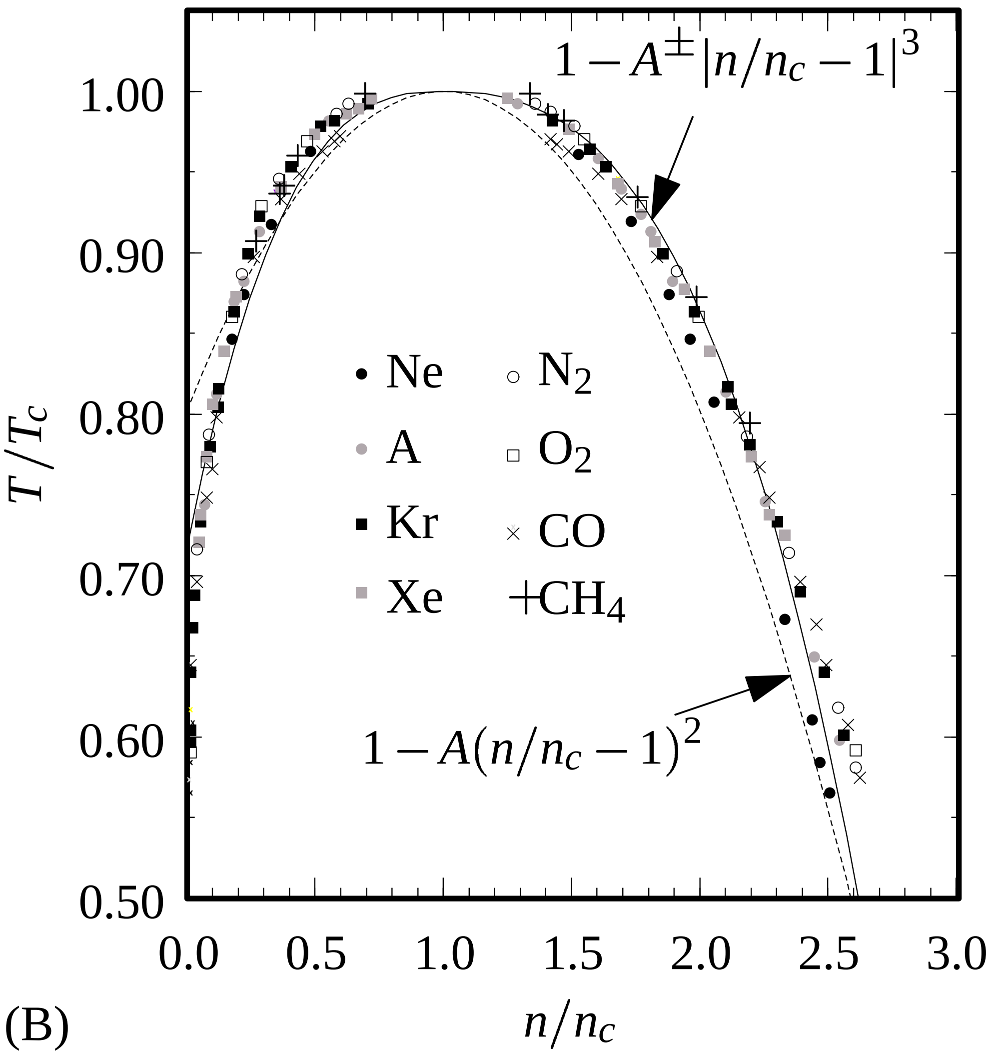


Figure 11: Shot noise for fractional quantum Hall effect [Source: Saminadayar et al. (1997), p. 2528.]



$1 - A^{\pm}|n/n_c - 1|^3$
1.00
0.90
0.80
0.70
0.60
0.50
T/T_c
Ne
A
Kr
Xe
N_2
O_2
CO
CH_4
$1 - A(n/n_c - 1)^2$
0.0
0.5
1.0
1.5
2.0
2.5
3.0
n/n_c
(B)

Definitions

☞ Phenomenology of Magnets

☞ Dipole Moments

☞ Ferromagnets, Ferrimagnets,and Antiferromagnets

☞ Mean Field Theory

☞ The Lenz–Ising Model

☞ Domains

☞ Hysteresis

☞ Order–Disorder Transitions

☞ Critical Phenomena

☞ Landau Free Energy

☞ Scaling and Universality

Magnetic Moments

$$\vec{j}_{\text{mag}} = c\vec{\nabla} \times \vec{M}. \tag{L1}$$

$$\vec{H} \equiv \vec{B} - 4\pi\vec{M} \tag{L2}$$

$$\begin{aligned}
\nabla \times \vec{B} &= \frac{4\pi\vec{j}_{\text{mag}}}{c} + \frac{4\pi\vec{j}_{\text{ext}}}{c} + \frac{1}{c}\frac{\partial\vec{D}}{\partial t} && \text{(L3)} \\
&= 4\pi\vec{\nabla} \times \vec{M} + \frac{4\pi\vec{j}_{\text{ext}}}{c} + \frac{1}{c}\frac{\partial\vec{D}}{\partial t} && \text{(L4)} \\
\Rightarrow \nabla \times \vec{H} &= \frac{4\pi\vec{j}_{\text{ext}}}{c} + \frac{1}{c}\frac{\partial\vec{D}}{\partial t}. && \text{(L5)}
\end{aligned}$$

$$\vec{B} = \mu\vec{H}, \tag{L6}$$

$$\chi = \frac{\partial M}{\partial H}. \tag{L7}$$

$$\vec{E}_{\mathrm{L}} = \frac{\vec{q}(\vec{E}\cdot\vec{q})}{q^2}, \quad \vec{E}_{\mathrm{T}} = \vec{E} - \vec{E}_{\mathrm{L}}. \tag{L8}$$

$$\vec{j} = \frac{c^2 q^2}{4\pi i\omega}\left(1-\frac{1}{\mu}\right)\vec{E}_{\mathrm{T}} \tag{L9}$$

$$\Rightarrow \frac{\partial\vec{j}}{\partial t} = -\frac{c^2}{4\pi}\left(1-\frac{1}{\mu}\right)\vec{\nabla}\times\vec{\nabla}\times\vec{E} \tag{L10}$$

$$= \frac{c}{4\pi}? \qquad ? \tag{L11}$$

$$\Rightarrow \vec{j} = \frac{c}{4\pi}? \qquad ? \tag{L12}$$

$$\Rightarrow \vec{\nabla}\times\vec{B} = ? \qquad ? \tag{L13}$$

$$\Rightarrow \vec{\nabla}\times\frac{\vec{B}}{\mu} = \vec{\nabla}\times\vec{H} = \frac{1}{c}\frac{\partial\vec{D}}{\partial t}. \tag{L14}$$

$$\mathcal{E}\{\vec{B}(\vec{r})\} \tag{L15}$$

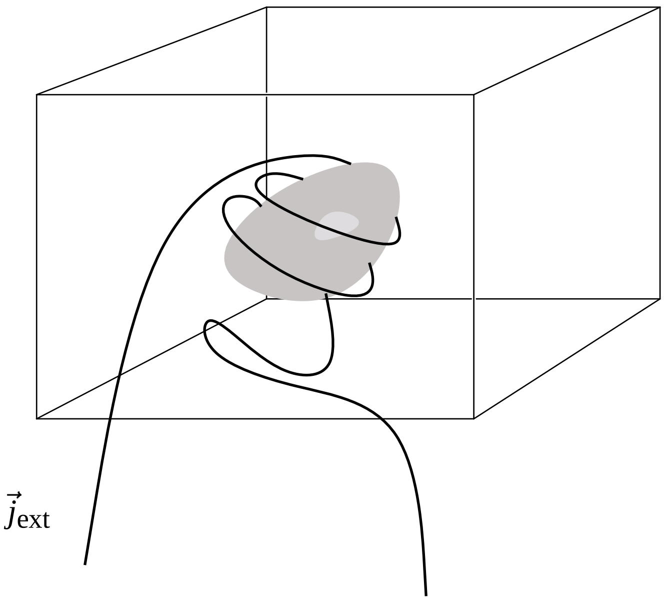


Figure 1: Sample influenced only by currents $\vec{j}_{\rm ext}$.

$$\frac{d\mathcal{E}}{dt} = -\int d\vec{r}\,\vec{E}(\vec{r})\cdot\vec{j}_{\rm ext}(\vec{r}). \tag{L16}$$

$$\vec{H}(\vec{r}) = 4\pi\frac{\delta\mathcal{E}\{\vec{B}\}}{\delta\vec{B}(\vec{r})}. \tag{L17}$$

$$\delta\mathcal{E} = \frac{1}{4\pi}\int d\vec{r}\,\vec{H}(\vec{r})\cdot\delta\vec{B}(\vec{r}). \tag{L18}$$

$$\frac{\partial\mathcal{E}}{\partial t} = \frac{1}{4\pi}\int d\vec{r}\,\vec{H}(\vec{r})\cdot\frac{\partial\vec{B}(\vec{r})}{\partial t} \tag{L19}$$

$$= -\frac{c}{4\pi}\int d\vec{r}\,\vec{H}\cdot\vec{\nabla}\times\vec{E} \tag{L20}$$

$$= -\frac{c}{4\pi}\int d\vec{r}\,\left[\vec{E}\cdot\vec{\nabla}\times\vec{H}-\vec{\nabla}\cdot(\vec{H}\times\vec{E})\right] \tag{L21}$$

$$= -\frac{c}{4\pi}\int d\vec{r}\,\vec{E}\cdot\vec{\nabla}\times\vec{H}. \tag{L22}$$

$$\vec{\nabla}\times\vec{H}(\vec{r}) = \frac{4\pi}{c}\vec{j}_{\text{ext}}. \tag{L23}$$

$$\vec{M}(\vec{r}) \equiv \frac{1}{4\pi}\left(\vec{B}(\vec{r})-\vec{H}(\vec{r})\right); \tag{L24}$$

Free Energy

$$\mathcal{F}(T,\vec{B}) = \mathcal{E}(\vec{B}) - TS. \tag{L25}$$

$$\delta\mathcal{F} = -S\delta T + \int d\vec{r}\,\vec{H}(\vec{r})\cdot\delta\vec{M}(\vec{r}) + \frac{1}{8\pi}\int d\vec{r}\,\delta H^2(\vec{r}). \tag{L26}$$

$$\tilde{\mathcal{G}} = \mathcal{F} - \frac{1}{4\pi}\int d\vec{r}\,\vec{B}(\vec{r})\cdot\vec{H}(\vec{r}). \tag{L27}$$

$$\delta\tilde{\mathcal{G}} = -\frac{1}{4\pi}\int d\vec{r}\,\vec{B}(\vec{r})\cdot\delta\vec{H}(\vec{r}) \tag{L28}$$

$$= -\int d\vec{r}\,\vec{M}(\vec{r})\cdot\delta\vec{H}(\vec{r}) - \frac{1}{4\pi}\int d\vec{r}\,\vec{H}(\vec{r})\cdot\delta\vec{H}(\vec{r}). \tag{L29}$$

$$\mathcal{G} = \tilde{\mathcal{G}} + \frac{1}{8\pi}\int d\vec{r}\,H^2(\vec{r}) \tag{L30}$$

$$\delta\mathcal{G} = -S\delta T - \int d\vec{r}\,\vec{M}\cdot\delta\vec{H}. \tag{L31}$$

Magnetic Dipole Moments

Element	χ $(10^{-6}\,\mathrm{cm}^3\,\mathrm{mole}^{-1})$	Element	χ $(10^{-6}\,\mathrm{cm}^3\,\mathrm{mole}^{-1})$
Ar	-19.18	N2	-12.04
As	-5.24	Ne	-7.02
B	-6.70	P	-26.63
C	-5.88	S	-15.39
Cl	-20.18	Se	-23.69
Ge	-7.99	Si	-3.09
H2	-4.00	Te	-37.00
He	-1.88	Tl	-43.42
I	-45.68	Xe	-43.33
Kr	-28.49		

$$\vec{m} = \int d\vec{r} \frac{1}{2c} \vec{r} \times \vec{j}(\vec{r}). \quad \text{(L32)}$$

$$\vec{F} = \frac{1}{c} \int d\vec{r}\, \vec{j}(\vec{r}) \times \vec{B}(\vec{r}). \quad \text{(L33)}$$

$$\vec{F} = \frac{1}{c} \int d\vec{r}\, \vec{j}(\vec{r}) \times [\vec{B}(0) + (\vec{r} \cdot \vec{\nabla})\vec{B}(0) + \ldots] \quad \text{(L34)}$$

$$= 0 + (\vec{m} \times \vec{\nabla}) \times \vec{B} \quad \text{(L35)}$$

$$= \vec{\nabla}(\vec{m} \cdot \vec{B}) \quad \text{(L36)}$$

$$\Rightarrow U = -\vec{m} \cdot \vec{B}. \quad \text{(L37)}$$

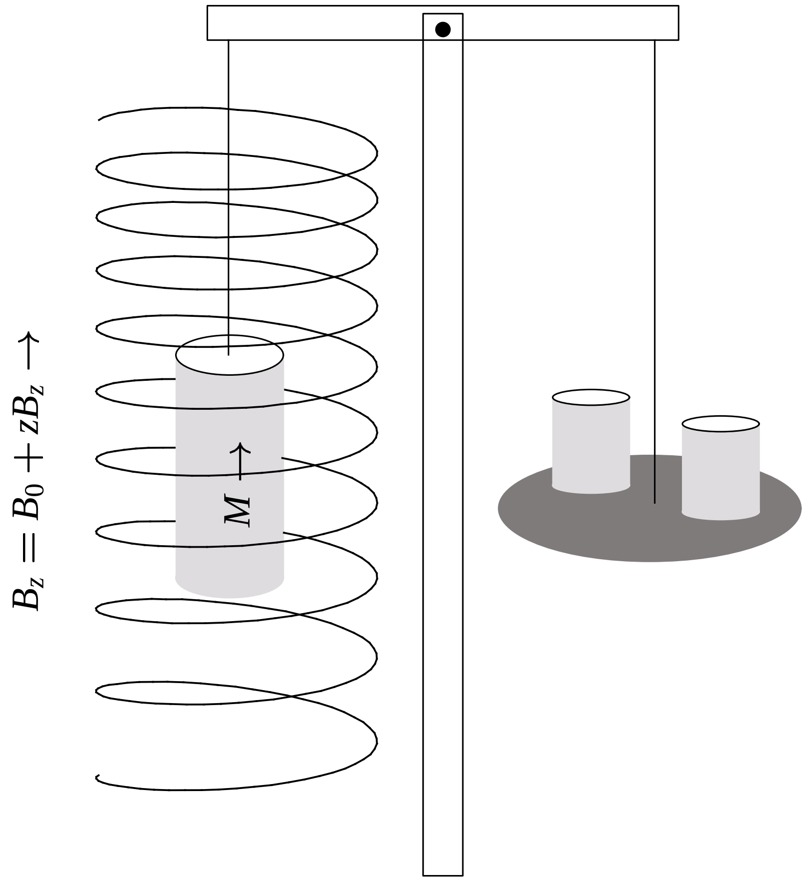


Figure 2: Schematic view of Faraday balance.

$$B_z(z) = B_0 + zB_1. \tag{L38}$$

Spontaneous Magnetization of Ferromagnets

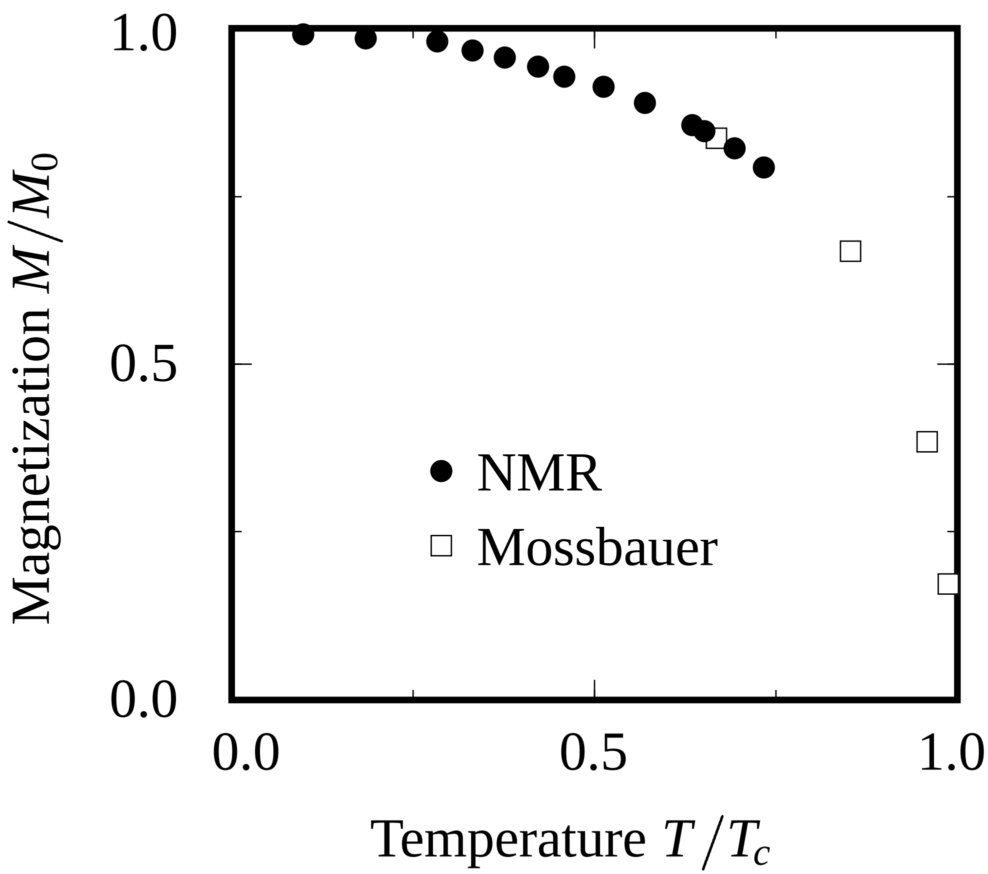


Figure 3: Internal magnetic fields in iron [Source:Preston et al. (1962).]

$$\mu_B = e\hbar/2mc, \tag{L39}$$

$$\mu_B = 9.27 \cdot 10^{-21}\text{cm esu} \; = \; 9.27 \cdot 10^{-21}\text{erg G}^{-1}. \tag{L40}$$

$$\chi \propto \frac{1}{T - \Theta}; \tag{L41}$$

Spontaneous Magnetization of Ferromagnets

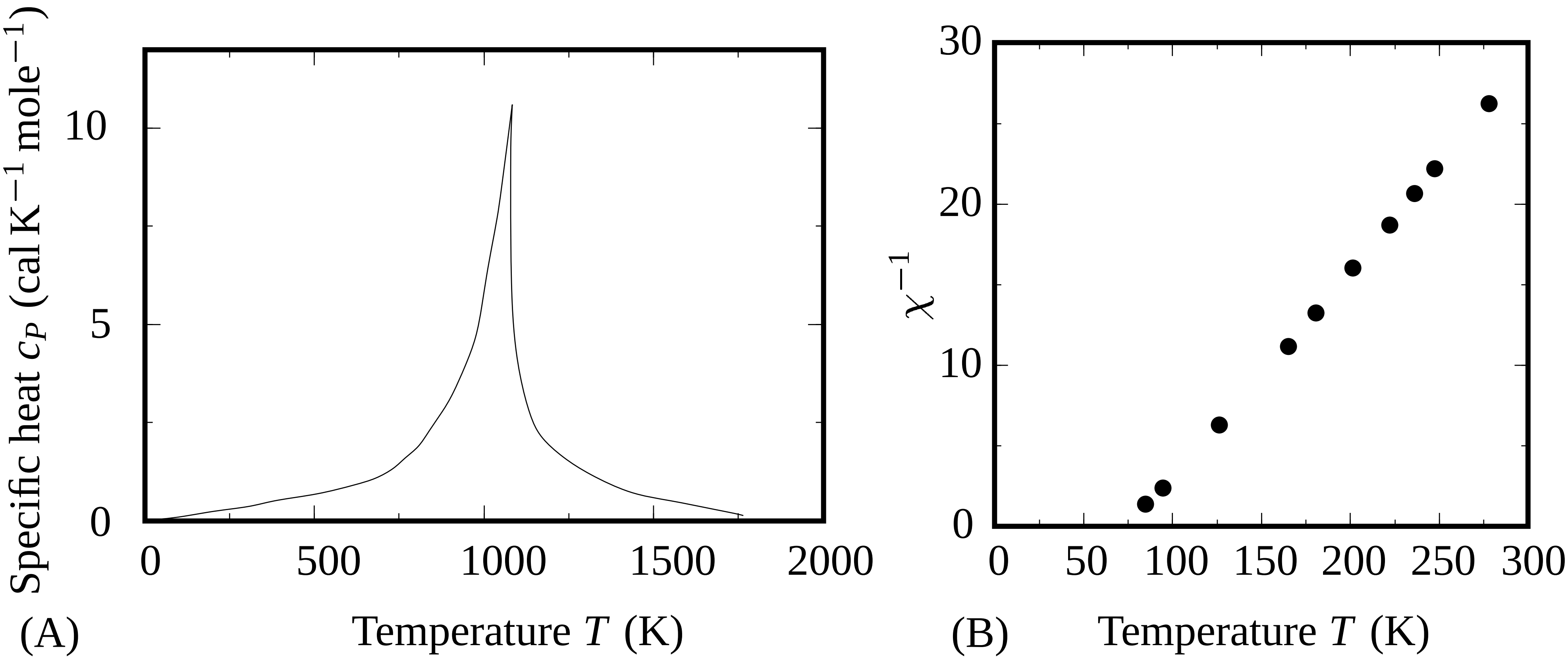


Figure 4: (A) Specific heat of iron. [Source: Hofmann et al. (1956) p. 53.] (B) Magnetic susceptibility χ of EuO. Source: Matthias et al. (1961), p. 160.]

Spontaneous Magnetization of Ferromagnets

Compound		T_c (K)	Θ (K)	m_I (μ_B)
Cr	a	312		0.59
CoO	a	291	−330	3.8
CuO	a	230	−745	0.5
Mn	a	100		0.5
MnO	a	122	−610	5
NiO	a	523	−2470	2
O_2	a	23.9		2
Co	f	1394	1415	1.72
Dy	f	85	157	10.65
Eu	f	289	108	7.12
Fe	f	1043	1100	2.2
Gd	f	302	289	7.97
Ho	f	20	87	10.9
Ni	f	628	650	0.6
Tb	f	20	87	10.9

Compound		T_c (K)	m_I (μ_B)
$FeFe_2O_4$ (magnetite)	fi	858	4.1
$FeNiFeO_4$	fi	858	2.3
$FeLiFeO_4$	fi	943	2.6
$FeCuFeO_4$	fi	728	1.3
$FeCoFeO_4$	fi	793	3.7

Ferrimagnets

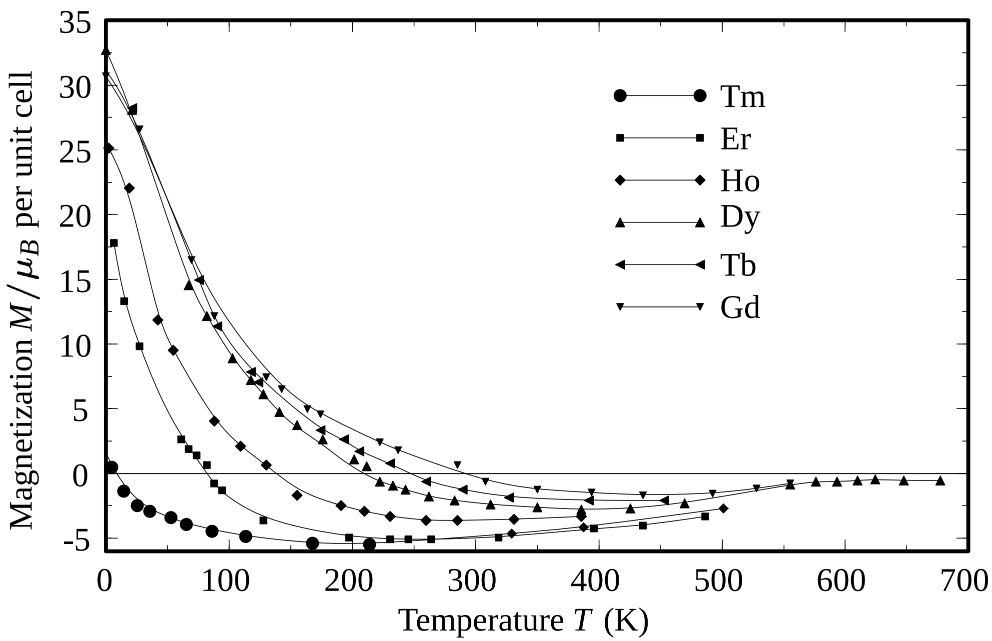


Figure 5: Spontaneous magnetization of rare earth iron garnets $5Fe_2O_3 \cdot R_2O_2$ [Source: Bertaut and Pauthenet (1957).]

$$\chi = \frac{1}{T + |\Theta|}. \tag{L42}$$

Antiferromagnets

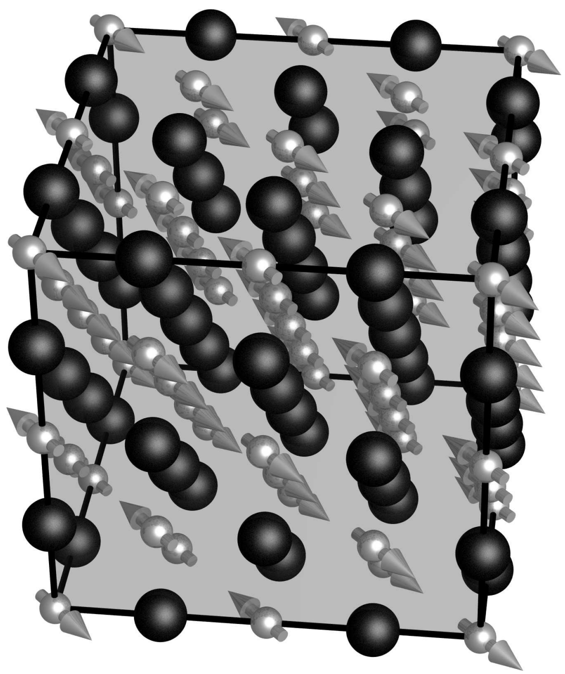


Figure 6: Spin structure of transition metal oxides such as CoO or NiO.

$$\mathcal{E} = -\sum_{\langle\vec{R}\vec{R}'\rangle} J\sigma_{\vec{R}}\sigma_{\vec{R}'} - \sum_{\vec{R}} H\mu_B\sigma_{\vec{R}}, \tag{L43}$$

$$\mathcal{P}(\sigma_{\vec{R}}) \propto \exp\left\{\beta\sum_{\langle\vec{R}\vec{R}'\rangle} J\sigma_{\vec{R}}\sigma_{\vec{R}'} + \beta\sum_{\vec{R}} H\mu_B\sigma_{\vec{R}}\right\}. \tag{L44}$$

$$\sigma_{\vec{R}} = \bar{\sigma} + (\sigma_{\vec{R}} - \bar{\sigma}), \tag{L45}$$

$$\sigma_{\vec{R}}\sigma_{\vec{R}'} = [\bar{\sigma} + (\sigma_{\vec{R}} - \bar{\sigma})][\bar{\sigma} + (\sigma_{\vec{R}'} - \bar{\sigma})] \approx \bar{\sigma}(\sigma_{\vec{R}} + \sigma_{\vec{R}'}) - \bar{\sigma}^2. \tag{L46}$$

$$-\sum_{\langle\vec{R}\vec{R}'\rangle} J\sigma_{\vec{R}}\sigma_{\vec{R}'} - \sum_{\vec{R}} H\mu_B\sigma_{\vec{R}} \approx NzJ\bar{\sigma}^2/2 - \sum_{\vec{R}} (H + \bar{H})\mu_B\sigma_{\vec{R}} \tag{L47}$$

$$\bar{H} = \frac{zJ\bar{\sigma}}{\mu_B}. \tag{L48}$$

$$Z \approx \sum_{\sigma_1\ldots\sigma_N} \exp\left[-\beta(NzJ\bar{\sigma}^2/2 - \sum_{\vec{R}}(H+\bar{H})\mu_B\sigma_{\vec{R}})\right] \tag{L49}$$

$$= e^{-\beta NzJ\bar{\sigma}^2/2}\left[\exp[\beta(H+\bar{H})\mu_B] + \exp[-\beta(H+\bar{H})\mu_B]\right]^N \tag{L50}$$

$$\Rightarrow \mathcal{F} = -k_BT\ln Z = NzJ\bar{\sigma}^2/2 - Nk_BT\ln[2\cosh\beta\mu_B(H+\bar{H})]. \tag{L51}$$

$$\bar{\sigma} = \frac{1}{Z}\sum_{\sigma_1\ldots\sigma_N}\frac{1}{N}\sum_{\vec{R}'}\sigma_{\vec{R}'}\exp[-\beta\mathcal{E}\{\sigma_{\vec{R}}\}] \tag{L52}$$

$$= \frac{1}{Z}\sum_{\sigma_1\ldots\sigma_N}\frac{1}{\beta N\mu_B}\frac{\partial}{\partial H}\exp[-\beta\mathcal{E}\{\sigma_{\vec{R}}\}] \tag{L53}$$

$$= -\frac{1}{N}\frac{1}{\mu_B}\frac{\partial\mathcal{F}}{\partial H} \tag{L54}$$

$$= ? \qquad\qquad ? \tag{L55}$$

$$\Rightarrow \bar{\sigma} = \tanh \beta[zJ\bar{\sigma} + \mu_B H]. \quad \text{(L56)}$$

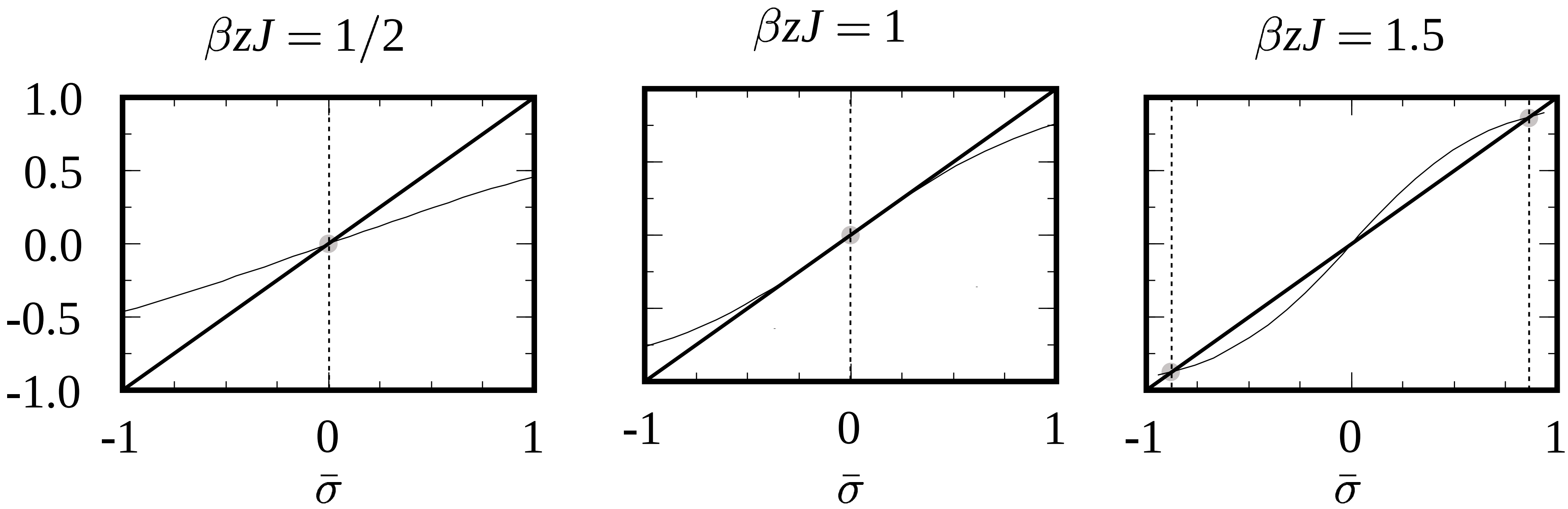


Figure 7: Graphical solution of Eq. (L56).

$$\mathcal{E} = -\sum_{\langle\vec{R}\vec{R}'\rangle} J\vec{\sigma}_{\vec{R}}\cdot\vec{\sigma}_{\vec{R}'} + \sum_{\vec{R}}\left[\alpha(\vec{\sigma}_{\vec{R}}\cdot\hat{x})^2 - \mu_B\vec{B}\cdot\vec{\sigma}_{\vec{R}}\right] + \frac{1}{8\pi}\int d\vec{r}\;\vec{B}\cdot\vec{B}. \tag{L57}$$

$$\mathcal{E} = \frac{JL}{la} + \frac{\alpha l}{a^2} \tag{L58}$$

$$\Rightarrow \frac{\partial\mathcal{E}}{\partial l} = \frac{\alpha}{a^2} - \frac{JL}{l^2 a} \tag{L59}$$

$$\Rightarrow l = a\sqrt{\frac{JL}{\alpha a}} \tag{L60}$$

$$\Rightarrow \frac{\mathcal{E}_{\rm min}}{L} = 2\frac{\sqrt{\alpha J}}{a^2}\sqrt{\frac{a}{L}}. \tag{L61}$$

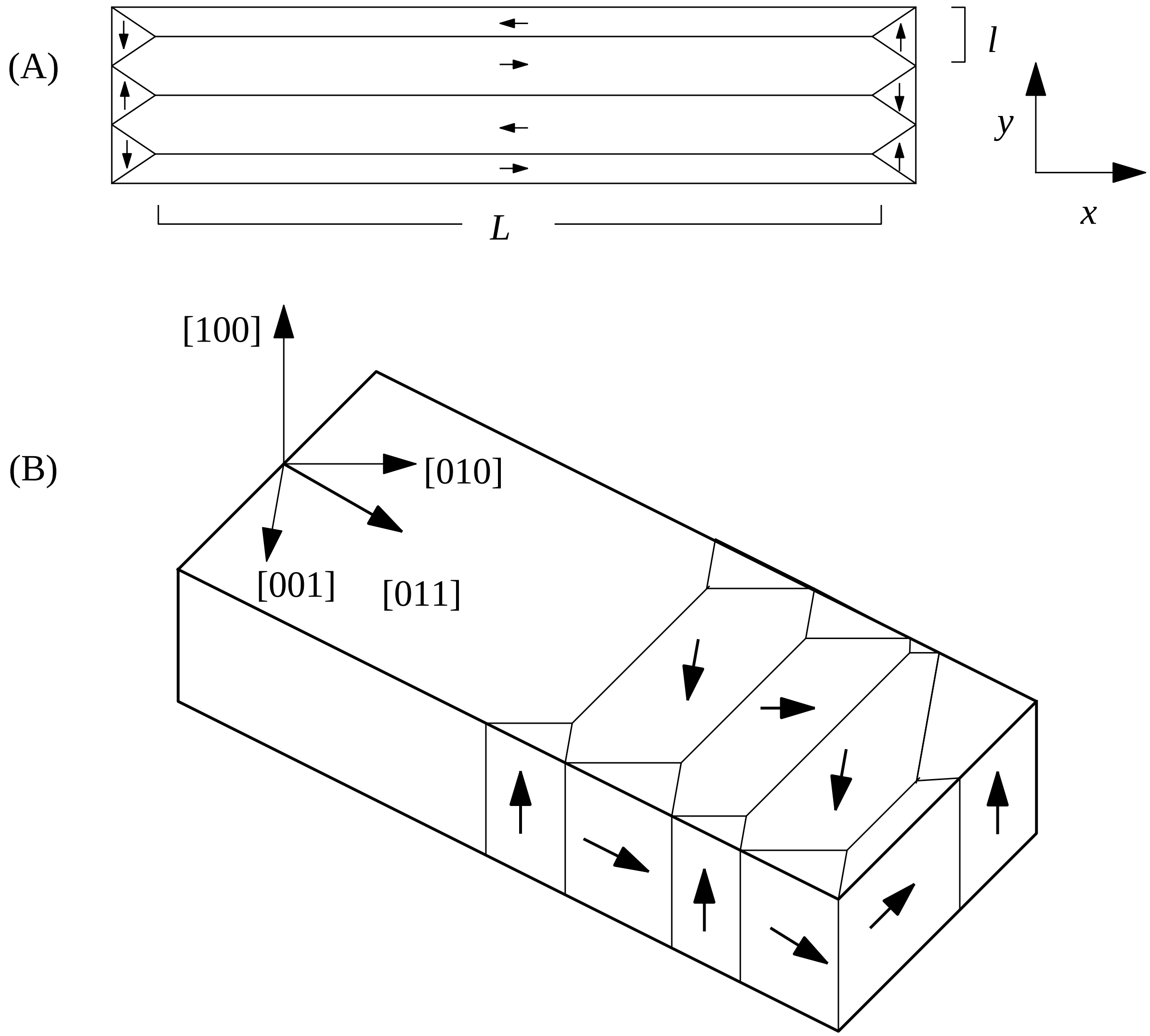


Figure 8: (A) Domain formation in a rectangular bar magnet. (B) In an anisotropic crystal

Hysteresis

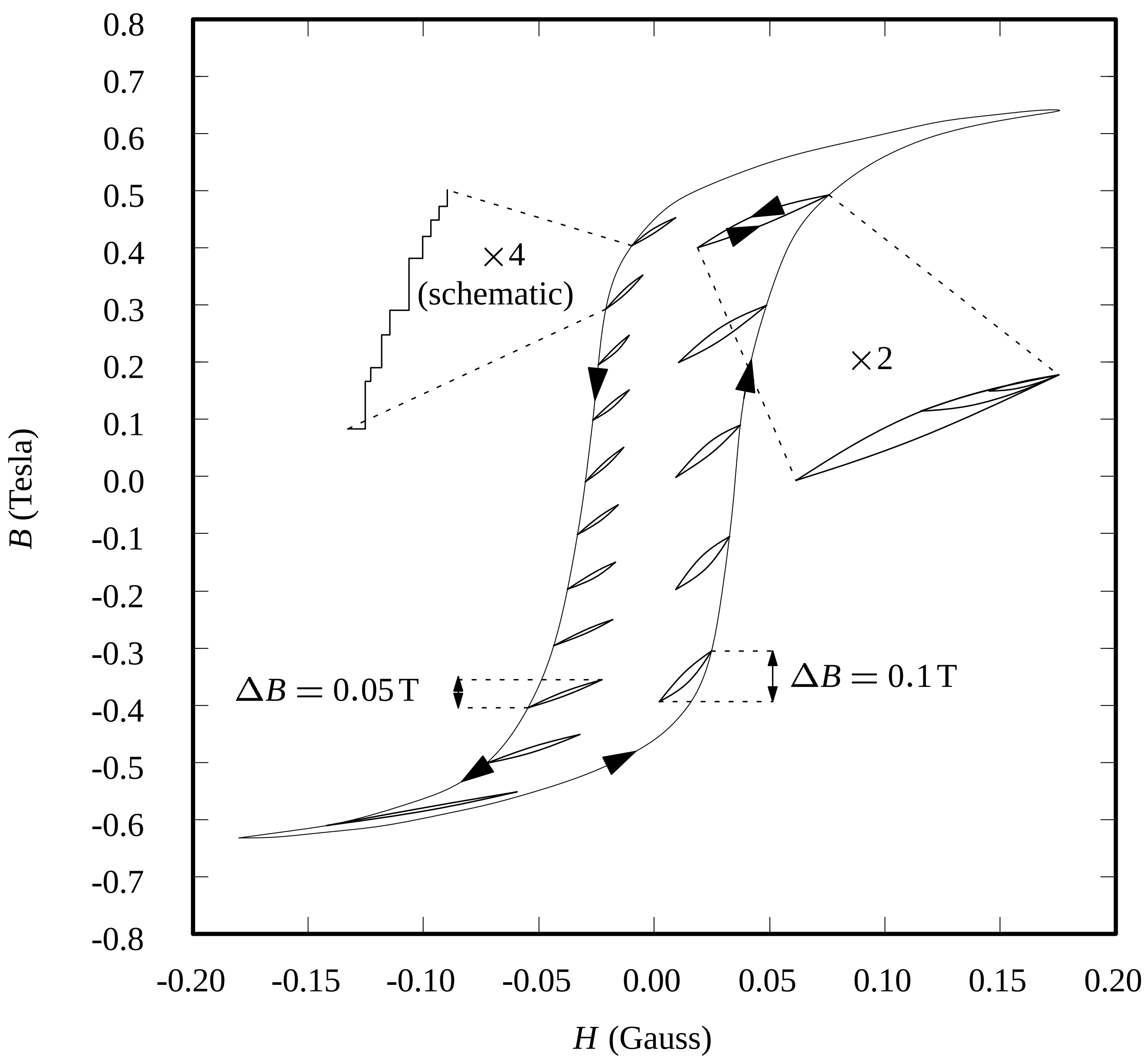


Figure 9: Hysteresis in the magnetization curve of Permalloy. [Source: Bozorth (1951)]

$$f(-1,-1)=\epsilon_{AA},\ f(1,-1)=f(-1,1)=\epsilon_{AB},\quad \text{and}\quad f(1,1)=\epsilon_{BB}. \tag{L62}$$

$$f(\sigma_{\vec{R}},\sigma_{\vec{R}'})=C_1+C_2(\sigma_{\vec{R}}+\sigma_{\vec{R}'})+C_3\sigma_{\vec{R}}\sigma_{\vec{R}'}, \tag{L63}$$

$$f(\sigma_{\vec{R}},\sigma_{\vec{R}'}) = \frac{\epsilon_{BB}+\epsilon_{AB}}{2}(\sigma_{\vec{R}}+\sigma_{\vec{R}'})-\epsilon_{AB}\sigma_{\vec{R}}\sigma_{\vec{R}'}. \tag{L64}$$

$$\mathcal{P}(\sigma_{\vec{R}}) = \exp\left\{\beta\mu\sum_{\vec{R}}\sigma_{\vec{R}}-\beta\sum_{\langle\vec{R}\vec{R}'\rangle}f(\sigma_{\vec{R}},\sigma'_{\vec{R}})\right\} \tag{L65}$$

$$= \exp\left\{\beta\mu_B H\sum_{\vec{R}}\sigma_{\vec{R}}+\beta J\sum_{\langle\vec{R}\vec{R}'\rangle}\sigma_{\vec{R}}\sigma_{\vec{R}'}\right\} \tag{L66}$$

where

$$\mu_B H \quad = \quad \mu - \frac{\epsilon_{BB}+\epsilon_{AB}}{2} z \quad \text{and} \quad J = \epsilon_{AB}. \tag{L67}$$

$$\sigma_{\vec{R}_A} = \sigma_A + (\sigma_{\vec{R}_A} - \sigma_A), \sigma_{\vec{R}_B} = \sigma_B + (\sigma_{\vec{R}_B} - \sigma_B) \tag{L68}$$

$$\begin{aligned} \mathcal{P} \quad &= \quad \exp\left\{\beta\mu_B H \sum_{\vec{R}} \sigma_{\vec{R}} + \beta J \sum_{\langle \vec{R}_A \vec{R}_B \rangle} (\sigma_A \sigma_{\vec{R}_B} + \sigma_B \sigma_{\vec{R}_A} - \sigma_A \sigma_B)\right\}, \\ &= \quad \prod_{\vec{R}_A} \exp\left\{\beta\mu_B H \sigma_{\vec{R}_A} + \beta J z (\sigma_B \sigma_{\vec{R}_A} - \sigma_A \sigma_B/2)\right\} \\ & \qquad \prod_{\vec{R}_B} \exp\left\{\beta\mu_B H \sigma_{\vec{R}_B} + \beta J z (\sigma_A \sigma_{\vec{R}_B} - \sigma_A \sigma_B/2)\right\}. \end{aligned} \tag{L70}$$

(L69)

Alloy Superlattices

$$\sigma_A = \left\langle \sigma_{\vec{R}_A} \right\rangle = \frac{e^{\{\beta\mu_B H + \beta J z \sigma_B\}} - e^{\{-\beta\mu_B H - \beta J z \sigma_B\}}}{e^{\{\beta\mu_B H + \beta J z \sigma_B\}} + e^{\{-\beta\mu_B H - \beta J z \sigma_B\}}}. \quad \text{(L71)}$$

$$\sigma_A = \tanh[\beta\mu_B H + \beta z \sigma_B J] \quad \text{(L72a)}$$

$$\sigma_B = \tanh[\beta\mu_B H + \beta z \sigma_A J]. \quad \text{(L72b)}$$

$$\sigma_A + \sigma_B = 0. \quad \text{(L73)}$$

$$\sigma_A = -\tanh(\beta J z \sigma_A) = \tanh(\beta |J| z \sigma_A). \quad \text{(L74)}$$

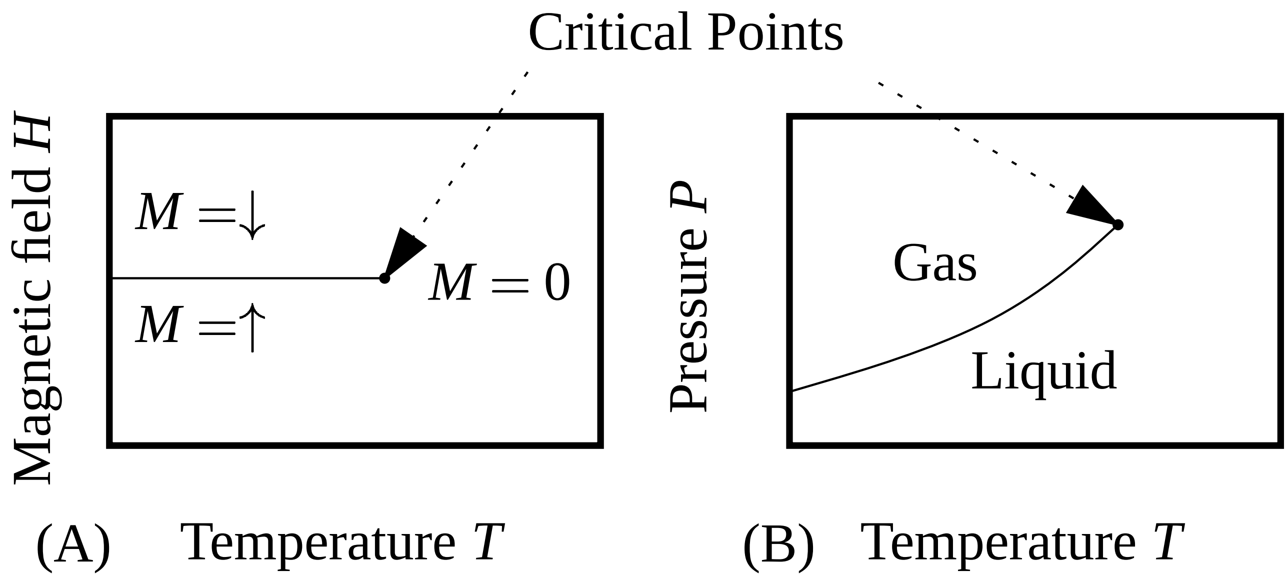


Figure 10: (A) Schematic phase diagram for a ferromagnet. (B) Schematic phase diagram of liquid–gas system. .

$$\mathcal{F}(M,T) = A_0(T) + A_2(T)M^2 + A_4(T)M^4 + HM. \tag{L75}$$

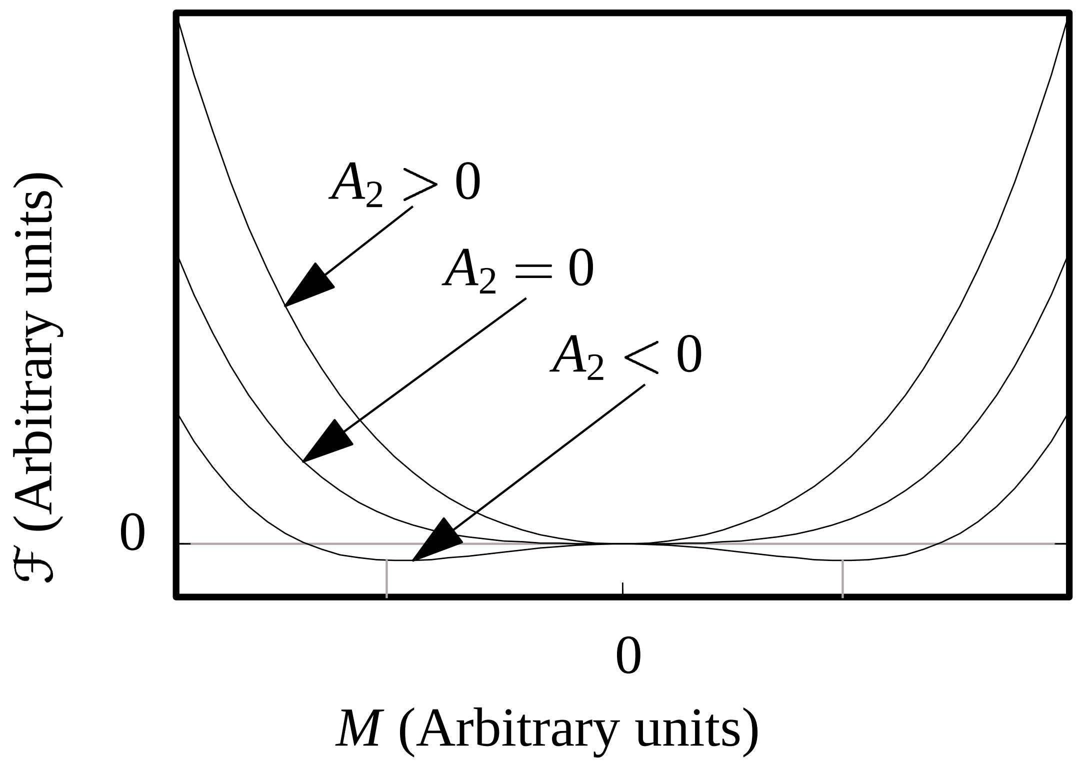


Figure 11: Landau free energy, Eq. (L75), for $A_2 > 0$, $A_2 = 0$, and $A_2 < 0$.

$$t \equiv \frac{T - T_c}{T_c}, \tag{L76}$$

$$\mathcal{F} = a_2 t M^2 + a_4 M^4 + HM. \tag{L77}$$

$$H + 2ta_2 M + 4a_4 M^3 = 0. \tag{L78}$$

$$M = \begin{cases} ? \qquad\qquad ? & \text{for } t < 0 \\ 0 & \text{for } t > 0. \end{cases} \tag{L79}$$

$$C_V = \frac{\partial \mathcal{E}}{\partial T} = \frac{\partial}{\partial T}\frac{\partial \beta \mathcal{F}}{\partial \beta} \tag{L80}$$

$$= -\frac{1}{T_c}\frac{\partial}{\partial t}(1+t)^2\frac{\partial}{\partial t}\left(\frac{\mathcal{F}}{1+t}\right) \tag{L81}$$

$$\approx -\frac{1}{T_c}\frac{\partial^2 \mathcal{F}}{\partial t^2} \tag{L82}$$

$$= \begin{cases} ? \qquad ? & \text{for } t < 0 \\ 0 & \text{for } t > 0. \end{cases} \tag{L83}$$

$$M = \sqrt{\frac{2|t|a_2}{4a_4}} + qH, \tag{L84}$$

$$q = -\frac{1}{4a_2|t|}. \tag{L85}$$

$$\frac{\partial M}{\partial H} \approx \begin{cases} -\frac{1}{4|t|a_2} & \text{for } t < 0 \\ -\frac{1}{2ta_2} & \text{for } t > 0. \end{cases} \tag{L86}$$

$$H + 4a_4M^3 = 0 \Rightarrow M \propto H^{1/3}. \tag{L87}$$

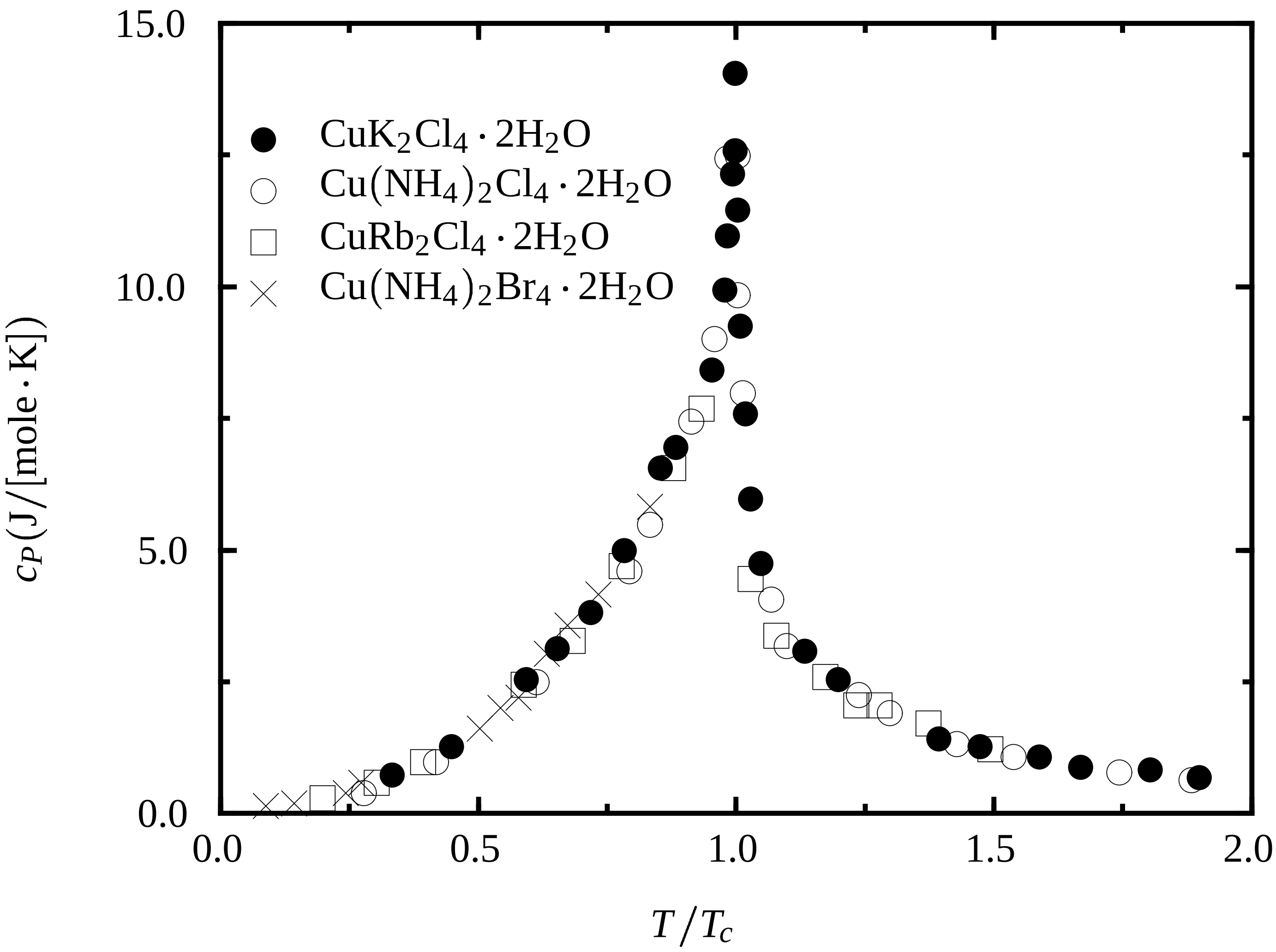


Figure 12: Molar heat capacities of four ferromagnetic copper salts versus scaled temperature T/T_c. [Source Jongh and Miedema (1974).]

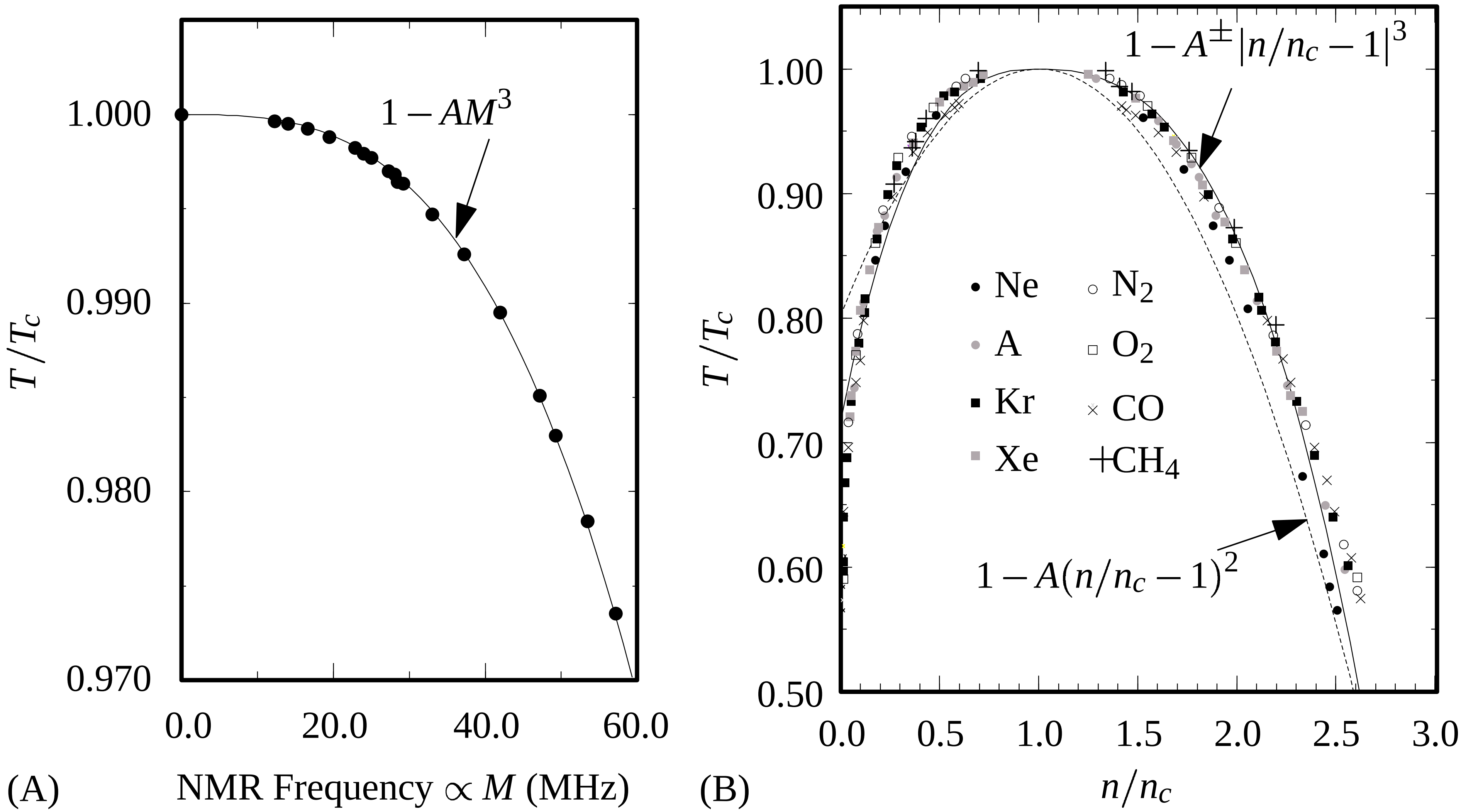


Figure 13: (A) Temperature versus magnetization, antiferromagnet Source: Heller and Benedek (1962) (B) Coexistence curve for eight fluids. Source: Guggenheim (1945).

$$dP = sdT + nd\mu, \tag{L88}$$

$$C_V(t) \sim |t|^{-\alpha}; \tag{L89}$$

$$M \sim |t|^{\beta} \quad \text{and} \quad \Delta n \sim |t|^{\beta}. \tag{L90}$$

$$K_T = \frac{1}{n}\frac{\partial n}{\partial P} \sim \frac{1}{n_c}\frac{\partial \Delta n}{\partial P} \sim |t|^{-\gamma}. \tag{L91}$$

$$\frac{\partial M}{\partial H} = \chi \sim |t|^{-\gamma}. \tag{L92}$$

$$P \sim |\Delta n|^{\delta}, \tag{L93}$$

$$|M| \sim |H|^{1/\delta}. \tag{L94}$$

$$g(r) - 1 \sim e^{-r/\xi} \tag{L95}$$

$$\begin{aligned} S(\vec{q}) - 1 &= n \int d\vec{r}\, e^{i\vec{q}\cdot\vec{r}} \left[g(r) - 1 \right] && \text{(L96)} \\ &\sim \int d\vec{r}\, e^{-r/\xi + i\vec{q}\cdot\vec{r}} \sim \frac{1}{1 + \xi^2 q^2}. && \text{(L97)} \end{aligned}$$

$$\xi \sim |t|^{-\nu}. \tag{L98}$$

$$g(r) \sim r^{-1-\eta}, \tag{L99}$$

Exponent	Fluid	Magnet	Mean Field Theory	Experiment	3d Ising
α	$C_V \sim \|t\|^{-\alpha}$	$C_V \sim \|t\|^{-\alpha}$	discontinuity	0.11–0.12	0.110
β	$\Delta n \sim \|t\|^{\beta}$	$M \sim \|t\|^{\beta}$	$\frac{1}{2}$	0.35–0.37	0.325
γ	$K_T \sim \|t\|^{-\gamma}$	$\chi \sim \|t\|^{-\gamma}$	1	1.21–1.35	1.241
δ	$P \sim \|\Delta n\|^{\delta}$	$\|H\| \sim \|M\|^{\delta}$	3	4.0–4.6	4.82
ν	$\xi \sim \|t\|^{-\nu}$	$\xi \sim \|t\|^{-\nu}$		0.61–0.64	0.63
η	$g(r) \sim r^{-1-\eta}$	$g(r) \sim r^{-1-\eta}$		0.02–0.06	0.032

Scaling Theory

$$\frac{\mathcal{G}}{\mathcal{V}k_BT} = |t|^{x_1} G(t,H), \tag{L100}$$

$$C_{\mathcal{V}} = \frac{\partial}{\partial T}\frac{\partial \beta \mathcal{G}}{\partial \beta} \sim t^{-\alpha} \tag{L101}$$

$$\Rightarrow x_1 = 2-\alpha. \tag{L102}$$

$$G(t,H) = G\left(\frac{H}{H_0|t|^{\Delta}}\right). \tag{L103}$$

$$\lim_{y\to\infty} G(y) \sim y^{x_2}. \tag{L104}$$

$$\frac{\mathcal{G}}{\mathcal{V}k_BT} \sim |t|^{2-\alpha}\left(\frac{H}{H_0|t|^{\Delta}}\right)^{x_2} \sim |t|^{2-\alpha-\Delta x_2}. \tag{L105}$$

$$x_2 = \frac{2-\alpha}{\Delta}. \tag{L106}$$

$$-M = \frac{\partial \mathcal{G}}{\partial H} = |t|^{2-\alpha} \frac{1}{H_0 |t|^{\Delta}} G'\left(\frac{H}{H_0|t|^{\Delta}}\right). \quad \text{(L107)}$$

$$|t|^{2-\alpha-\Delta} \quad \sim \quad |t|^{\beta} \quad \text{(L108)}$$

$$\Rightarrow \Delta \quad = \quad 2-\alpha-\beta. \quad \text{(L109)}$$

$$\left.\frac{\partial M}{\partial H}\right|_{H=0} \quad = \quad \chi \sim \frac{|t|^{2-\alpha}}{H_0^2|t|^{2\Delta}} G''(\frac{H}{H_0|t|^{\Delta}})\Big|_{H=0} \quad \text{(L110)}$$

$$\Rightarrow |t|^{2-\alpha-2\Delta} \quad \sim \quad |t|^{-\gamma} \quad \text{(L111)}$$

$$\Rightarrow \gamma \quad = \quad \alpha+2\Delta-2. \quad \text{(L112)}$$

$$2 = \alpha + 2\beta + \gamma. \quad \text{(L113)}$$

$$M \sim \frac{1}{H_0|t|^\Delta}|t|^{2-\alpha}\left(\frac{H}{H_0|t|^\Delta}\right)^{x_2-1} \quad \text{(L114)}$$

$$\sim H^{x_2-1} = H^{(2-\alpha-\Delta)/\Delta} \quad \text{(L115)}$$

$$\Rightarrow \frac{1}{\delta} = \frac{2-\alpha-\gamma}{2-\alpha+\gamma} \quad \text{(L116)}$$

$$\Rightarrow \delta = 1+\frac{\gamma}{\beta}, \quad \text{(L117)}$$

$$\langle \Delta N^2 \rangle = -\frac{k_B T N^2}{\mathcal{V}^2}\frac{\partial \mathcal{V}}{\partial P} = k_B T n^2 \mathcal{V} K_T \quad \text{(L118)}$$

$$= \left[\int d\vec{r}d\vec{r}'\ \langle n(\vec{r})n(\vec{r}')\rangle\right] - \langle N\rangle^2 \quad \text{(L119)}$$

$$= \mathcal{V}n\left\{1+n\int d\vec{r}(g(r)-1)\right\}. \quad \text{(L120)}$$

$$g(r) \sim \frac{e^{-r/\xi}}{r^{1+\eta}}, \quad \text{(L121)}$$

one has

$$K_T \sim \int d\vec{r}\, g(r). \tag{L122}$$

$$K_T \sim \xi^3 \xi^{-1-\eta} \int d\vec{s}\, \frac{e^{-s}}{s^{1+\eta}} \tag{L123}$$

$$\sim \xi^{2-\eta} \sim |t|^{-\nu(2-\eta)}. \tag{L124}$$

$$(2-\eta)\nu = \gamma, \tag{L125}$$

$$\frac{\mathcal{G}}{k_B T \mathcal{V}} \sim |t|^{2-\alpha} \sim \xi^{-3} \tag{L126}$$

$$\Rightarrow 2-\alpha = 3\nu, \tag{L127}$$

Scaling Theory

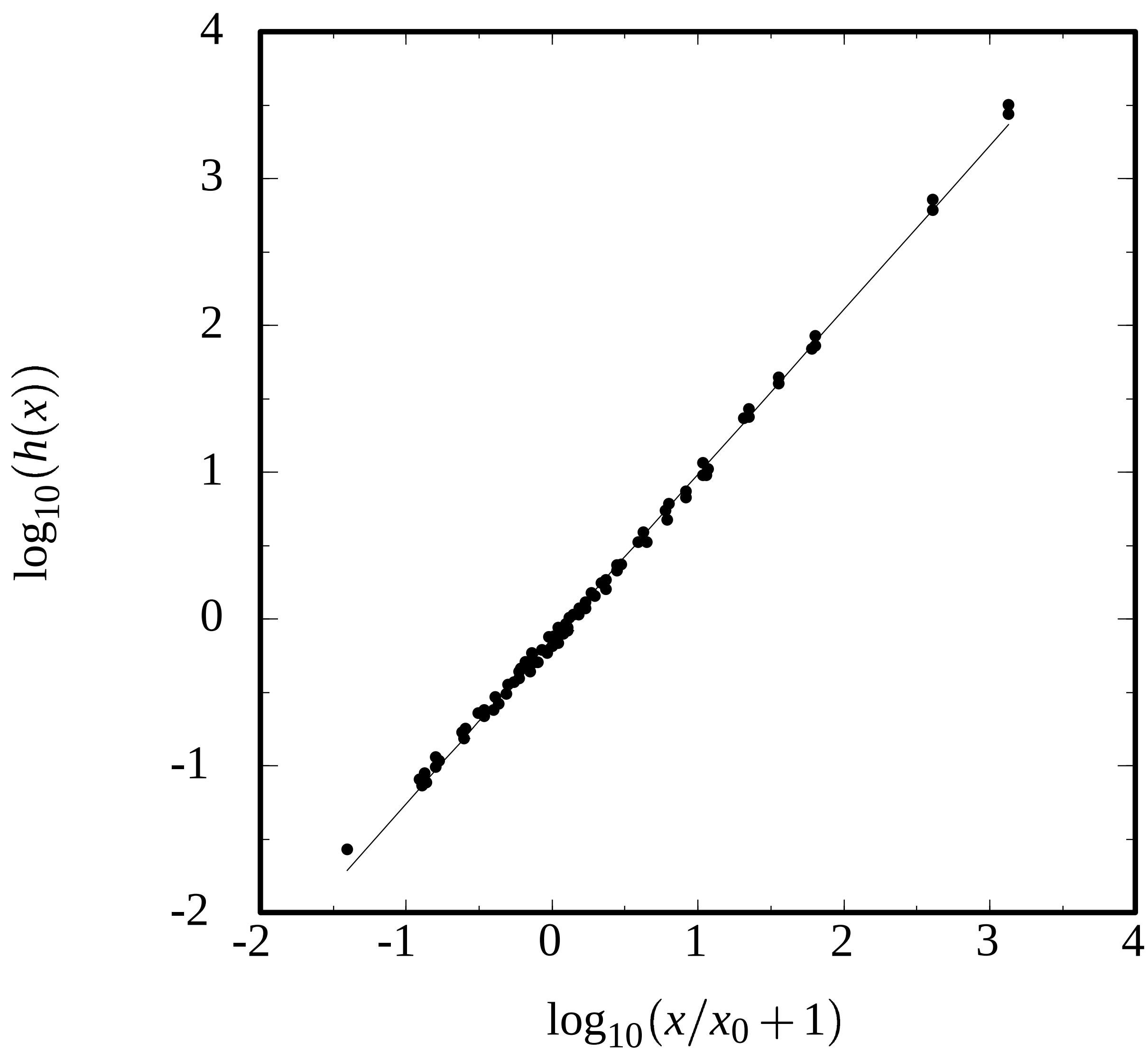
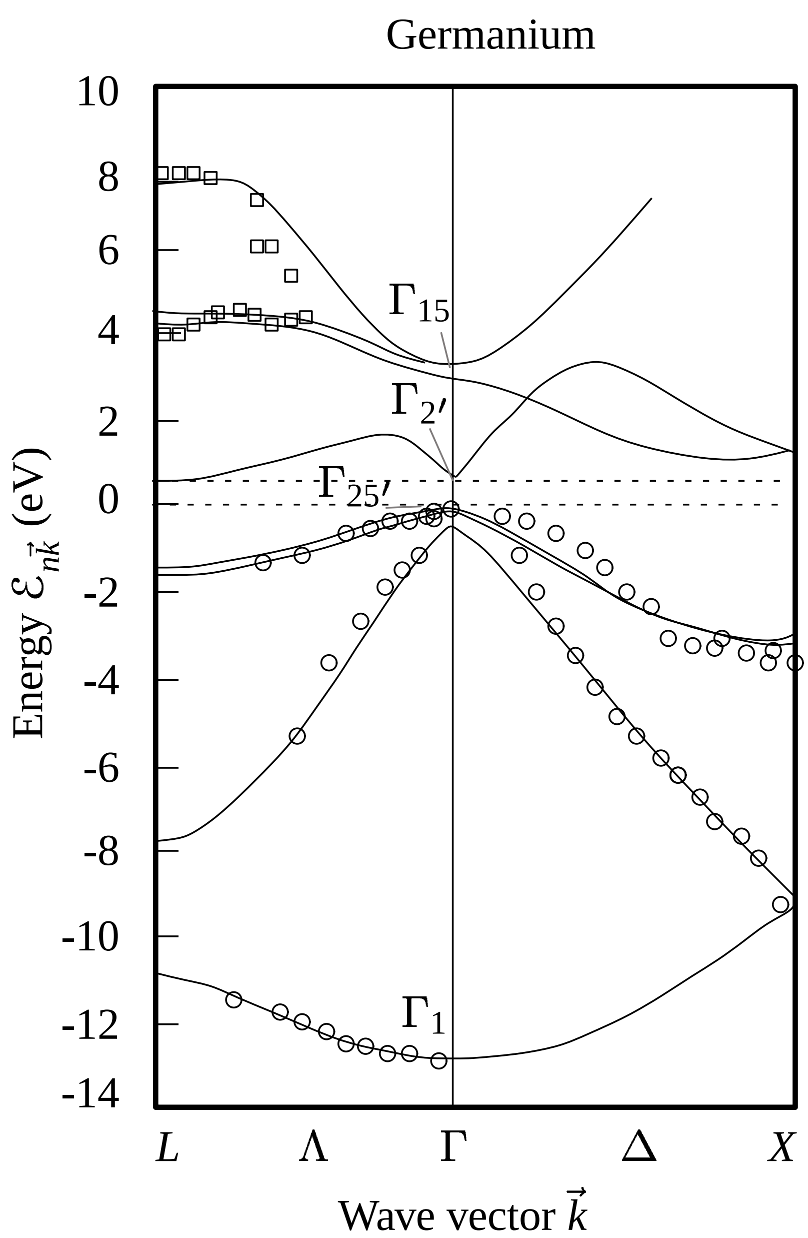


Figure 14: Scaling function $h = |H|/|M|^{\delta}$ versus $x = t/|M|^{1/\beta}$ [Source: Vicentini-Missoni (1972), p. 68.]

Optical Properties of Metals



Definitions

- ☞ Phenomenology of Metals
- ☞ Anomalous Skin Effect
- ☞ Plasmons
- ☞ Interband Transitions
- ☞ Brillouin and Raman Scattering
- ☞ Photoemission
- ☞ Work Function
- ☞ Angle–Resolved Photoemission Spectroscopy (ARPES)
- ☞ Charge–Transfer Insulators

$$1\,\mathrm{eV} \Rightarrow \omega \sim 10^{15}\,\mathrm{Hz} \Rightarrow \lambda \sim 1\,\mu\mathrm{m}. \tag{L1}$$

$$\epsilon(\omega) = 1 - \frac{\omega_\mathrm{p}^2}{\omega(\omega + i/\tau)} \tag{L2}$$

$$\omega_\mathrm{p} = \sqrt{\frac{4\pi n e^2}{m}} = 5.64 \cdot 10^{15}\ \mathrm{Hz}\ \left[\frac{n}{10^{22}\mathrm{cm}^{-3}}\right]^{1/2}. \tag{L3}$$

Plasma Frequency

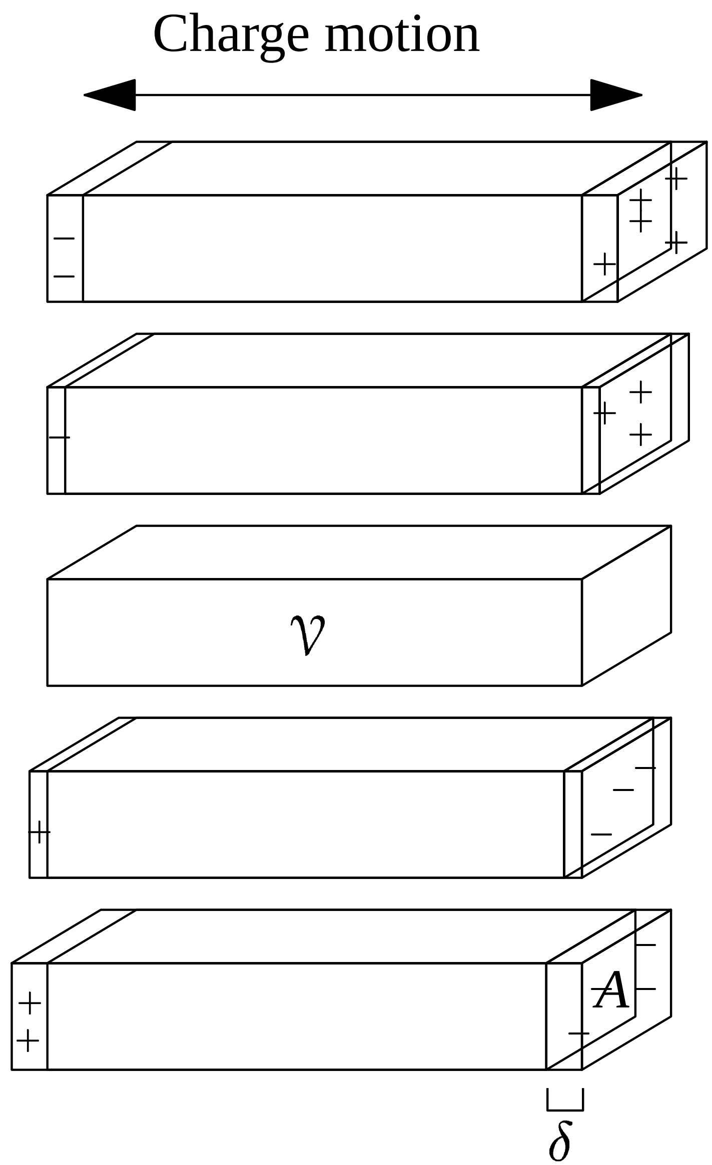


Figure 1: Plasma oscillations

Plasma Frequency

$$\epsilon(\omega) = 1 - \left(\frac{\omega_{\text{p}}}{\omega}\right)^2. \quad \text{(L4)}$$

$$en\mathcal{V}E = ? \qquad\qquad ?. \quad \text{(L5)}$$

$$\ddot{\delta} = -? \qquad\qquad ? \quad \text{(L6)}$$

$$\omega_{\text{p}}^2 = \frac{4\pi ne^2}{m}. \quad \text{(L7)}$$

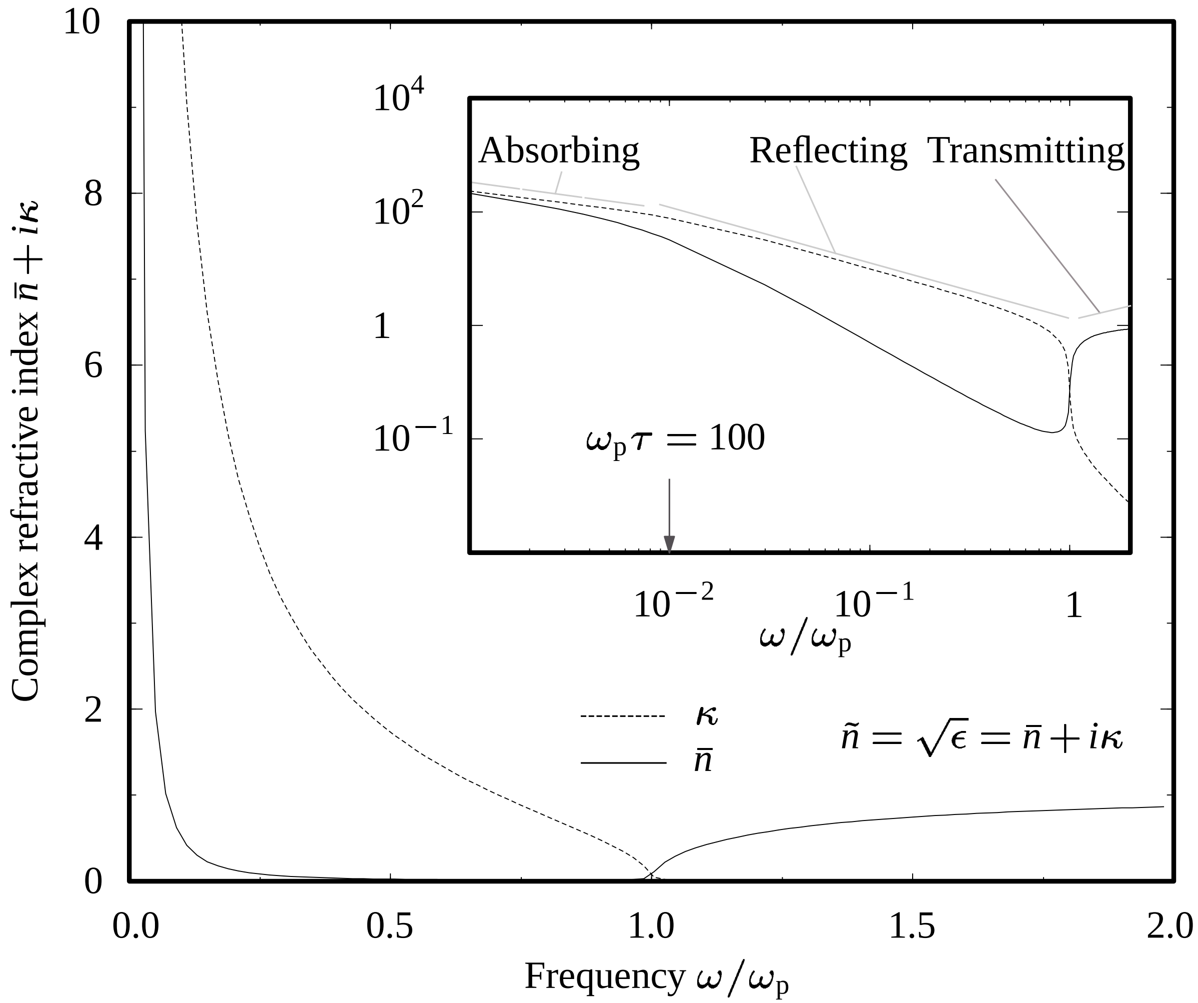


Figure 2: Index of refraction $\bar{n}$ and extinction coefficient κ for metal

Plasma Frequency

$$\epsilon \quad \approx \quad 1 + i\tau \frac{\omega_{\rm p}^2}{\omega}(1 + i\omega\tau) \Rightarrow \bar{n} \approx \kappa \approx \sqrt{\tau\omega_{\rm p}^2/2\omega}. \tag{L8}$$

$$\frac{(\omega^2 - \omega_{\rm p}^2)}{\omega^2} \tag{L9}$$

$$\kappa \approx \sqrt{\omega_{\rm p}^2/\omega^2 - 1} \text{ and } \bar{n} \approx \frac{\omega_{\rm p}^2}{2\tau\omega^2\sqrt{\omega_{\rm p}^2 - \omega^2}}. \tag{L10}$$

$$\bar{n} \approx \sqrt{1 - \omega_{\rm p}^2/\omega^2} \;\; \kappa \approx \frac{\omega_{\rm p}^2}{2\tau\omega^2\sqrt{\omega^2 - \omega_{\rm p}^2}}. \tag{L11}$$

$$\frac{\partial g}{\partial t} = -\vec{v}\cdot\nabla g - e\vec{E}\cdot\vec{v}\frac{\partial g}{\partial \mu} - \frac{g}{\tau}. \tag{L12}$$

$$\vec{E} = \vec{E}(\vec{q},\omega)e^{i\vec{q}\cdot\vec{r}-i\omega t}. \tag{L13}$$

$$g_{\vec{r}\vec{k}} = g_{\vec{k}}(\vec{q},\omega)e^{i\vec{q}\cdot\vec{r}-i\omega t} \tag{L14}$$

$$g_{\vec{k}}(\vec{q},\omega)[-i\omega] = [-i\vec{v}\cdot\vec{q} - 1/\tau]g_{\vec{k}}(\vec{q},\omega) - e\vec{E}\cdot\vec{v}\frac{\partial f}{\partial \mu} \tag{L15}$$

$$\Rightarrow g_{\vec{k}}(\vec{q},\omega) = \quad ? \qquad\qquad ?. \tag{L16}$$

$$\vec{j} = -e\int[d\vec{k}]\,\vec{v}g_{\vec{k}} \tag{L17}$$

$$= e^2\int[d\vec{k}]\,\frac{\partial f}{\partial \mu}\frac{\vec{v}[\vec{v}\cdot\vec{E}(\vec{q},\omega)]}{1/\tau - i(\omega - \vec{q}\cdot\vec{v})} \tag{L18}$$

$$\Rightarrow \sigma_{\alpha\beta} = e^2 \int [d\vec{k}] \frac{\partial f}{\partial \mu} \frac{v_\alpha v_\beta}{1/\tau - i(\omega - \vec{q}\cdot\vec{v})} \quad \text{(L19)}$$

$$= e^2 \int \frac{d\Sigma}{4\pi^3 \hbar v} \frac{v_\alpha v_\beta}{1/\tau - i(\omega - \vec{q}\cdot\vec{v})} \quad \text{(L20)}$$

$$\Rightarrow \epsilon_{\alpha\beta} = \delta_{\alpha\beta} + \frac{4\pi i e^2}{\omega} \int \frac{d\Sigma}{4\pi^3 \hbar v} \frac{v_\alpha v_\beta}{1/\tau - i(\omega - \vec{q}\cdot\vec{v})} \quad \text{(L21)}$$

$$q = \frac{\sqrt{\epsilon}\omega}{c} = (\bar{n} + i\kappa)\frac{\omega}{c}. \quad \text{(L22)}$$

$$\frac{1}{\tau} - i\omega + i(\bar{n} + i\kappa)\frac{\omega v_F}{c} \approx \frac{1}{\tau} - i\omega \quad \text{(L23a)}$$

$$\Rightarrow \frac{\bar{n} v_F}{c} \ll 1 \quad \text{(L23b)}$$

and

$$\kappa \omega v_F \tau / c \ll 1 \quad \text{or equivalently} \quad l_T \ll \delta, \quad \text{(L23c)}$$

$$\delta \equiv \frac{c}{\kappa\omega} \tag{L24}$$

$$\epsilon = 1 - \frac{\omega_{\rm p}^2}{\omega(\omega + i/\tau)} \tag{L25}$$

with

$$\omega_{\rm p}^2 = \frac{4\pi n e^2}{m_{\rm opt}}, \tag{L26}$$

$$\frac{1}{m_{\rm opt}} = \frac{1}{m}\frac{\int [d\vec{k}]\, \frac{\partial f}{\partial \mu} m v_x^2}{\int [d\vec{k}]\, f_k} = \int \frac{d\Sigma}{12\pi^3 \hbar n}\, v. \tag{L27}$$

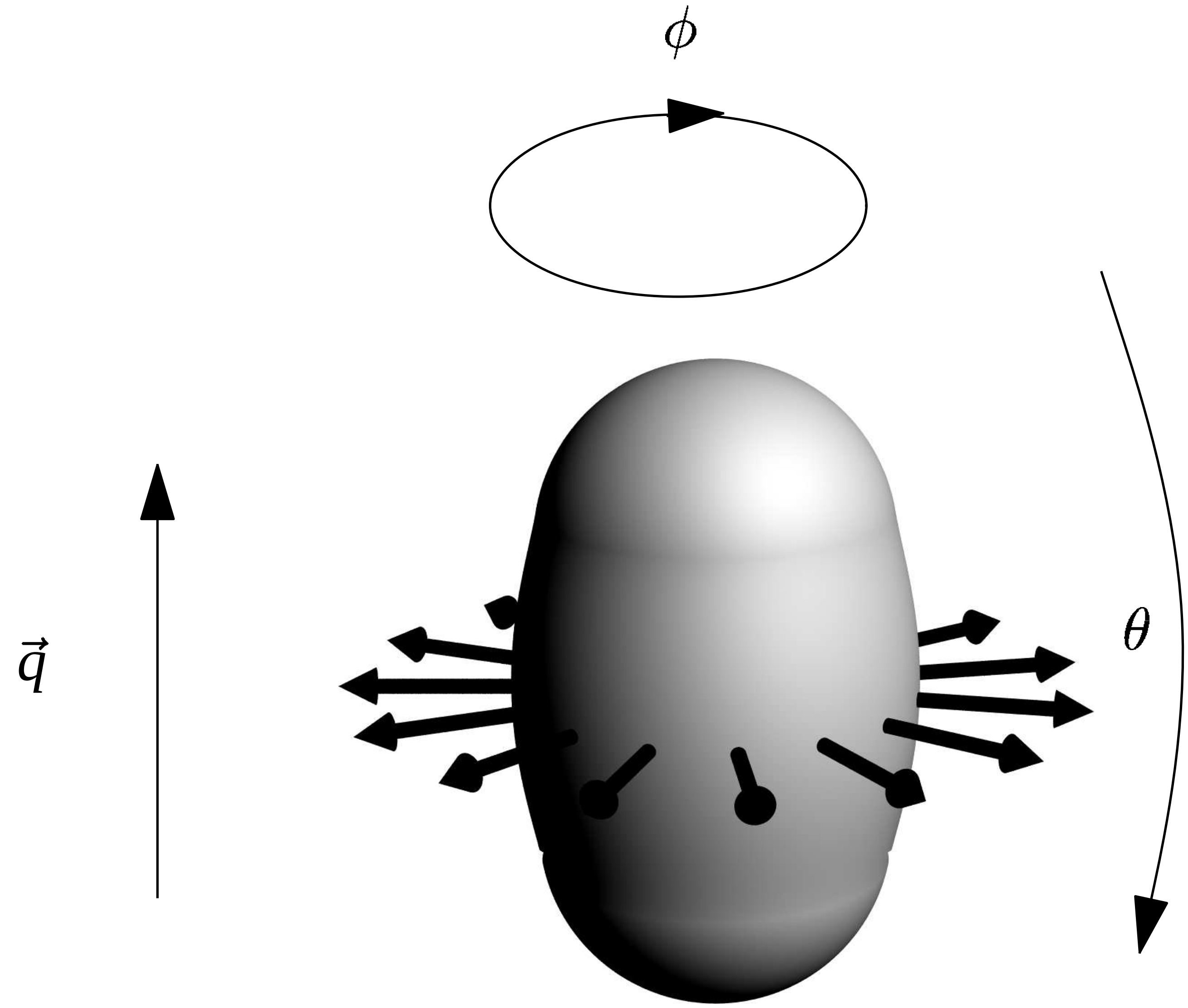


Figure 3: Anomalous skin effect

$$d\Sigma \approx \mathcal{R}_\phi \mathcal{R}_\theta d\theta d\phi, \quad v_x \approx v_F \cos\phi \tag{L28}$$

$$\sigma_{xx} = e^2 \int \frac{\mathcal{R}_\phi \mathcal{R}_\theta d\theta d\phi}{4\pi^3 \hbar v_F} \frac{v_F^2 \cos^2\phi}{1/\tau + iqv_F\theta} \tag{L29}$$

$$= \frac{e^2}{4\pi\hbar q} \mathcal{R}_\phi \mathcal{R}_\theta. \tag{L30}$$

Plasmons

$$\chi_c = \frac{e^2}{\hbar \mathcal{V}} \sum_{\vec{k}} f_{\vec{k}} [\frac{1}{\omega_{\vec{k}} - \omega_{\vec{q}+\vec{k}} - \omega} + \frac{1}{\omega_{\vec{k}} - \omega_{\vec{q}+\vec{k}} + \omega}] \tag{L31}$$

$$= \frac{e^2}{\hbar \mathcal{V}} \sum_{\vec{k}} \frac{2 f_{\vec{k}} (\omega_{\vec{k}} - \omega_{\vec{k}+\vec{q}})}{\left(\omega_{\vec{k}} - \omega_{\vec{k}+\vec{q}}\right)^2 - \omega^2} \tag{L32}$$

$$= \frac{e^2}{\mathcal{V}} \sum_{\vec{k}} \frac{2 f_{\vec{k}} \left[\frac{q^2}{2m} + \frac{\vec{q}\cdot\vec{k}}{m}\right]}{\omega^2 - \hbar^2 \left[\frac{\vec{q}\cdot\vec{k}}{m} + \frac{q^2}{2m}\right]^2}. \tag{L33}$$

$$\chi_c(\vec{q},\omega) \approx \frac{e^2}{\mathcal{V}} \sum_{\vec{k}} \frac{f_{\vec{k}}}{\omega^2} \frac{q^2}{m} \left[1 + \frac{3(\vec{q}\cdot\vec{k})^2 \hbar^2}{m^2 \omega^2}\right]. \tag{L34}$$

$$\chi_c(\vec{q},\omega) = \frac{e^2}{\mathcal{V}} \sum_{\vec{k}} \frac{f_{\vec{k}}}{\omega^2} \frac{q^2}{m} \left[1 + \frac{(qk)^2 \hbar^2}{m^2 \omega^2}\right]. \tag{L35}$$

Plasmons

$$N = \sum_{\vec{k}\sigma} f_{\vec{k}} = \mathcal{V} \int \frac{dk}{4\pi^3} 4\pi k^2 \, f_{\vec{k}}. \tag{L36}$$

$$\sum_{\vec{k}\sigma} f_{\vec{k}} k^2 = \frac{3}{5} N k_F^2. \tag{L37}$$

$$\epsilon(\vec{q},\omega) = 1 - \frac{4\pi n e^2}{m\omega^2}\left[1 + \frac{3}{5}\frac{\hbar^2 k_F^2 q^2}{m^2\omega^2}\right]. \tag{L38}$$

$$1 = \frac{\omega_{\mathrm{p}}^2}{\omega^2}\left[1 + \frac{3}{5}\frac{\hbar^2 k_F^2 q^2}{m^2\omega^2}\right] \tag{L39}$$

$$\Rightarrow \omega^2 = \omega_p^2 + \frac{6}{5}\frac{\mathcal{E}_F q^2}{m}. \tag{L40}$$

Experimental Observation of Plasmons

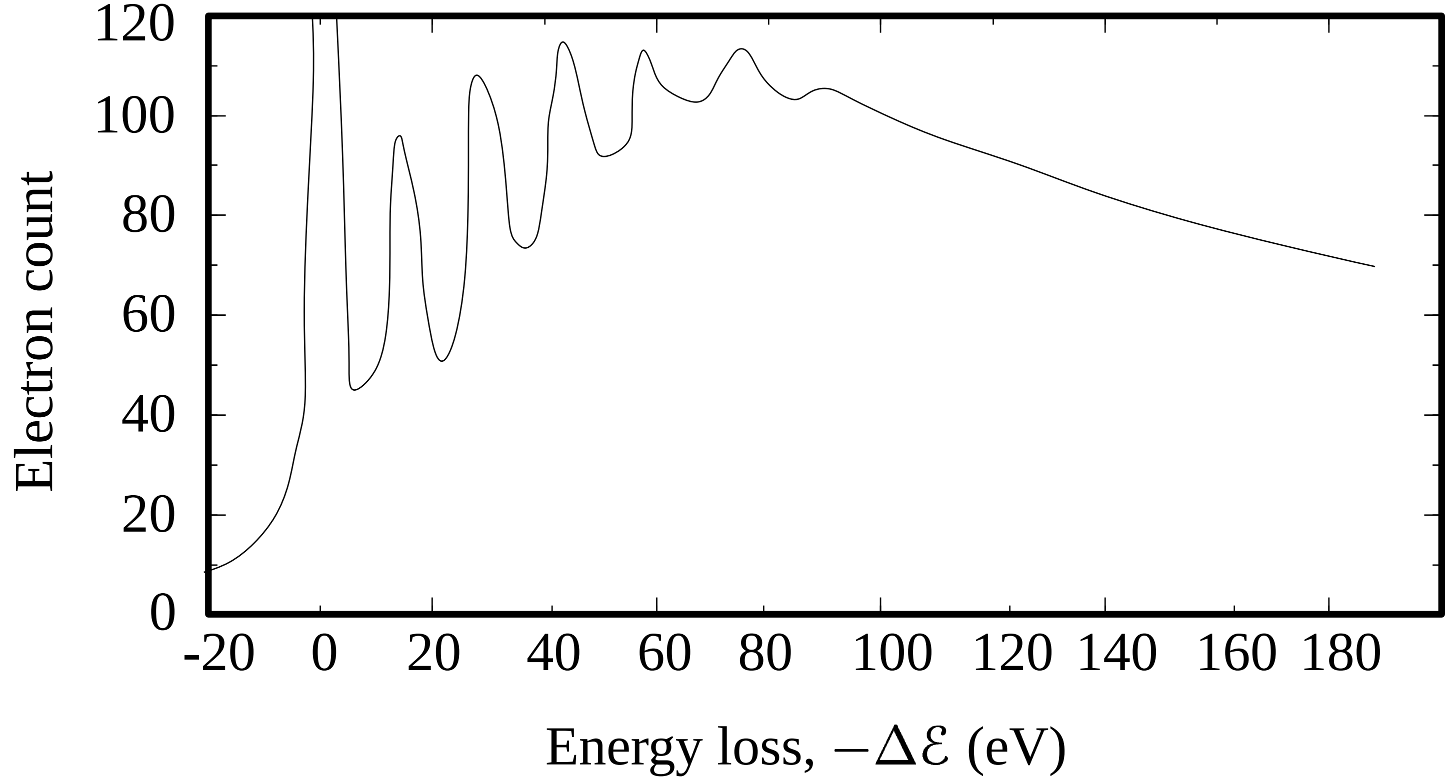


Figure 4: Electron energy loss to plasma oscillations [Lang (1948)]

Experimental Observation of Plasmons

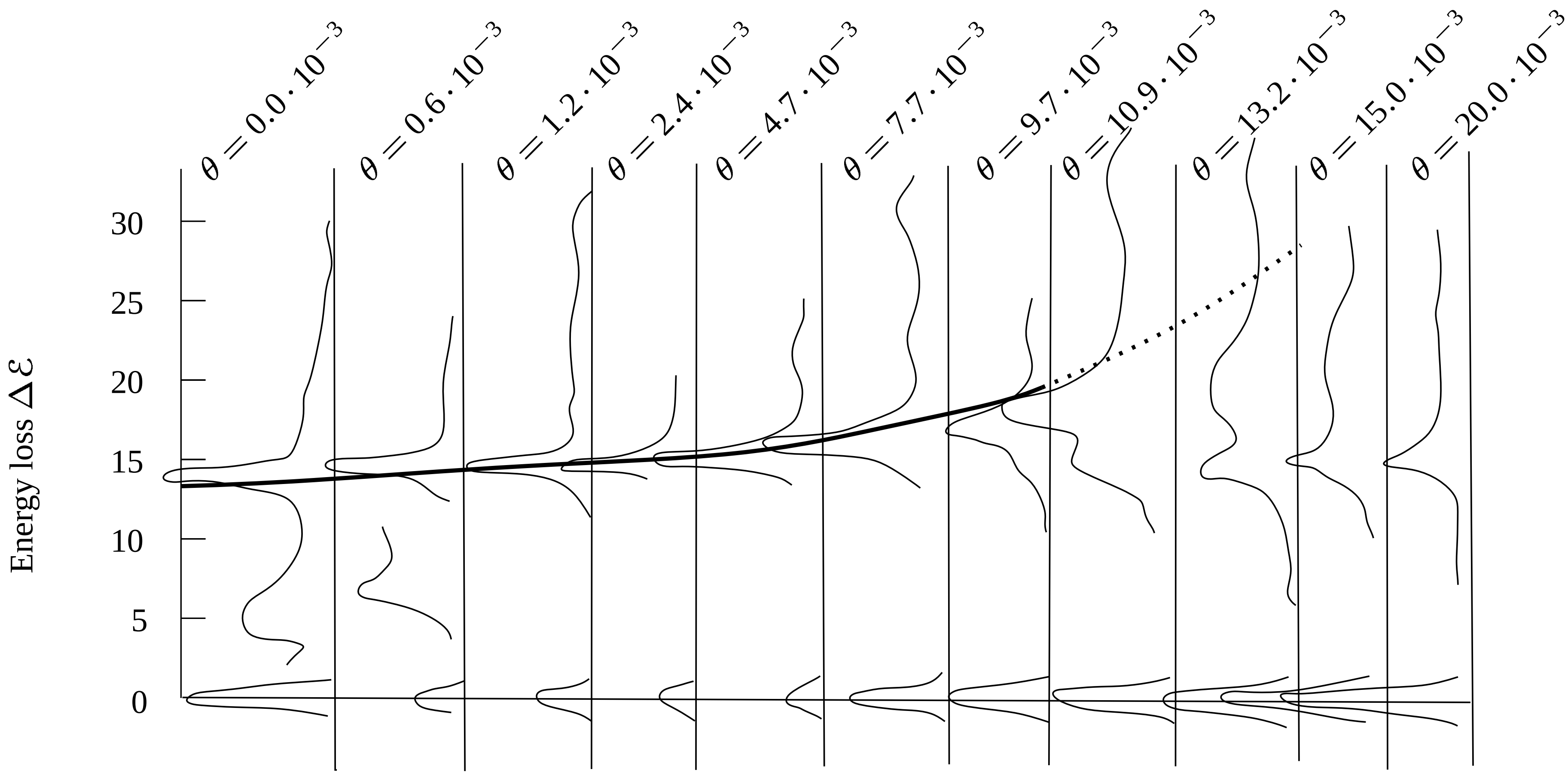


Figure 5: Electron energy loss to plasmons as a function of angle [Kunz (1962)]

$$\hbar\omega(\vec{k}-\vec{k}') = \Delta\mathcal{E} \qquad \text{(L41)}$$

$$\Rightarrow \hbar\omega(2k\sin\theta/2) \quad \approx \quad \hbar\omega_{\rm p} + \alpha_{\rm pl}\frac{\hbar^2 k^2}{m}\theta^2 \tag{L42}$$

$$\alpha_{\rm pl} = \frac{3}{5}\frac{\hbar^2 k_F^2}{2m\hbar\omega_{\rm p}}. \tag{L43}$$

Element	Be	Al	Mg	Sb	Na
$\alpha_{\rm pl}$ [from Eq. (L43)]	0.47	0.44	0.39	0.44	0.32
$\alpha_{\rm pl}$ (experiment)	0.42	0.35	0.39	0.37	0.29

Interband Transitions

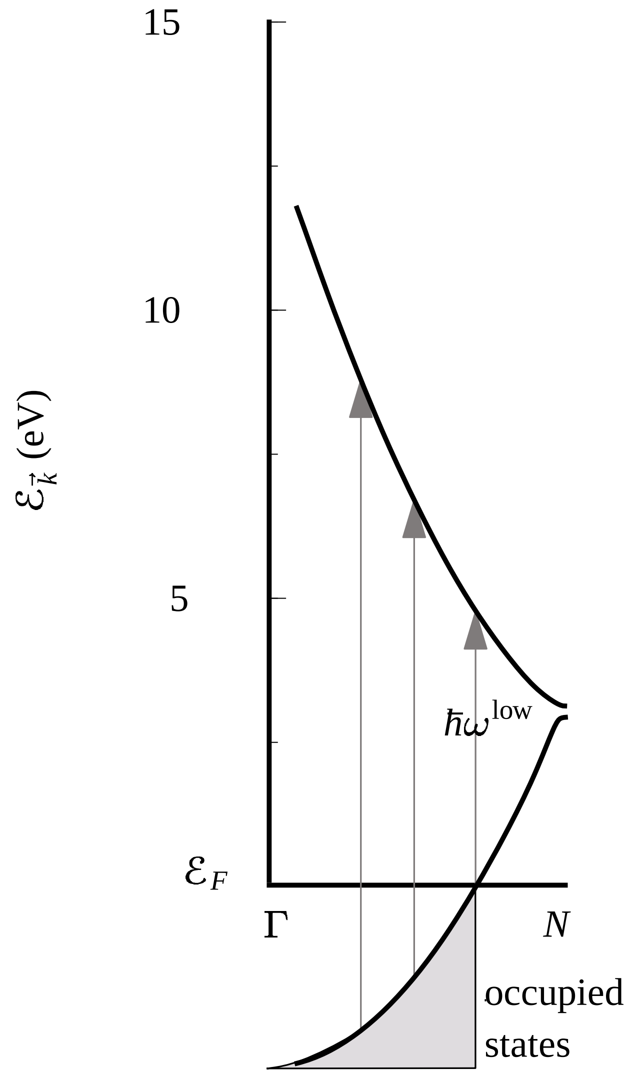


Figure 6: The sodium electron bands.

$$\langle n_1\vec{k}|\hat{P}_\alpha|n_2\vec{k}\rangle. \tag{L44}$$

$$\psi^{\text{low}}_{\vec{k}}(\vec{r}) \approx \frac{1}{\sqrt{\mathcal{V}}}\left[e^{i\vec{k}\cdot\vec{r}} + \frac{e^{i(\vec{k}-\vec{K})\cdot\vec{r}}U_{-\vec{K}}}{\mathcal{E}^0_{\vec{k}} - \mathcal{E}^0_{\vec{k}-\vec{K}}}\right] \tag{L45}$$

$$\psi^{\text{high}}_{\vec{k}}(\vec{r}) \approx \frac{1}{\sqrt{\mathcal{V}}}\left[e^{i(\vec{k}-\vec{K})\cdot\vec{r}} + \frac{e^{i\vec{k}\cdot\vec{r}}U_{\vec{K}}}{\mathcal{E}^0_{\vec{k}-\vec{K}} - \mathcal{E}^0_{\vec{k}}}\right]. \tag{L46}$$

$$\text{Re}[\sigma_{\alpha\beta}](\omega) = \frac{\pi}{\omega}\frac{e^2\hbar^2}{m^2}\frac{1}{\mathcal{V}}\sum_{\vec{k}\vec{K}\in\langle 110\rangle} f_{\vec{k}}\frac{|U_{\vec{K}}|^2 K_\alpha K_\beta}{(\mathcal{E}^0_{\vec{k}-\vec{K}} - \mathcal{E}^0_{\vec{k}})^2}\delta(\mathcal{E}^0_{\vec{k}-\vec{K}} - \mathcal{E}^0_{\vec{k}} - \hbar\omega) \tag{L47}$$

Interband Transitions

$$\Rightarrow \sigma(\omega) = \frac{4e^2\pi}{m^2\omega^3} K^2 |U_{\vec{K}}|^2 D_{\rm j}(\hbar\omega), \tag{L49}$$

$$D_{\rm j}(\hbar\omega) = \frac{1}{\mathcal{V}} \sum_{\vec{k},\vec{K}\in\langle 110\rangle} f_{\vec{k}}\,\delta(\mathcal{E}^0_{\vec{k}-\vec{K}} - \mathcal{E}^0_{\vec{k}} - \hbar\omega) \tag{L50}$$

$$= \frac{m^3}{4\pi^2\hbar^4K^3}(\omega^{\rm high} - \omega)(\omega - \omega^{\rm low}) \tag{L51}$$

with

$$\omega^{\rm high} = \frac{\hbar^2 K(K+2k_F)}{2\hbar m} \quad \omega^{\rm low} = \frac{\hbar^2 K(K-2k_F)}{2\hbar m}. \tag{L52}$$

Interband Transitions

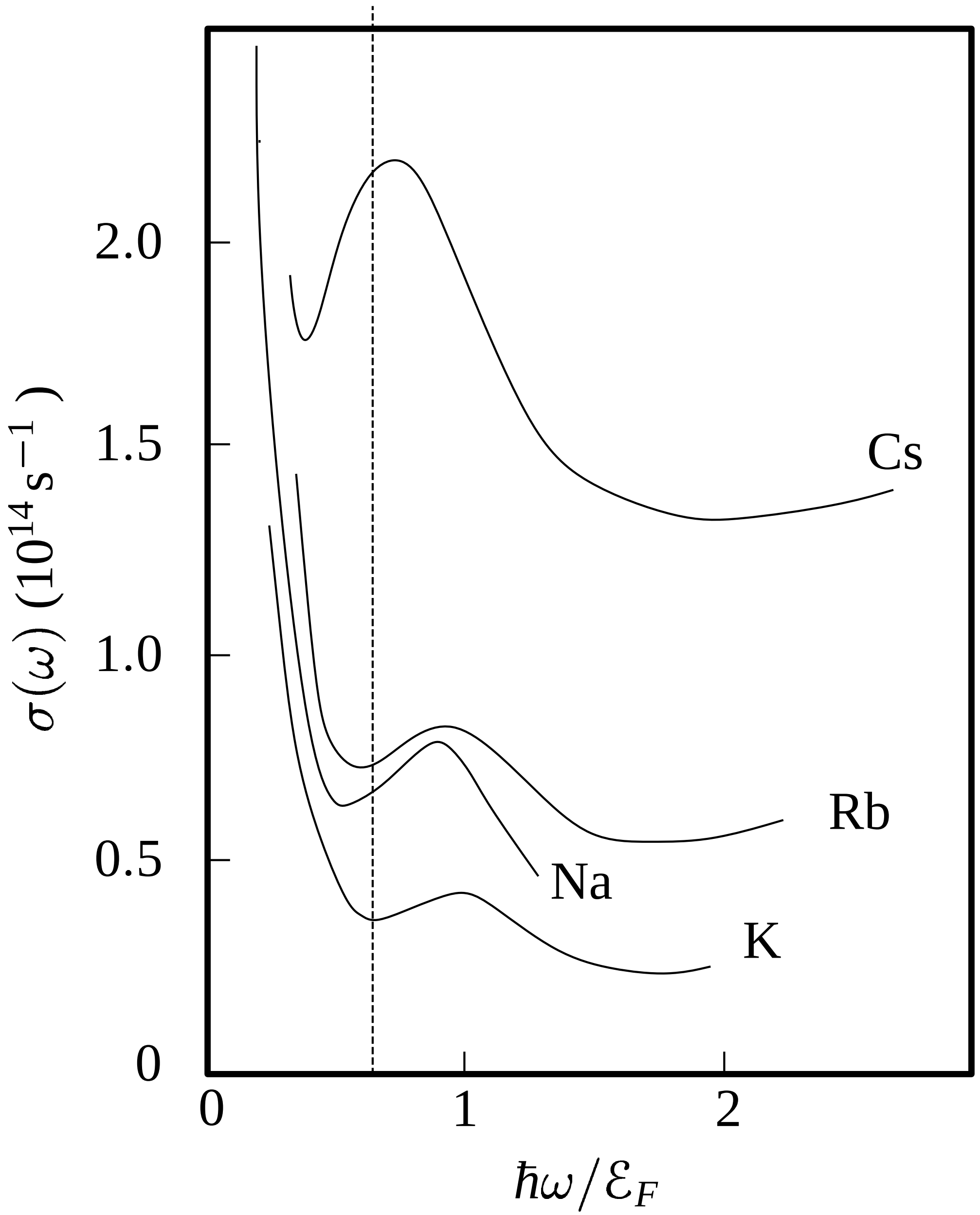


Figure 7: Absorption of alkali metals [Smith (1970)]

Interband Transitions

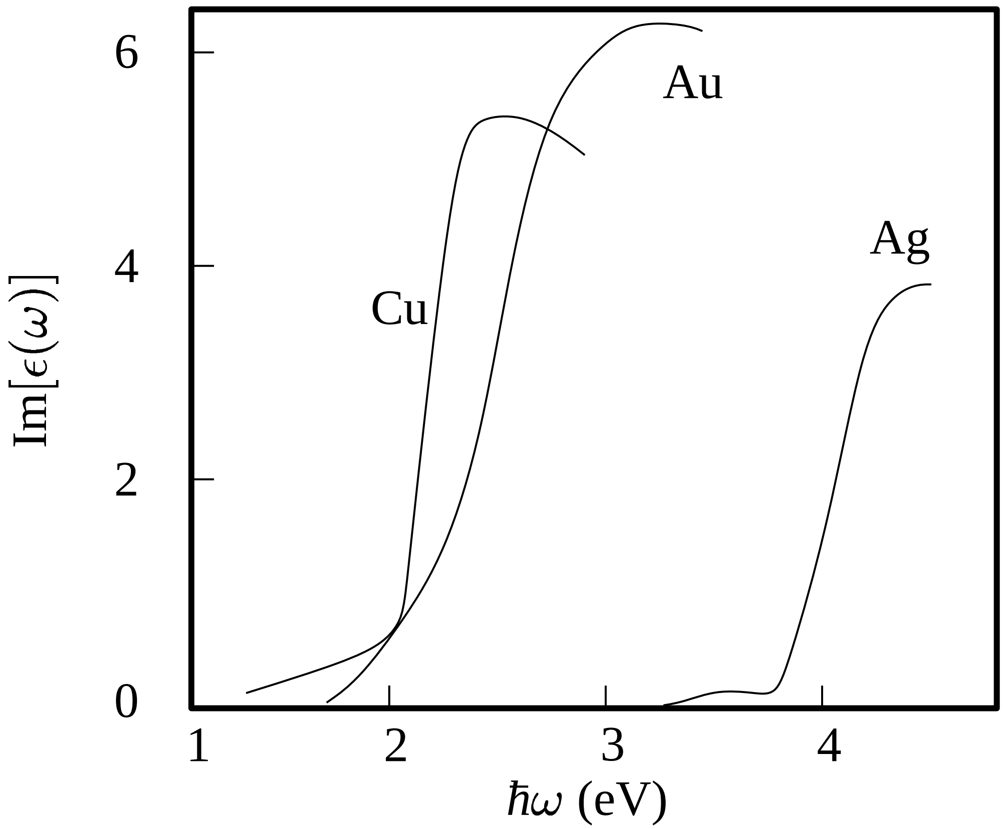


Figure 8: Noble metal absorption [Thèye (1968)]

Brillouin and Raman Scattering

Conserve (Crystal) Momentum:

$$\vec{k}_f = ? \qquad ? \tag{L53}$$

Conserve Energy:

$$\frac{c}{\bar{n}}(k_f - k_0) = ? \qquad ?. \tag{L54}$$

Brillouin Scattering

$$\omega_1 = c_p k. \tag{L55}$$

$$\begin{aligned}
(k_f - k_0) &= -\frac{\bar{n} c_p}{c}\sqrt{k_f^2 + k_0^2 - 2k_f k_0 \cos\theta} && \text{(L56)}\\
\Rightarrow k_0 - k_f &\approx k_0 \frac{2\bar{n} c_p}{c}\sqrt{\frac{1-\cos\theta}{2}}. && \text{(L57)}\\
\Rightarrow \omega_0 - \omega_f &= \frac{2\bar{n}\omega_0 c_p}{c}\sin\theta/2 && \text{(L58)}
\end{aligned}$$

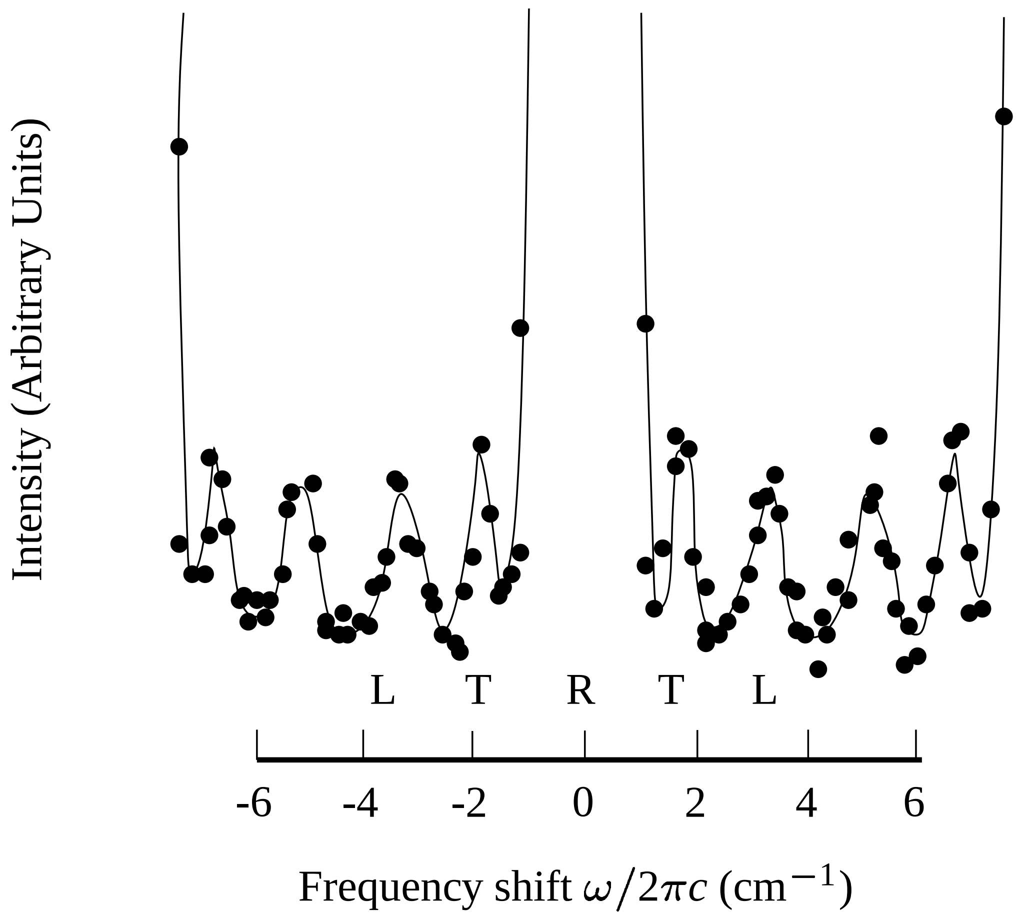


Figure 9: Brillouin scattering from the (111) surface of germanium [Sandercock (1972).]

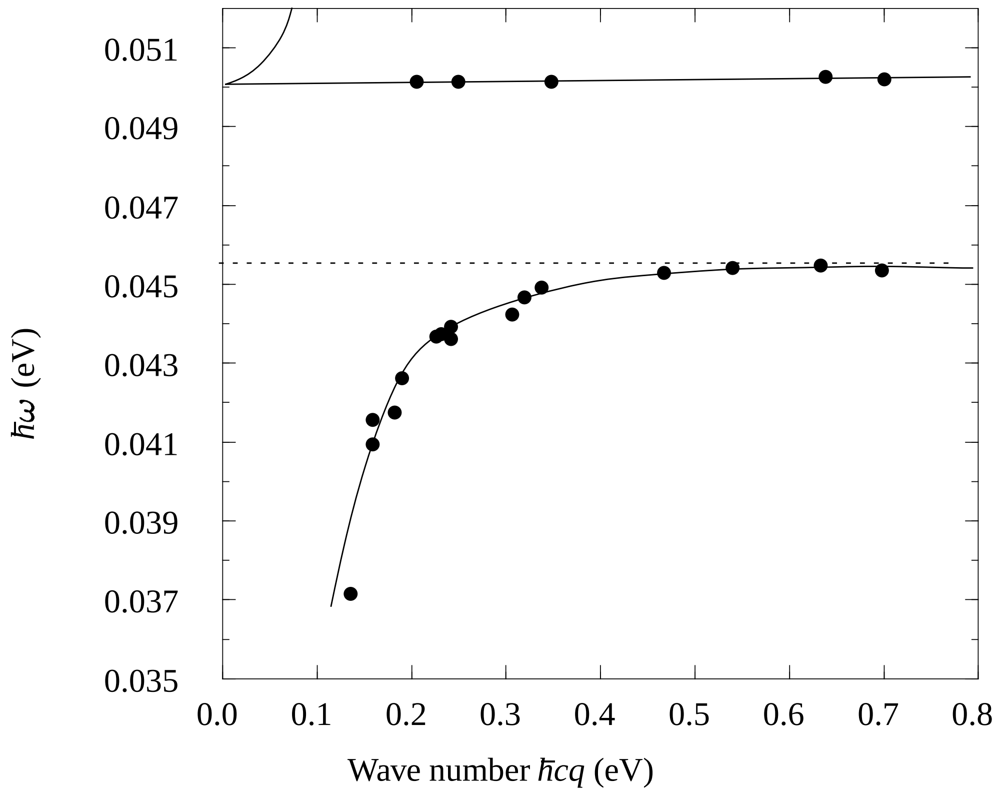


Figure 10: Dispersion relation of polaritons in GaP [Henry and Hopfield (1965)]

Inelastic X-Ray Scattering

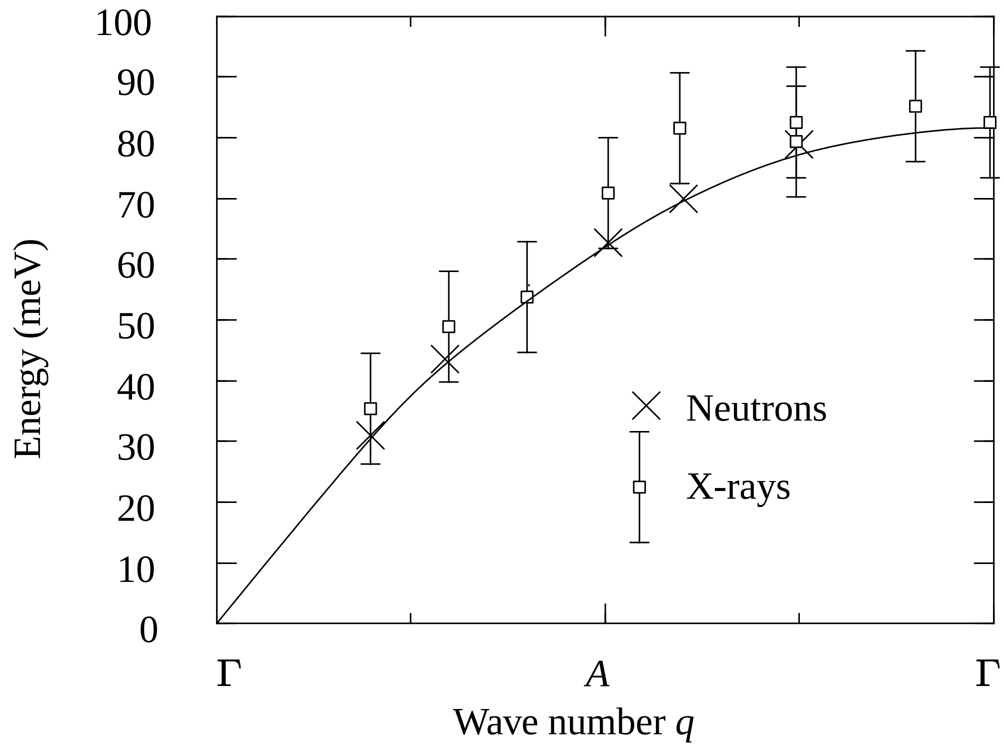


Figure 11: Dispersion relation of longitudinal phonons in beryllium [Dorner et al. (1987).]

Measurement of Work Functions

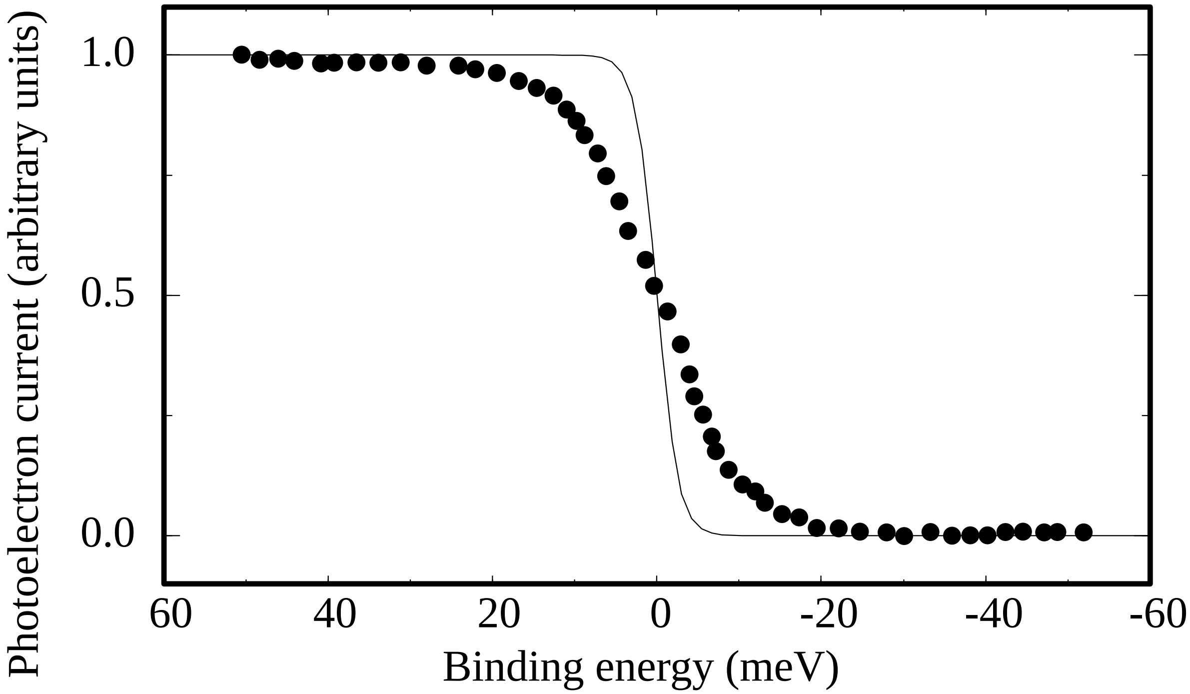


Figure 12: Measurement of Fermi function [Patthey et al. (1990)]

Work Functions

Compound	Surface	ϕ (eV)	Compound	Surface	ϕ (eV)
Ag	(100)	4.64	Na	(110)	2.9
	(110)	4.52	Nb	(100)	4.02
	(111)	4.74		(110)	4.87
Al	(100)	4.20		(111)	4.36
	(110)	4.06	Ni	(100)	5.22
	(111)	4.26		(110)	5.04
Au	(100)	5.47		(111)	5.35
	(110)	5.37	Pt	(100)	5.84
	(111)	5.31	Si	(111) 2×1	4.85
Be	(0001)	5.1		(111) 7×7	4.50
Cu	(100)	5.10		(100) 2×1	4.87
	(110)	4.48	W	(100)	4.63
	(111)	4.94		(110)	5.25
Fe	(100)	4.67		(111)	4.47
Ge	(111) 2×1	4.68	SiC	(0001)	4.6
	(111) 2×8	4.53	AlN	(100)	5.35
K	(110)	2.39	GaAs	(110)	5.56
Mg	(100)	3.71	GaSb	(110)	4.91
Mo	(100)	4.53	InP	(110)	5.85
	(110)	4.95			
	(111)	4.55			

Angle-Resolved Photoemission

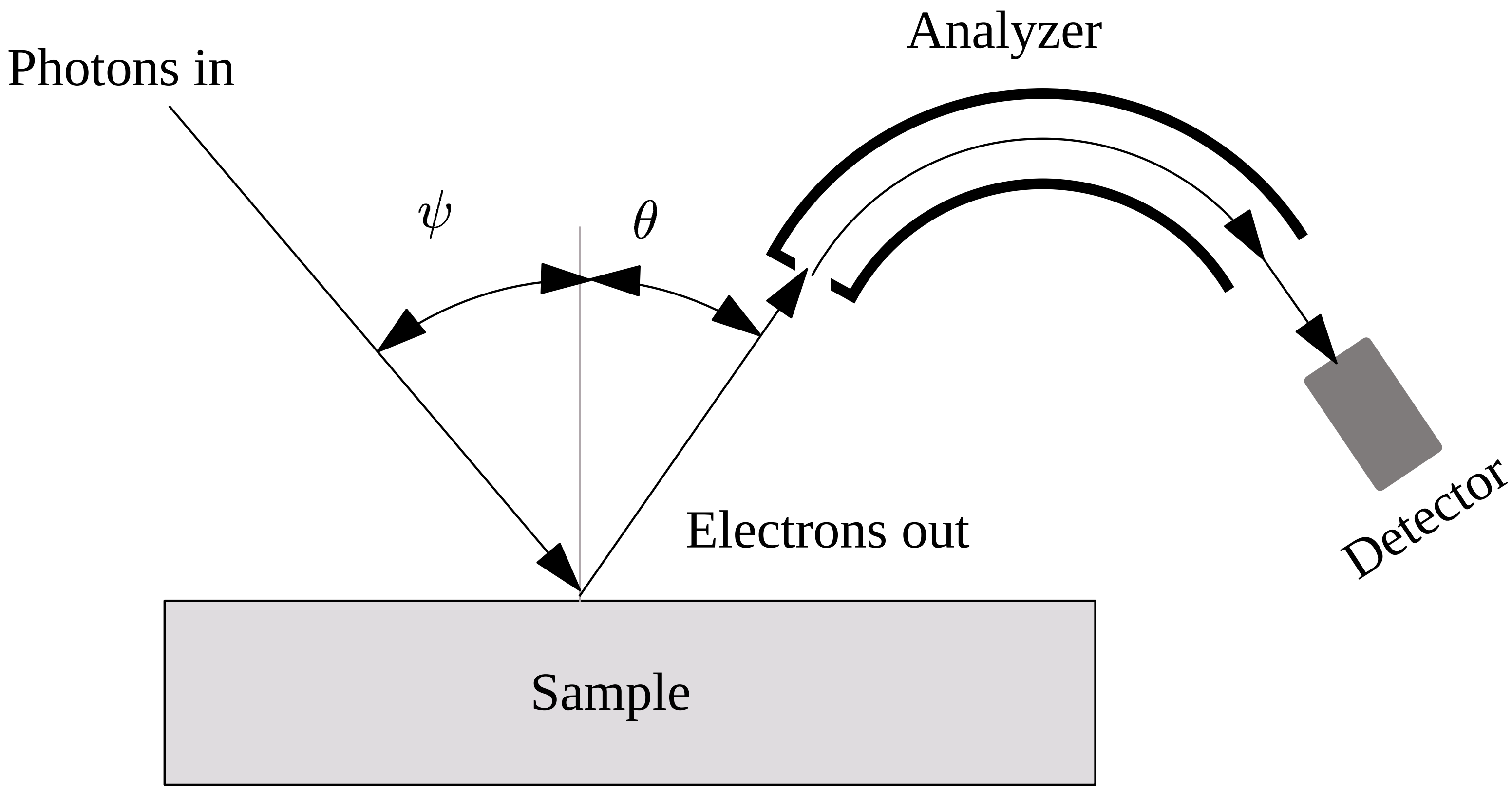


Figure 13: Angle-resolved photoemission experiment.

$$\phi + \mathcal{E}_{\text{kin}} - (-\mathcal{E}_B) = \hbar\omega, \tag{L59}$$

$$\mathcal{E}_B(\vec{k}_{\text{final}}) = \hbar\omega - \phi - \mathcal{E}_{\text{kin}}, \tag{L60}$$

$$\Delta p = \int -\frac{\partial U}{\partial x} dt \approx -\frac{\Delta U}{v}, \tag{L61}$$

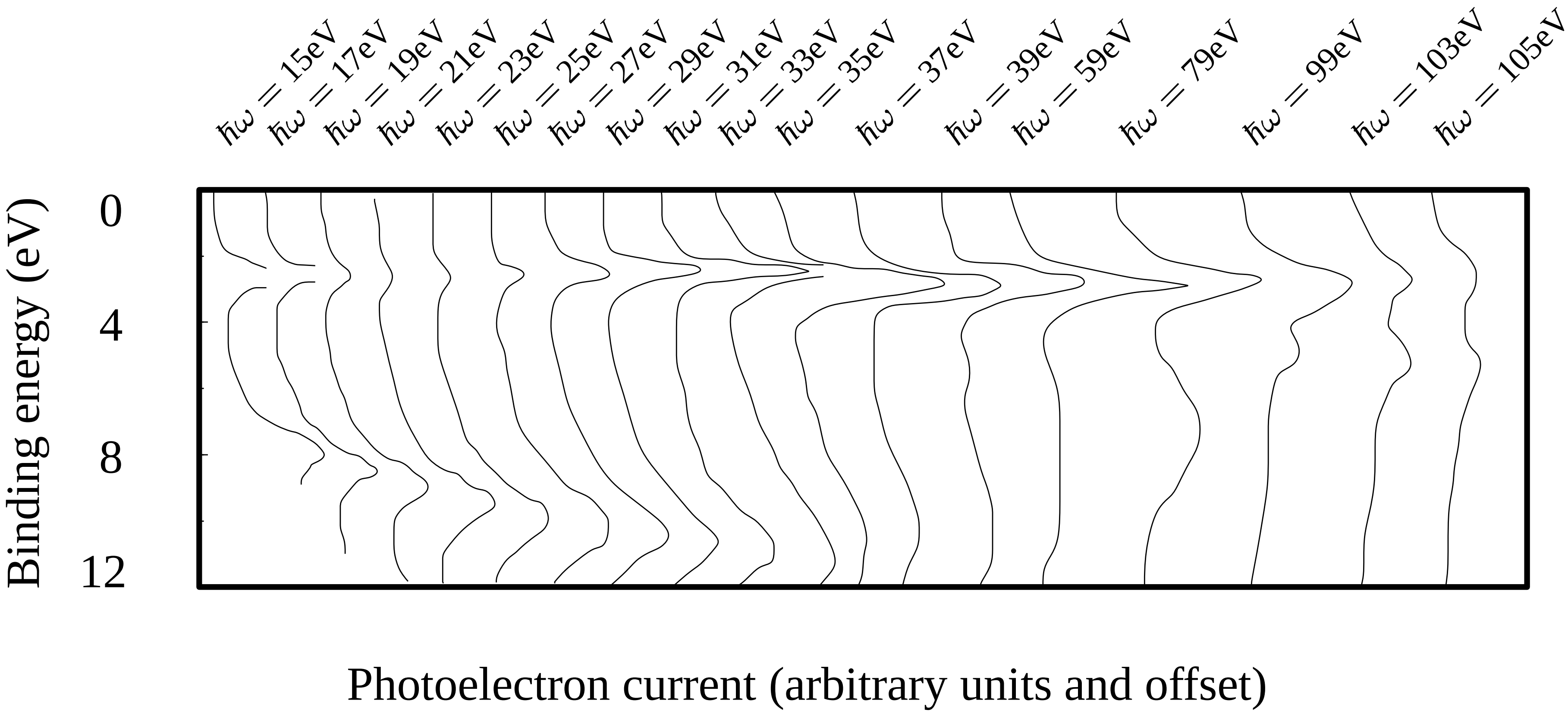


Figure 14: Photon injection and electron emission in beryllium along [0001]. [Jensen et al. (1984)]

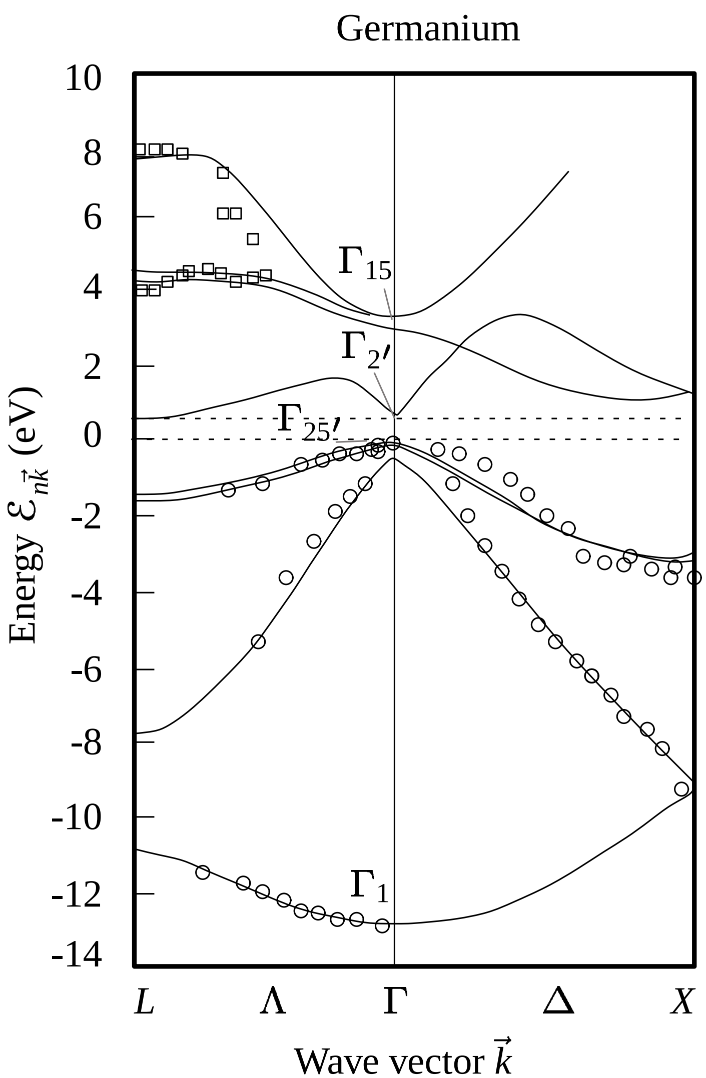


Figure 15: Theoretical calculations of Louie (1992). Experiments of Wachs et al. (1985) and Straub et al. (1986).

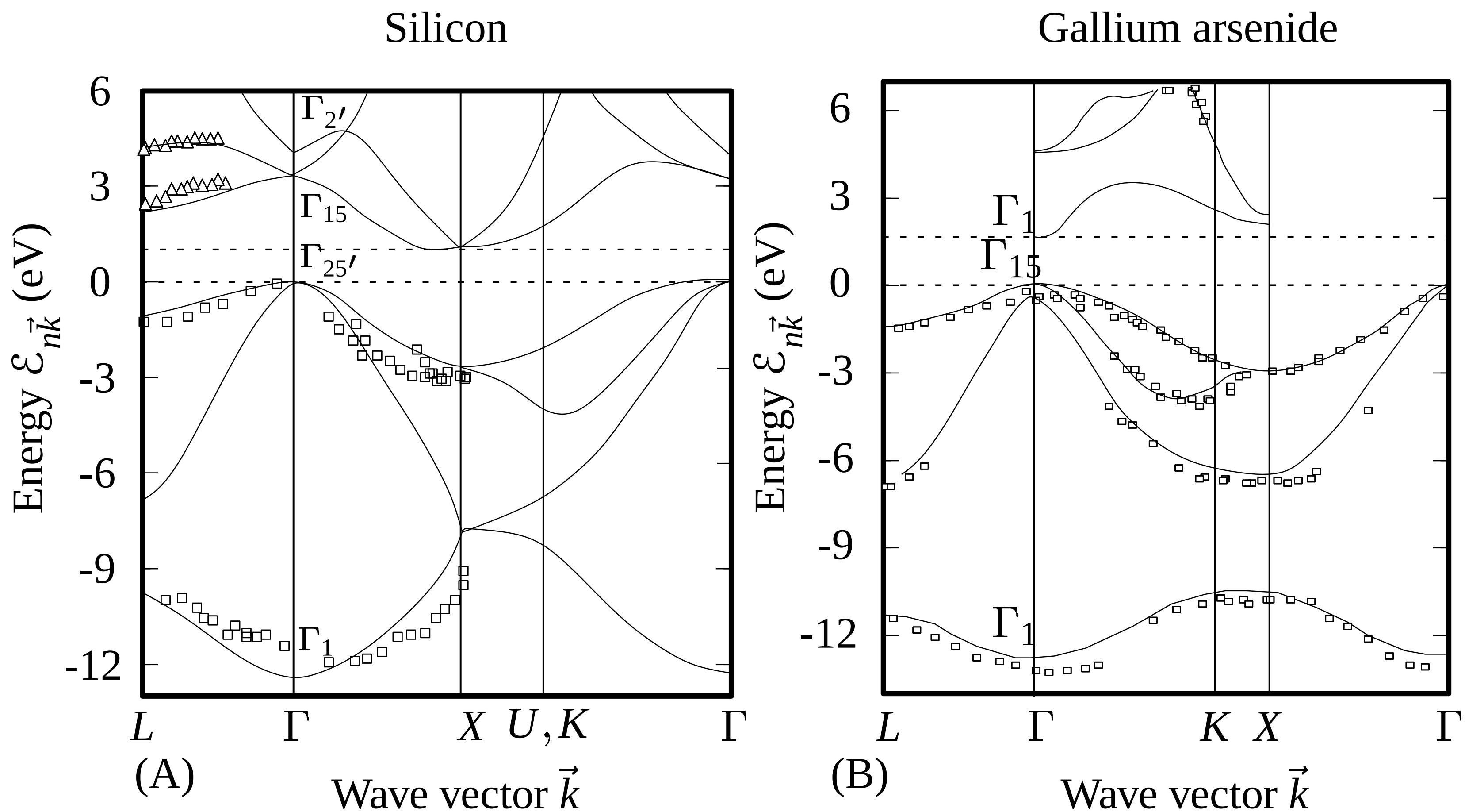


Figure 16: (A) Silicon: theory of Chelikowsky and Cohen (1976), experiments of Straub et al. (1986) and Rich et al. (1989). (B) GaAs: Theory of Pandey and Phillips (1974), experiments of Chiang et al. (1980) and Williams et al. (1986).

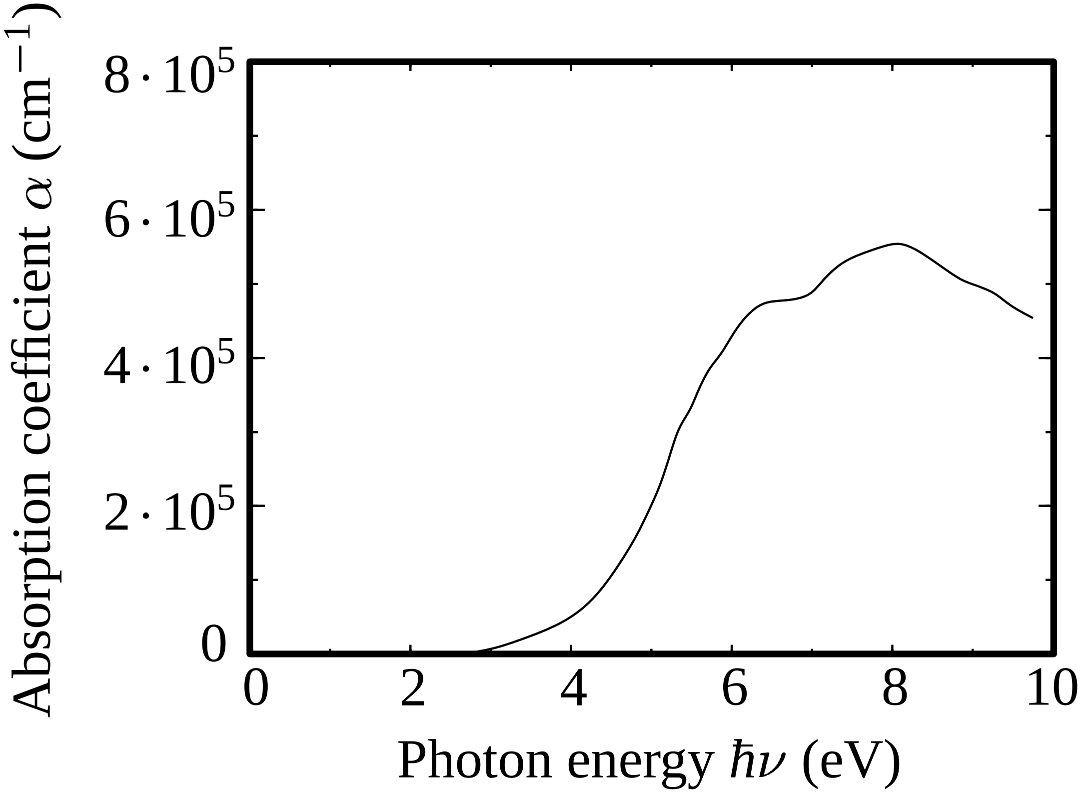


Figure 17: Optical absorption of CoO. [Powell and Spicer (1970).]

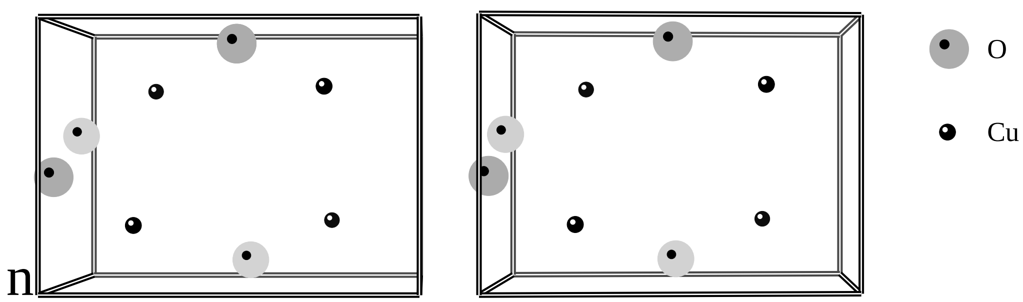


Figure 18: Structure of CuO [Åsbrink and Norrby (1970)].

$$\langle d^9\mathrm{O}^{-\mathrm{II}}|\hat{\mathcal{H}}|d^9\mathrm{O}^{-\mathrm{II}}\rangle \equiv 0 \quad \text{(L62a)}$$

$$\langle d^{10}\mathrm{O}^{-\mathrm{I}}|\hat{\mathcal{H}}|d^{10}\mathrm{O}^{-\mathrm{I}}\rangle \equiv \Delta. \quad \text{(L62b)}$$

$$\langle d^9\mathrm{O}^{-\mathrm{II}}|\hat{\mathcal{H}}|d^{10}\mathrm{O}^{-\mathrm{I}}\rangle = \langle d^{10}\mathrm{O}^{-\mathrm{I}}|\hat{\mathcal{H}}|d^9\mathrm{O}^{-\mathrm{II}}\rangle \equiv T, \quad \text{(L63)}$$

$$\begin{pmatrix} 0 & T \\ T & \Delta \end{pmatrix}. \quad \text{(L64)}$$

$$|\Psi_{\mathrm{i0}}\rangle = \cos\theta_i|d^9\mathrm{O}^{-\mathrm{II}}\rangle - \sin\theta_i|d^{10}\mathrm{O}^{-\mathrm{I}}\rangle \quad \text{(L65a)}$$

where

$$\tan 2\theta_i = \frac{2T}{\Delta}. \quad \text{(L65b)}$$

$$\langle c^{\mathrm{I}}d^9\mathrm{O}^{-\mathrm{II}}|\hat{\mathcal{H}}|c^{\mathrm{I}}d^9\mathrm{O}^{-\mathrm{II}}\rangle \equiv \mathcal{E}_{\mathrm{core}} \quad \text{(L66a)}$$

$$\langle c^{\mathrm{I}}d^{10}\mathrm{O}^{-\mathrm{I}}|\hat{\mathcal{H}}|c^{\mathrm{I}}d^{10}\mathrm{O}^{-\mathrm{I}}\rangle = \mathcal{E}_{\mathrm{core}} + \Delta - U_{\mathrm{cd}}. \quad \text{(L66b)}$$

$$\begin{pmatrix} \mathcal{E}_{\rm core} & T \\ T & \mathcal{E}_{\rm core}+\Delta-U_{\rm cd} \end{pmatrix}. \quad \text{(L67)}$$

$$|\Psi_{f0}\rangle = \cos\theta_f|c^{\rm I}d^9{\rm O}^{-\rm II}\rangle - \sin\theta_f|c^{\rm I}d^{10}{\rm O}^{-\rm I}\rangle \quad \text{(L68a)}$$

$$|\Psi_{f1}\rangle = \sin\theta_f|c^{\rm I}d^9{\rm O}^{-\rm II}\rangle + \cos\theta_f|c^{\rm I}d^{10}{\rm O}^{-\rm I}\rangle, \quad \text{(L68b)}$$

where the label f indicates final states of the valence electrons and

$$\tan 2\theta_f = \frac{2T}{\Delta - U_{cd}}. \quad \text{(L68c)}$$

$$\langle c^0|\hat{P}|c^{\rm I}\rangle\langle\Psi_{i0}|\Psi_{f\,0,1}\rangle \quad \text{(L69)}$$

$$\Delta\mathcal{E} = \sqrt{(\Delta - U_{cd})^2 + 4T^2}, \quad \text{(L70)}$$

$$\frac{|\langle\Psi_{i0}|\Psi_{f1}\rangle|^2}{|\langle\Psi_{i0}|\Psi_{f0}\rangle|^2} = \tan^2(\theta_i - \theta_f). \quad \text{(L71)}$$

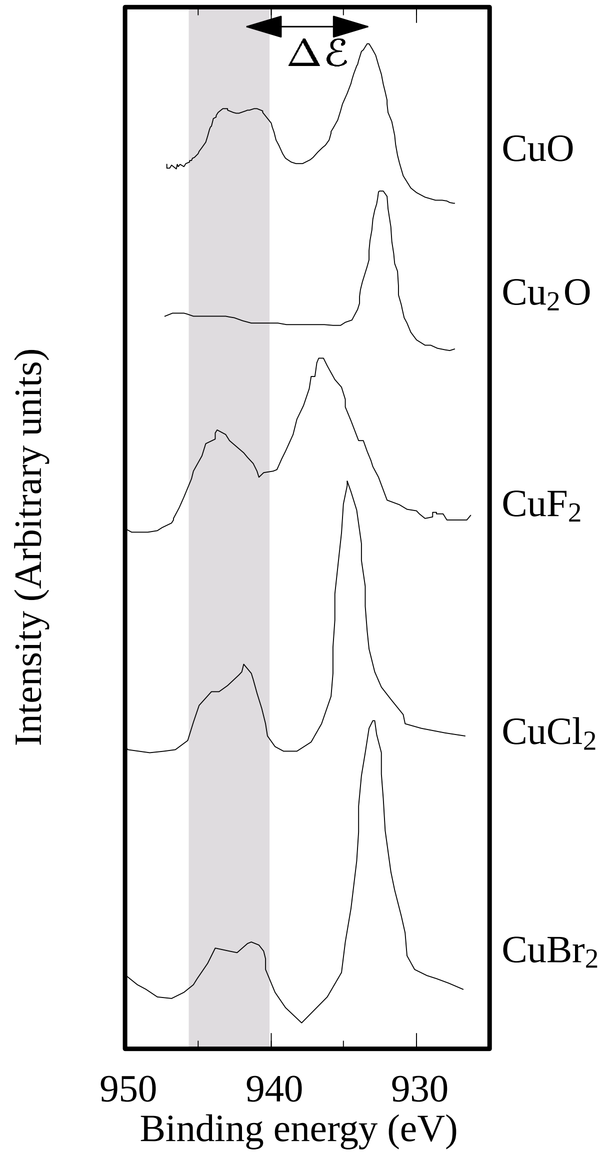
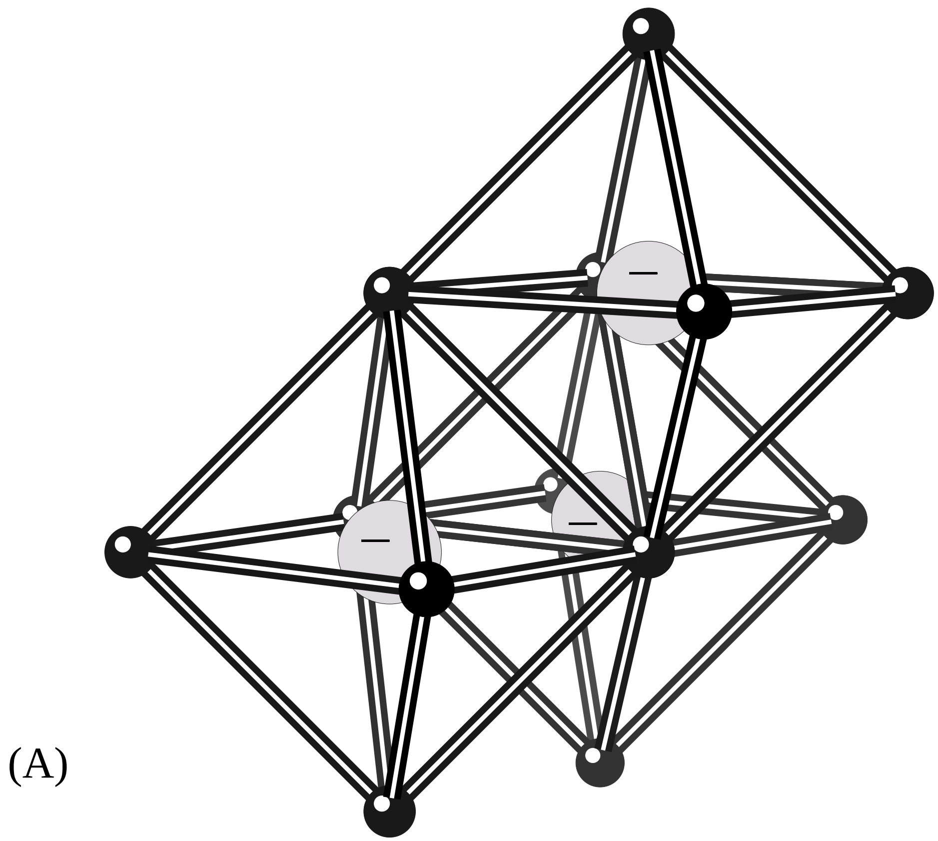
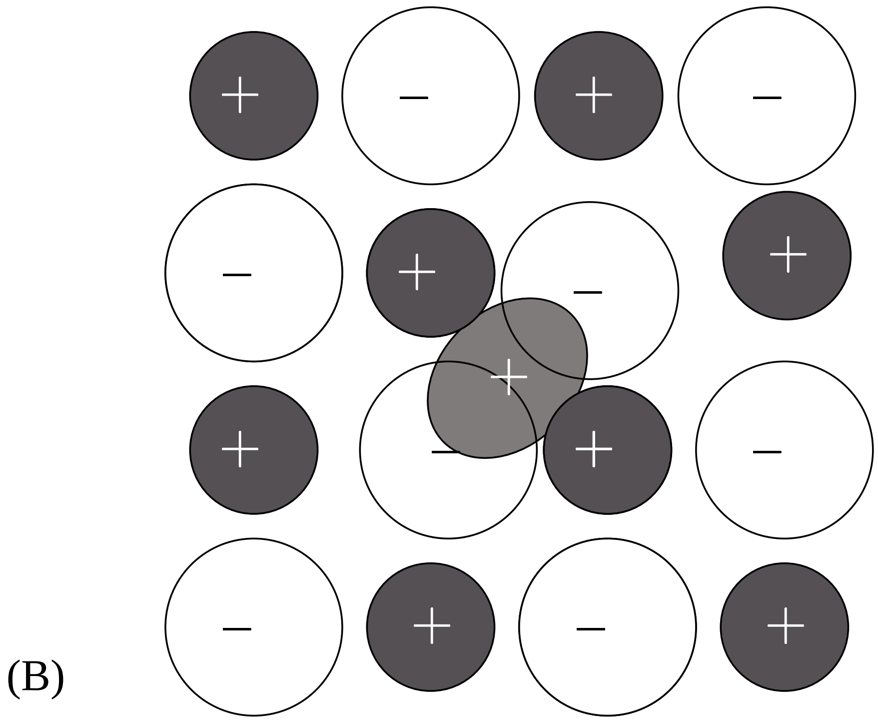


Figure 19: Core-level photoemission from CuO [Ghijsen et al. (1988), and van der Laan et al. (1981) .]

F_3 or R center



V_K center



Definitions

- ☞ Polarization
- ☞ Optical Modes
- ☞ Polaritons
- ☞ Polarons
- ☞ Point Defects
- ☞ Color Centers
- ☞ Electron Spin Resonance
- ☞ Franck–Condon Effect
- ☞ Urbach Tails

Polarization

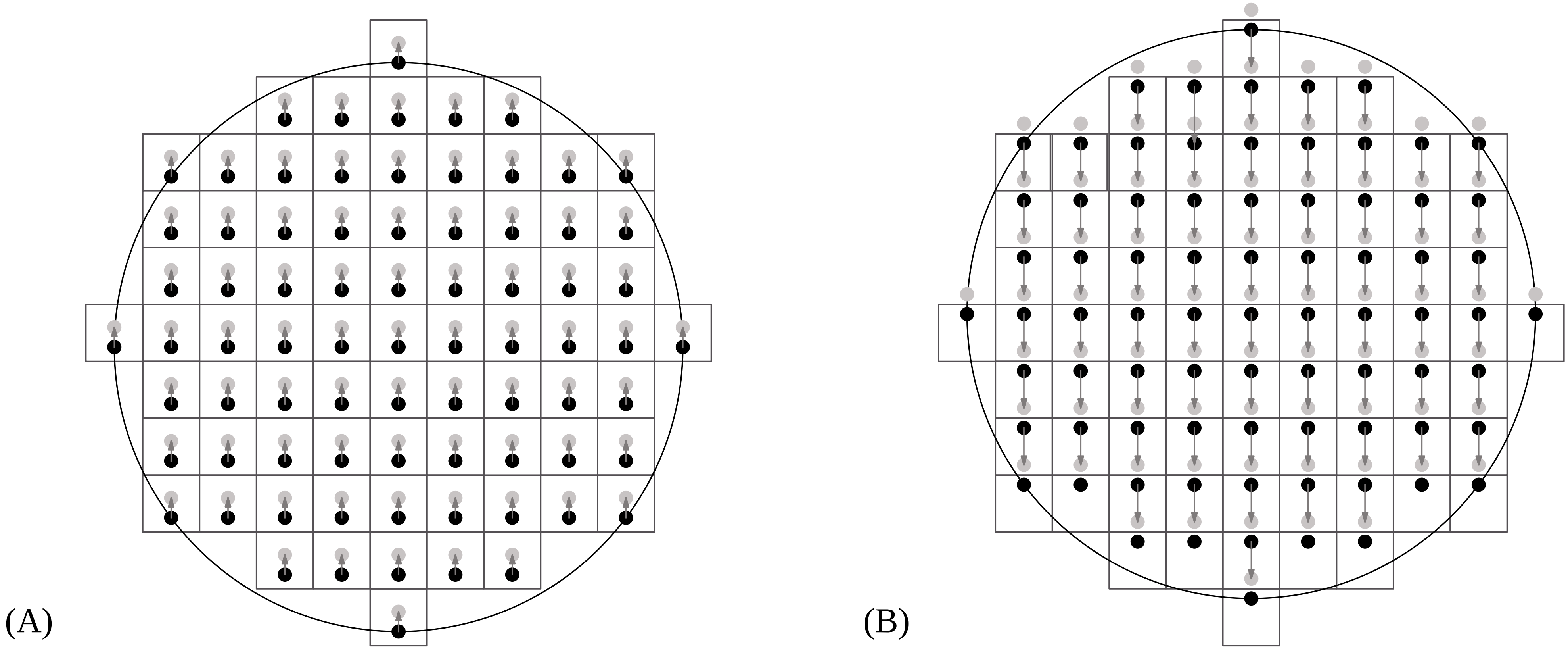


Figure 1: Ambiguity of dielectric

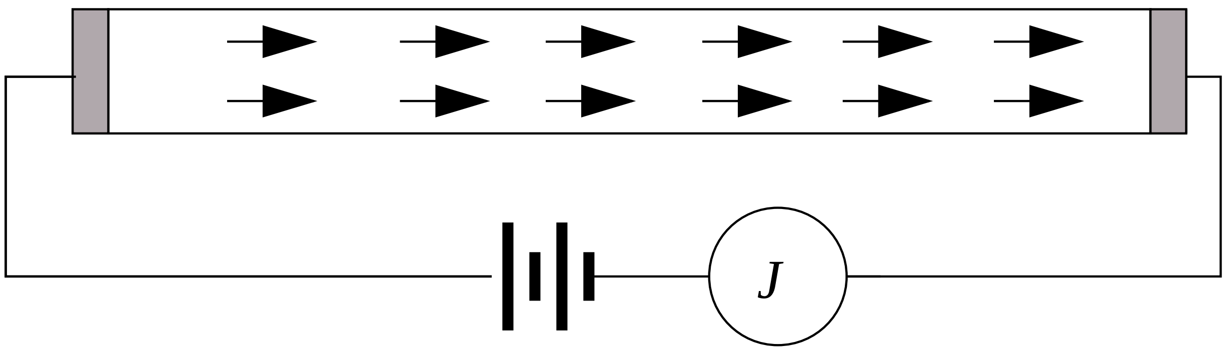


Figure 2: Measuring the spontaneous electric polarization of a sample.

$$\vec{E} = \vec{E}_0 - \frac{4\pi}{3}\vec{P}. \tag{L1}$$

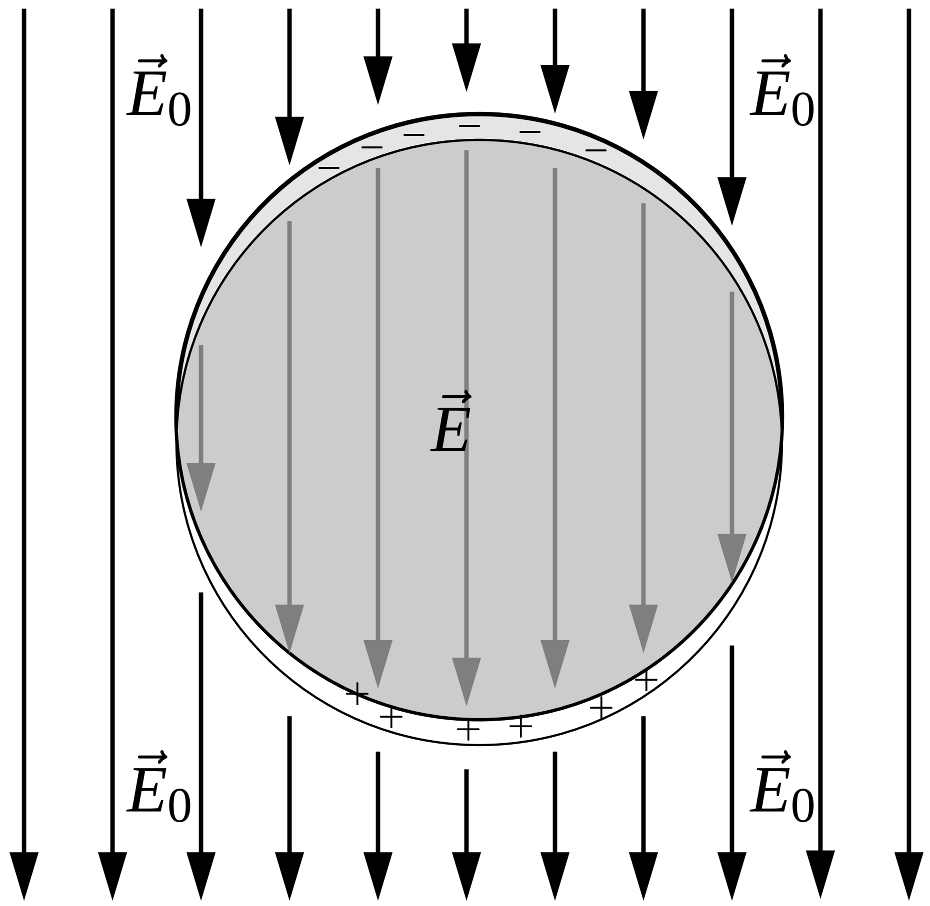


Figure 3: A dielectric sphere placed in a uniform electric field $\vec{E}_0$.

Clausius–Mossotti Relation

$$\vec{E}_1 = -\sum_{\vec{R}\neq 0} \vec{\nabla}_{\vec{R}} \frac{\vec{p}\cdot\vec{R}}{R^3} = \sum_{\vec{R}\neq 0} 3\frac{\vec{R}(\vec{R}\cdot\vec{p})}{R^5} - \frac{\vec{p}}{R^3} \tag{L2}$$

$$\vec{p} = \alpha\vec{E}_{\text{cell}} \Rightarrow \vec{p} = \alpha\vec{E}_0. \tag{L3}$$

$$\vec{P} = n\alpha\vec{E}_0. \tag{L4}$$

$$\frac{E+4\pi P}{E} = \quad ? \qquad\qquad ? \tag{L5}$$

$$\Rightarrow \epsilon = \quad ? \qquad\qquad ?. \tag{L6}$$

$$\vec{E} = \vec{E}_0 - \mathcal{N}\vec{P}, \tag{L7}$$

Clausius–Mossotti Relation

$$\vec{E}_{\text{cell}} = \vec{E}_0 - \mathcal{N}\vec{P} + \frac{4\pi}{3}\vec{P} = \vec{E} + \frac{4\pi}{3}\vec{P} \tag{L8}$$

$$\Rightarrow \vec{E}_{\text{cell}} = \frac{4\pi}{3}\frac{\epsilon+2}{\epsilon-1}\vec{P} \tag{L9}$$

$$= \frac{4\pi}{3}\frac{\epsilon+2}{\epsilon-1}n\alpha\vec{E}_{\text{cell}} \tag{L10}$$

$$\Rightarrow \alpha = \frac{3}{4\pi n}\left(\frac{\epsilon-1}{\epsilon+2}\right) \tag{L11}$$

$$\Rightarrow \epsilon = \frac{3+8\pi n\alpha}{3-4\pi n\alpha}. \tag{L12}$$

Optical Modes in Ionic Crystals

$$\vec{u} = \vec{u}_1 - \vec{u}_2 \tag{L13}$$

$$\bar{\omega} \equiv \sqrt{\frac{2\mathcal{K}}{M}}, \text{ where } M = \frac{M_1 M_2}{(M_1 + M_2)}. \tag{L14}$$

$$M\ddot{\vec{u}} = -M\bar{\omega}^2\vec{u} - M\dot{\vec{u}}/\tau + e^\star \vec{E}_{\text{cell}}. \tag{L15}$$

$$\Rightarrow \vec{u} = -\frac{e^\star}{M(\omega^2 - \bar{\omega}^2 + i\omega/\tau)}\vec{E}_{\text{cell}}. \tag{L16}$$

$$\vec{p} = e^\star \vec{u} + \alpha^\infty \vec{E}_{\text{cell}}. \tag{L17}$$

$$\vec{P} = n\left[\frac{(e^\star)^2}{M(\bar{\omega}^2 - \omega^2 - i\omega/\tau)} + \alpha^\infty\right]\vec{E}_{\text{cell}} \tag{L18}$$

$$\Rightarrow \frac{3}{4\pi}\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = n\left[\frac{(e^\star)^2}{M(\bar{\omega}^2 - \omega^2 - i\omega/\tau)} + \alpha^\infty\right]. \tag{L19}$$

$$\alpha^\infty = \frac{3}{4\pi n}\left(\frac{\epsilon^\infty - 1}{\epsilon^\infty + 2}\right). \tag{L20}$$

$$\vec{u} = \frac{e^\star \vec{E}_{\text{cell}}}{M\bar{\omega}^2} \tag{L21}$$

$$(e^\star)^2 = \frac{9M\bar{\omega}^2}{4\pi n}\left(\frac{\epsilon^0 - \epsilon^\infty}{(\epsilon^0 + 2)(\epsilon^\infty + 2)}\right). \tag{L22}$$

$$\epsilon(\omega) = \epsilon^\infty + \frac{\epsilon^\infty - \epsilon^0}{\left(\frac{\omega^2}{\bar{\omega}^2} + i\frac{\omega}{\tau\bar{\omega}^2}\right)\left(\frac{\epsilon^0 + 2}{\epsilon^\infty + 2}\right) - 1}. \tag{L23}$$

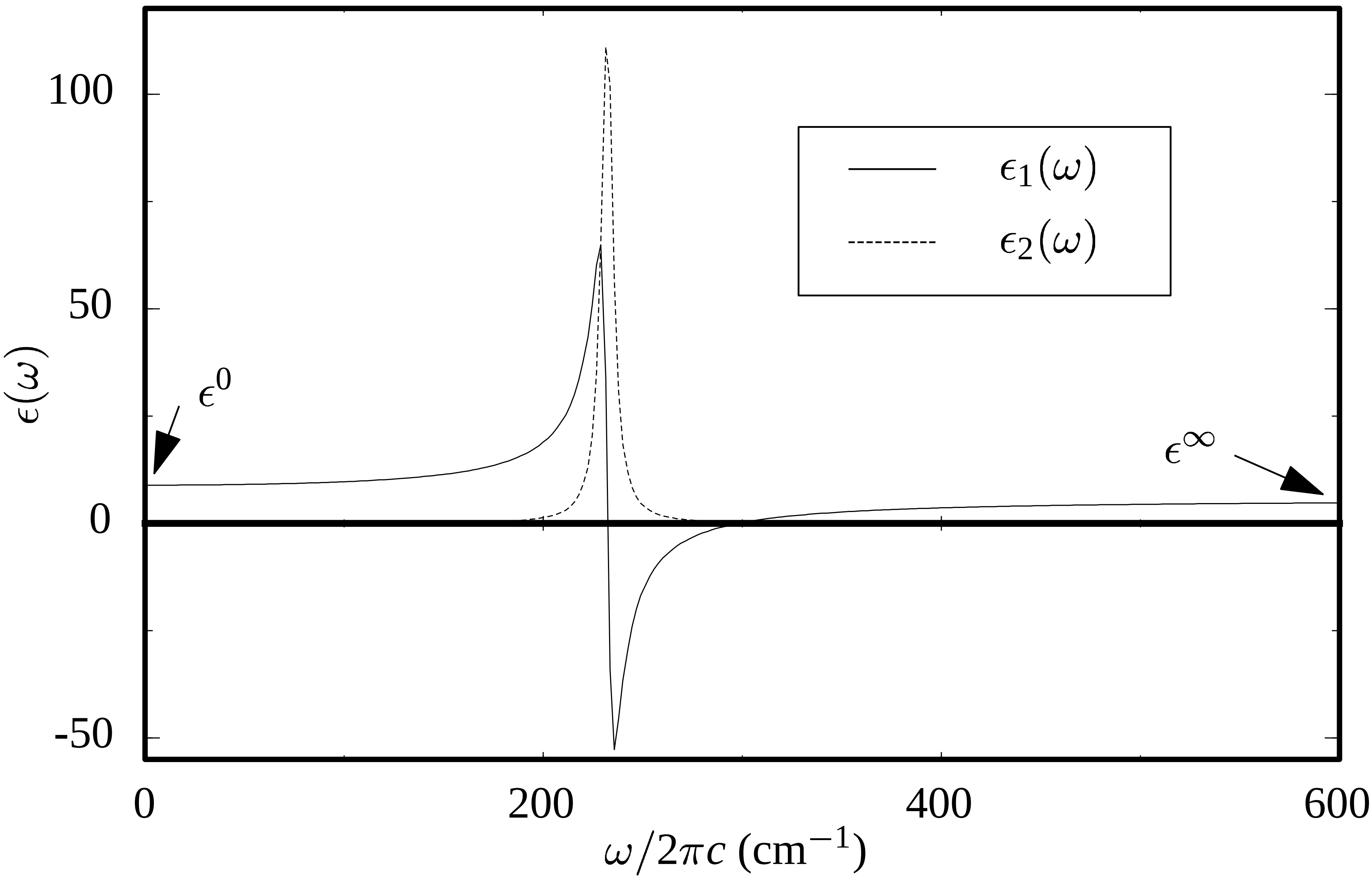


Figure 4: Dielectric function for CdS, deduced from reflection data by Balkanski (1972).

Polaritons

$$\omega_T^2 = \bar{\omega}^2 \left(\frac{\epsilon^\infty + 2}{\epsilon^0 + 2} \right) \tag{L24}$$

$$\omega_{\mathrm{L}}^2 = \omega_{\mathrm{T}}^2 \left[\frac{\epsilon^0}{\epsilon^\infty} \right] \tag{L25}$$

$$\Rightarrow \epsilon(\omega) = \epsilon^\infty \left[\frac{\omega^2 + i\omega/\tau - \omega_{\mathrm{L}}^2}{\omega^2 + i\omega/\tau - \omega_{\mathrm{T}}^2} \right]. \tag{L26}$$

$$\frac{\omega^2 \epsilon(\omega)}{c^2} = q^2, \tag{L27}$$

$$\epsilon(\omega) = 0. \tag{L28}$$

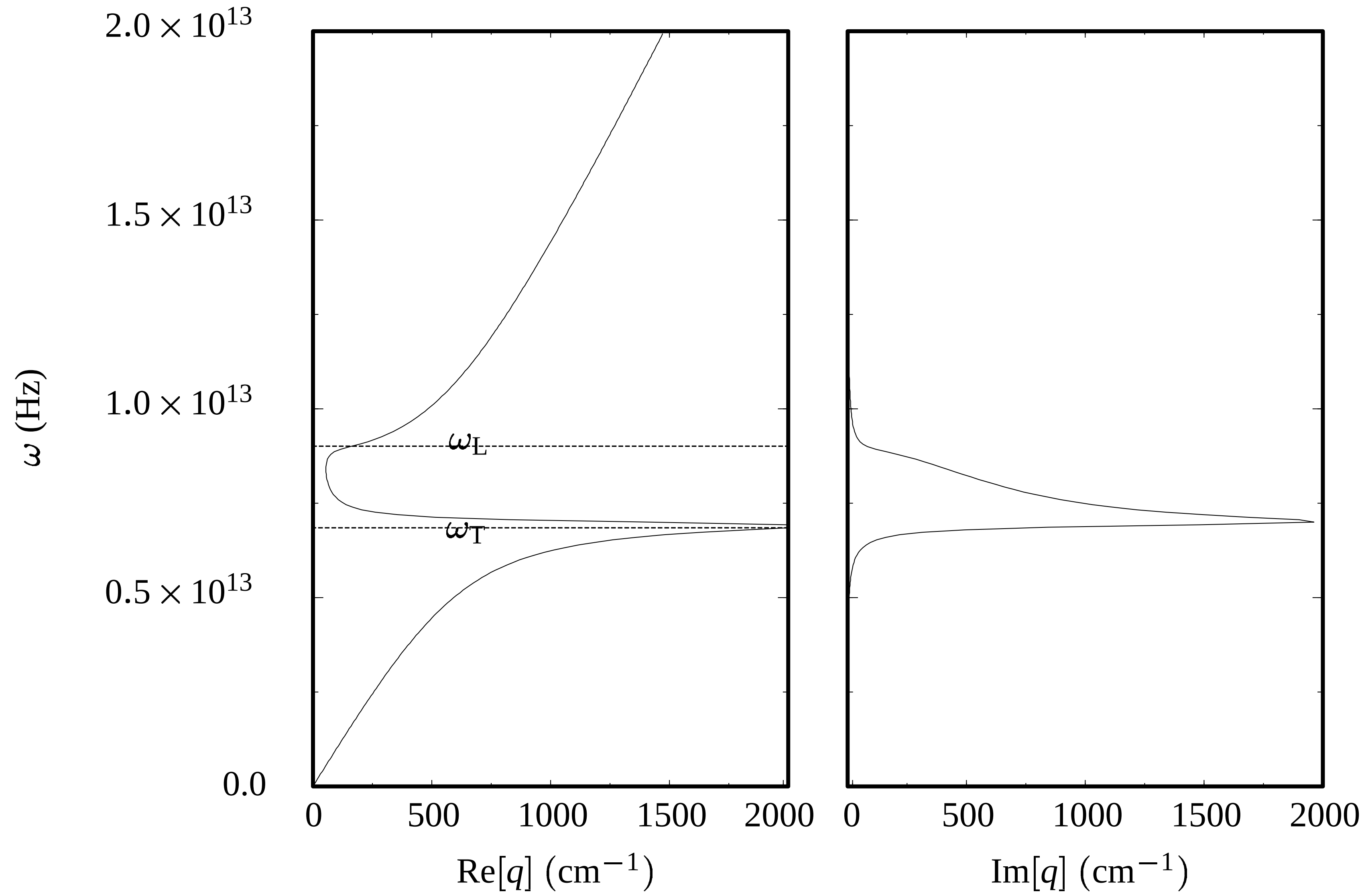


Figure 5: Frequency ω of transverse waves as a function of complex wave vector q.

Compound	ϵ^{∞}	ϵ^{0}	$\frac{\omega_T}{2\pi c}$ (cm^{-1})	$\frac{\omega_L}{2\pi c}$ (cm^{-1})	$\frac{m^\star}{m}$	α_p	$\frac{m^\star}{m}(1+\frac{\alpha_p}{6})$	$\frac{m^\star_{pol}}{m}$
LiF	1.93	8.50	318	667				
LiH	3.60	12.90	590	1116				
NaF	1.75	4.73	262	431				
NaI	3.08	6.60	124	182				
KF	1.86	5.11	202	334				
KI	2.68	4.68	102	144	0.325	2.51	0.461	0.540
RbF	1.94	5.99	163	286				
RbI	2.61	4.55	76	108	0.368	3.16	0.562	0.720
CsF	2.17	7.27	134	245				
CsCl	2.67	6.68	107	168				
CsBr	2.83	6.38	78	118				
CsI	3.09	6.32	66	94	0.420	3.67	0.677	0.960
GaAs	10.90	12.83	273	296	0.066	0.07	0.067	0.066
GaSb	14.40	15.69	231	240	0.047	0.03	0.047	0.047
GaP	8.46	10.28	365	403	0.338	0.20	0.349	0.350
InAs	11.80	14.61	219	243	0.023	0.05	0.023	0.023
InSb	15.68	17.88	185	197	0.014	0.02	0.014	0.013
CdS	5.27	8.42	244	308	0.155	0.53	0.169	0.170
CdSe	6.10	9.30	174	214	0.130	0.46	0.140	0.140
CdTe	7.21	10.23	141	168	0.091	0.32	0.096	0.096
ZnS	5.14	8	282	352	0.280	0.65	0.310	0.313
ZnSe	5.90	8.33	207	246	0.171	0.43	0.183	0.184
ZnTe	7.28	9.86	177	205	0.160	0.33	0.169	0.169
ZnO	4	8.15	414	591	0.240	0.85	0.274	0.279
PbS	18.50	190	67	214	0.082	0.32	0.086	0.087
PbSe	25.20	280	44	147	0.047	0.21	0.049	0.049
PbTe	36.90	450	32	110	0.034	0.15	0.035	0.035

$$\vec{P} = n[e^\star \vec{u} + \alpha^\infty \vec{E}_{\text{cell}}]. \tag{L29}$$

$$\vec{E} = -4\pi\vec{P}, \tag{L30}$$

$$\vec{E}_{\text{cell}} = \frac{2}{3}\vec{E} = -\frac{8\pi}{3}\vec{P} \tag{L31}$$

$$\Rightarrow \vec{P} = \frac{ne^\star}{1 + n\alpha^\infty 8\pi/3}\vec{u}. \tag{L32}$$

$$\frac{ne^\star}{1 + n\alpha^\infty 8\pi/3} = n\frac{\sqrt{\frac{9M\bar{\omega}^2}{4\pi n}\frac{\epsilon^0 - \epsilon^\infty}{(\epsilon^0 + 2)(\epsilon^\infty + 2)}}}{1 + 2(\epsilon^\infty - 1)/(\epsilon^\infty + 2)} \tag{L33}$$

$$= \sqrt{\frac{M\omega_{\text{L}}^2 n}{4\pi}\left(\frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0}\right)}. \tag{L34}$$

$$\vec{P} = \beta \vec{u}, \tag{L35}$$

$$\beta = \sqrt{\frac{M\omega_L^2 n}{4\pi}\left(\frac{1}{\epsilon^\infty} - \frac{1}{\epsilon^0}\right)}. \tag{L36}$$

$$\hat{U}_{\text{el-phon}} = e\int d\vec{r}'\, \vec{P}(\vec{r}') \cdot \nabla_{\vec{r}'} \frac{1}{|\hat{R} - \vec{r}'|}. \tag{L37}$$

$$\hat{U}_{\text{el-phon}} = e\beta\int d\vec{r}' \sqrt{\frac{\hbar}{2M\omega_L N}} \sum_{\vec{k}} \frac{\vec{k}}{k} \cdot \left[\nabla_{\vec{r}'} \frac{1}{|\vec{r}' - \hat{R}|}\right] [e^{i\vec{k}\cdot\vec{r}'}\hat{a}_{\vec{k}} + e^{-i\vec{k}\cdot\vec{r}'}\hat{a}^\dagger_{\vec{k}}] \tag{L38}$$

$$= -e\beta\int d\vec{r}' \sqrt{\frac{\hbar}{2M\omega_L N}} \sum_{\vec{k}} \frac{i\vec{k}\cdot\vec{k}}{k} \frac{1}{|\vec{r}' - \hat{R}|} [e^{i\vec{k}\cdot\vec{r}'}\hat{a}_{\vec{k}} - e^{-i\vec{k}\cdot\vec{r}'}\hat{a}^\dagger_{\vec{k}}]. \tag{L39}$$

$$\hat{U}_{\text{el-phon}} = e\beta 4\pi i \sum_{\vec{k}} \sqrt{\frac{\hbar}{2M\omega_L N}} \frac{1}{k} [e^{-i\vec{k}\cdot\hat{R}}\hat{a}^\dagger_{\vec{k}} - e^{i\vec{k}\cdot\hat{R}}\hat{a}_{\vec{k}}]. \tag{L40}$$

Polarons

$$\alpha_{\rm p} \equiv \frac{e^2}{2}\sqrt{\frac{2m^\star\omega_L}{\hbar}}\frac{1}{\hbar\omega_L}\left(\frac{1}{\epsilon^\infty}-\frac{1}{\epsilon^0}\right) = 1.44\cdot 10^8\left(\frac{1}{\epsilon^\infty}-\frac{1}{\epsilon^0}\right)\sqrt{\frac{m^\star/m}{\omega_{\rm L}\cdot {\rm s}}}. \qquad \text{(L41)}$$

$$\hat{U}_{\rm el-phon} = i\sqrt{4\pi\alpha_{\rm p}}\frac{1}{\sqrt{\mathcal{V}}}\left(\frac{\hbar^5\omega_L^3}{2m^\star}\right)^{1/4}\sum_{\vec{k}}\frac{1}{k}[e^{-i\vec{k}\cdot\hat{R}}\hat{a}^\dagger_{\vec{k}} - e^{i\vec{k}\cdot\hat{R}}\hat{a}_{\vec{k}}]. \qquad \text{(L42)}$$

$$\hat{U}_{\rm el-phon} = \sum_{\vec{q}\vec{q}'}\hat{c}^\dagger_{\vec{q}'}\langle\vec{q}'|\hat{U}_{\rm el-phon}|\vec{q}\rangle\hat{c}_{\vec{q}} \qquad \text{(L43)}$$

$$\hat{U}_{\rm el-phon} = i\sqrt{4\pi\alpha_{\rm p}}\frac{1}{\sqrt{\mathcal{V}}}\left(\frac{\hbar^5\omega_L^3}{2m^\star}\right)^{1/4}\sum_{\vec{q}''\vec{k}}\frac{1}{k}[\hat{c}^\dagger_{\vec{q}''-\vec{k}}\hat{c}_{\vec{q}''}\hat{a}^\dagger_{\vec{k}} - \hat{c}^\dagger_{\vec{q}''+\vec{k}}\hat{c}_{\vec{q}''}\hat{a}_{\vec{k}}]. \qquad \text{(L44)}$$

$$\Delta\mathcal{E}^{(2)} = \sum_{\Phi'\vec{q}'}\frac{|\langle\vec{q}|\langle\Phi_0|\hat{U}_{\rm el-phon}|\Phi'\rangle|\vec{q}'\rangle|^2}{\mathcal{E}(\vec{q},\Phi_0)-\mathcal{E}(\vec{q}',\Phi')}. \qquad \text{(L45)}$$

$$\Delta\mathcal{E}^{(2)} = 4\pi\alpha_{\rm p}\frac{1}{\mathcal{V}}\sqrt{\frac{\hbar^5\omega_{\rm L}^3}{2m^\star}}\sum_{\vec{q}'}\frac{1}{|\vec{q}-\vec{q}'|^2}\left[\frac{1}{\frac{\hbar^2q^2}{2m^\star}-\left(\frac{\hbar^2q'^2}{2m^\star}+\hbar\omega_{\rm L}\right)}\right] \quad \text{(L46)}$$

$$= 4\pi\alpha_{\rm p}\frac{1}{\mathcal{V}}\sqrt{\frac{\hbar^5\omega_{\rm L}^3}{2m^\star}}\int dq'\,\frac{d(\cos\theta)}{(2\pi)^3}\,\frac{2\pi\mathcal{V}}{\frac{\hbar^2q^2}{2m^\star}-\left(\frac{\hbar^2|\vec{q}'+\vec{q}|^2}{2m^\star}+\hbar\omega_{\rm L}\right)} \quad \text{(L47)}$$

$$= \frac{\alpha_{\rm p}}{\pi}\sqrt{\frac{\hbar^5\omega_{\rm L}^3}{2m^\star}}\int_{-1}^{1}ds\int_0^\infty dq'\,\frac{1}{\frac{\hbar^2q^2}{2m^\star}-\left(\frac{\hbar^2(q'^2+q^2+2qq's)}{2m^\star}+\hbar\omega_{\rm L}\right)} \quad \text{(L48)}$$

$$= -\alpha_{\rm p}\sqrt{m^\star\hbar\omega_{\rm L}^3}\,\frac{\sqrt{2}}{q}\sin^{-1}\sqrt{\frac{\hbar^2q^2}{2m^\star\hbar\omega_{\rm L}}}. \quad \text{(L49)}$$

$$\Delta\mathcal{E}^{(2)} = -\alpha_{\rm p}\hbar\omega_{\rm L} - \alpha_{\rm p}\frac{\hbar^2q^2}{12m^\star}. \quad \text{(L50)}$$

Polarons

$$\frac{m^\star_{\text{pol}}}{m^\star} = 1 + \frac{\alpha_{\text{p}}}{6}.$$ Table of data.

$$\Delta\mathcal{E}^{(2)} = -\alpha_{\text{p}}\sqrt{m^\star\hbar\omega_{\text{L}}^3}\frac{\sqrt{2}}{q}\left[\pi/2 + i\cosh^{-1}\sqrt{\frac{\hbar^2 q^2}{2m^\star\hbar\omega_{\text{L}}}}\right]. \quad \text{(L51)}$$

$$\exp\left[-\frac{i}{\hbar}(\mathcal{E}^{(0)} + \Delta\mathcal{E}^{(2)})t\right], \quad \text{(L52)}$$

$$\exp\left[\frac{2}{\hbar}\text{Im}(\Delta\mathcal{E}^{(2)})t\right]. \quad \text{(L53)}$$

$$2\alpha_{\text{p}}\sqrt{m^\star\hbar\omega_{\text{L}}^3}\frac{\sqrt{2}}{\hbar q}\cosh^{-1}\sqrt{\frac{\hbar^2 q^2}{2m^\star\hbar\omega_{\text{L}}}}. \quad \text{(L54)}$$

Vacancies

Crystal	Cohesive Energy $\mathcal{E}/N$ (eV)	Vacancy Energy (eV)
Na	1.16	0.42
Au	3.8	0.97
Al	3.4	0.76
Pt	5.3	1.4
Ne	0.021	0.020
Kr	0.11	0.077
Ge	3.9	2.0

F Centers

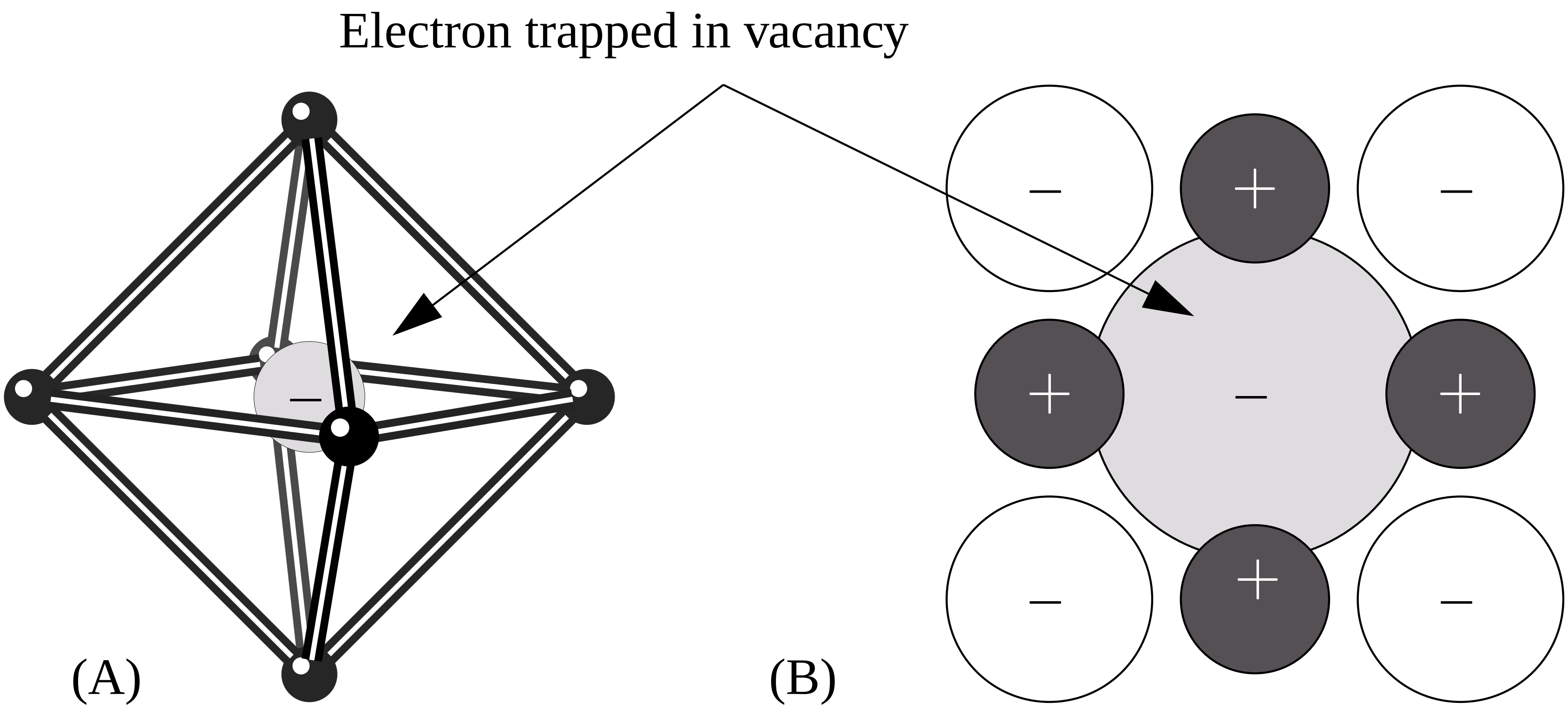


Figure 6: The F center is a halogen ion vacancy that has trapped an electron.

F Centers

Compound	$\mathcal{E}_{abs}$ (eV)	$\mathcal{E}_{em}$ (eV)	Compound	$\mathcal{E}_{abs}$ (eV)	$\mathcal{E}_{em}$ (eV)
NaF	3.72	1.67	RbCl	2.05	1.09
NaCl	2.77	0.98	RbBr	1.86	0.87
KF	2.85	1.66	RbI	1.71	0.81
KCl	2.31	1.22	CsF	1.89	1.42
KBr	2.06	0.92	CsCl	2.17	1.26
KI	1.87	0.83	CsBr	1.96	0.91
RbF	2.43	1.33	CsI	1.68	0.74

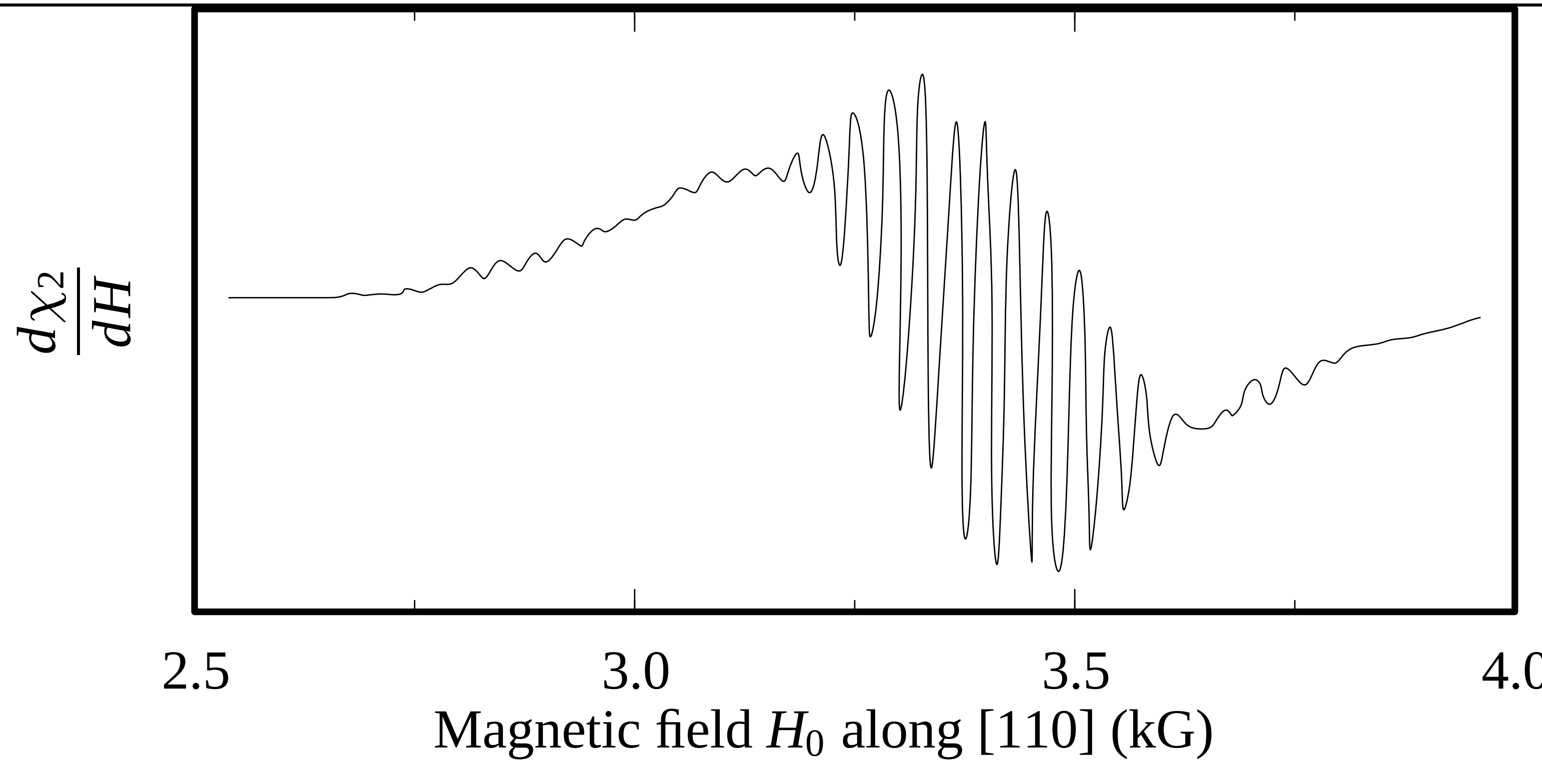


Figure 7: Electron spin resonance in RbCl F centers at a temperature of 90 K. [Source: Pick (1972)]

$$\vec{B} = \vec{B}_0 + \sum_l \vec{B}_l, \tag{L55}$$

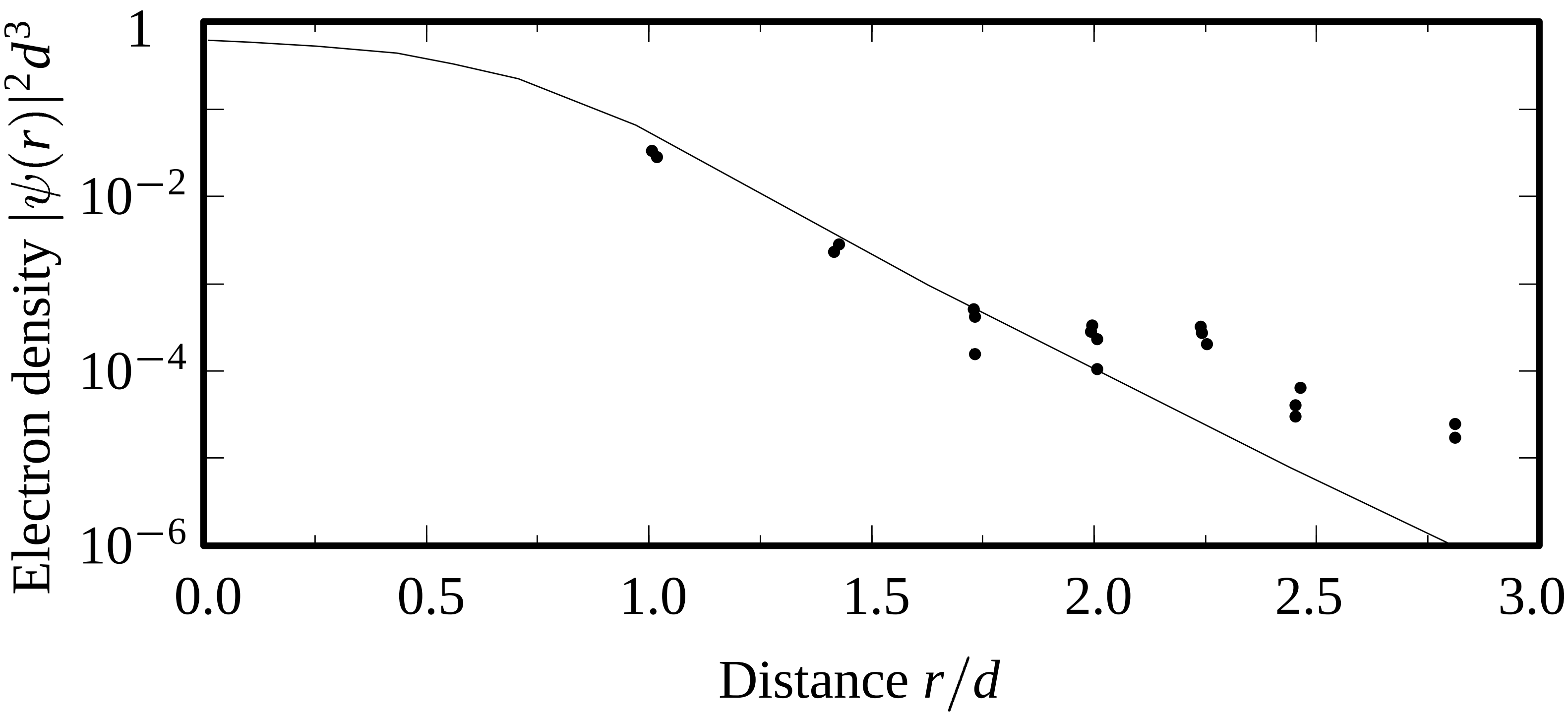


Figure 8: Electron density versus distance from vacancy center [Seidel and Wolf (1968)]

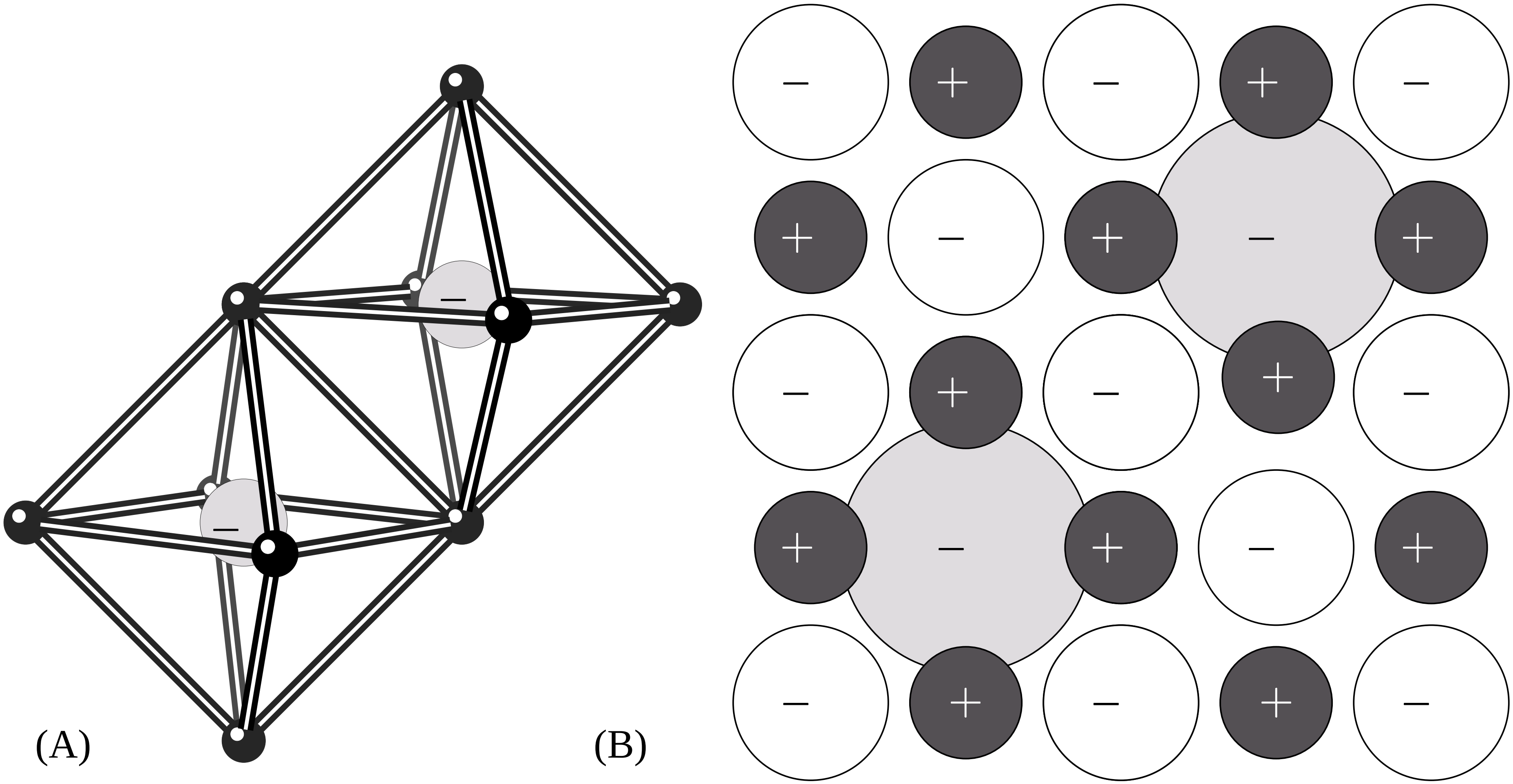


Figure 9: The F_2 or M center.

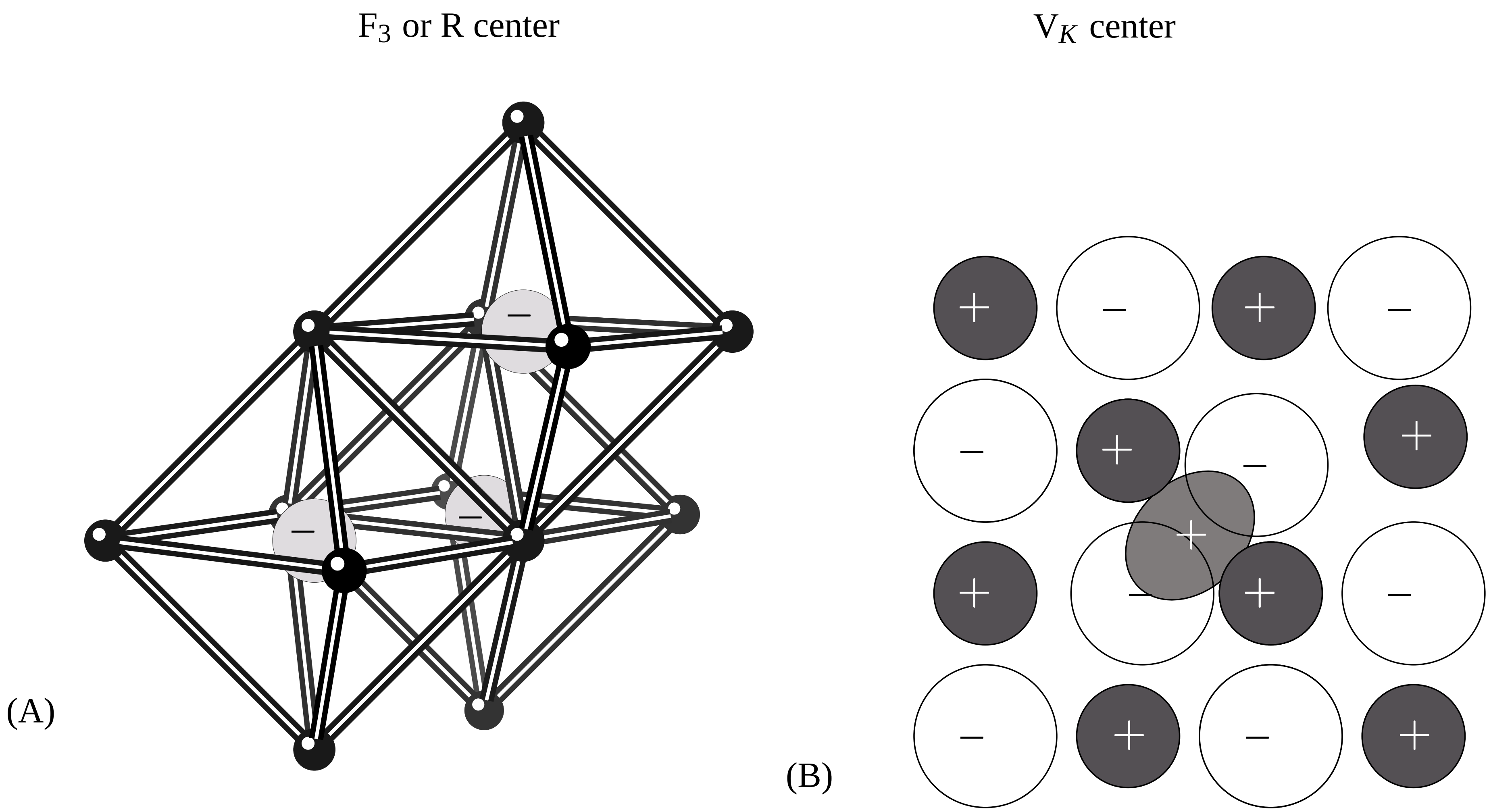


Figure 10: F_3 center [Lüty (1961)]

Franck–Condon Effect

$$\hat{\mathcal{H}}_{\mathrm{F}}|F_0\rangle = \mathcal{E}_0|F_0\rangle = 0 \tag{L56a}$$

$$\hat{\mathcal{H}}_{\mathrm{F}}|F_1\rangle = \mathcal{E}_1|F_1\rangle. \tag{L56b}$$

$$\hat{\mathcal{H}}_{\mathrm{ion}} = \frac{\hat{P}^2}{2M} + \frac{M\omega_{\mathrm{i}}^2}{2}\hat{x}^2. \tag{L57}$$

$$\hat{\mathcal{H}}_{\mathrm{int}} = g\hat{x}\hat{\mathcal{H}}_{\mathrm{F}}, \tag{L58}$$

$$\left\{\hat{\mathcal{H}}_{\mathrm{F}}(1+g\hat{x}) + \hat{\mathcal{H}}_{\mathrm{ion}}\right\}|\psi\rangle = \mathcal{E}_{\mathrm{tot}}|\psi\rangle. \tag{L59}$$

$$\phi_l(x) \equiv \langle x, \mathcal{E}_l|\psi\rangle. \tag{L60}$$

$$\left\{\mathcal{E}_l(1+gx) + \frac{-\hbar^2\nabla^2}{2M} + \frac{M\omega_{\mathrm{i}}^2}{2}x^2\right\}\phi_l(x) = \mathcal{E}_{\mathrm{tot}}\phi_l(x). \tag{L61}$$

Franck–Condon Effect

$$\mathcal{D}_l = \frac{\mathcal{E}_l g}{M\omega_{\rm i}^2}. \tag{L62}$$

$$\left\{ \mathcal{E}_l + \frac{-\hbar^2\nabla^2}{2M} + \frac{M\omega_{\rm i}^2}{2}\left[(x+\mathcal{D}_l)^2 - \mathcal{D}_l^2\right] \right\} \phi_l(x) = \mathcal{E}_{\rm tot}\phi_l(x). \tag{L63}$$

$$\mathcal{E}_{l,n} = \mathcal{E}_l + \hbar\omega_{\rm i}(n+\tfrac{1}{2}) - \tfrac{1}{2}\mathcal{D}_l^2 M\omega_{\rm i}^2. \tag{L64}$$

Franck–Condon Effect

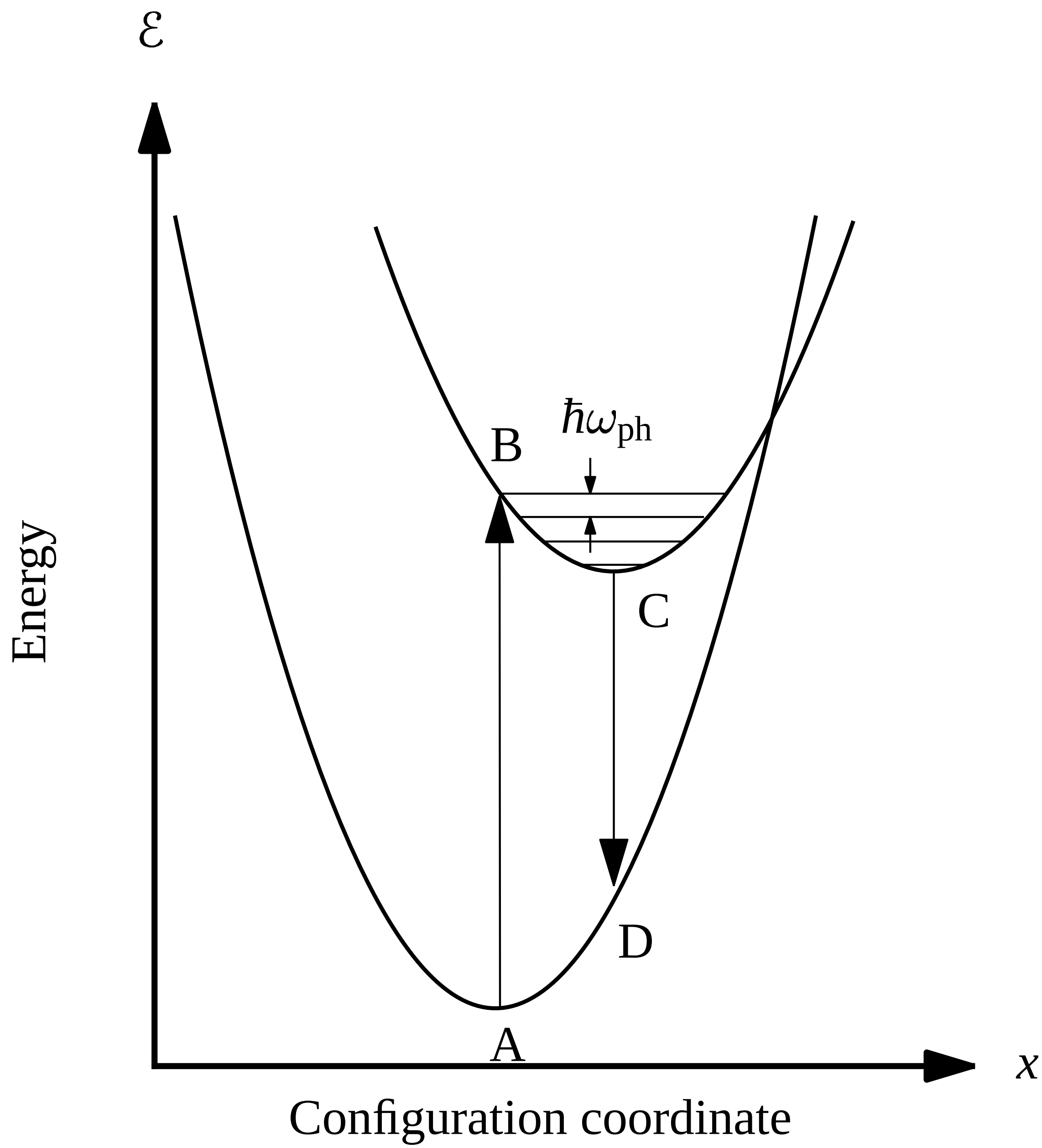


Figure 11: Franck–Condon effect

$$\sum_{\text{final}} \delta(\mathcal{E}_{\text{tot,final}} - \mathcal{E}_{\text{tot},0} - \hbar\omega) |\langle \psi_0 | \hat{U}_{\text{int}} | \psi_{\text{final}} \rangle|^2, \tag{L65}$$

$$\hbar\omega = \mathcal{E}_1 + n\hbar\omega_{\text{i}} - \tfrac{1}{2}\mathcal{D}_1^2 M\omega_{\text{i}}^2, \tag{L66}$$

$$|\int dx\, \phi_0(x)\phi_n(x + \mathcal{D}_1)|^2. \tag{L67}$$

$$x_0 = \sqrt{\frac{\hbar}{M\omega_{\text{i}}}} \quad \gg \quad \mathcal{D}_1 \tag{L68}$$

$$\Rightarrow 1 \quad \gg \quad \frac{\mathcal{E}_1 g}{\sqrt{\hbar M\omega_{\text{i}}^3}}. \tag{L69}$$

$$\mathcal{D}_1 \gg x_0, \tag{L70}$$

$$\int dx\,\phi_0(x)\phi_n(x+\mathcal{D}_1) \tag{L71}$$

$$= \int d\chi\,\sqrt{\frac{1}{\pi 2^n n!}}e^{\chi\mathcal{D}_1/x_0-(\mathcal{D}_1/x_0)^2/2}(-1)^n\frac{d^n}{d\chi^n}e^{-\chi^2} \tag{L72}$$

$$= \int d\chi\,\sqrt{\frac{1}{\pi 2^n n!}}\left(\frac{\mathcal{D}_1}{x_0}\right)^n e^{\chi\mathcal{D}_1/x_0-(\mathcal{D}_1/x_0)^2/2}e^{-\chi^2} \tag{L73}$$

$$= \sqrt{\frac{1}{2^n n!}}\left(\frac{\mathcal{D}_1}{x_0}\right)^n e^{-(\mathcal{D}_1/x_0)^2/4}. \tag{L74}$$

$$n = \tfrac{1}{2}(\mathcal{D}_1/x_0)^2. \tag{L75}$$

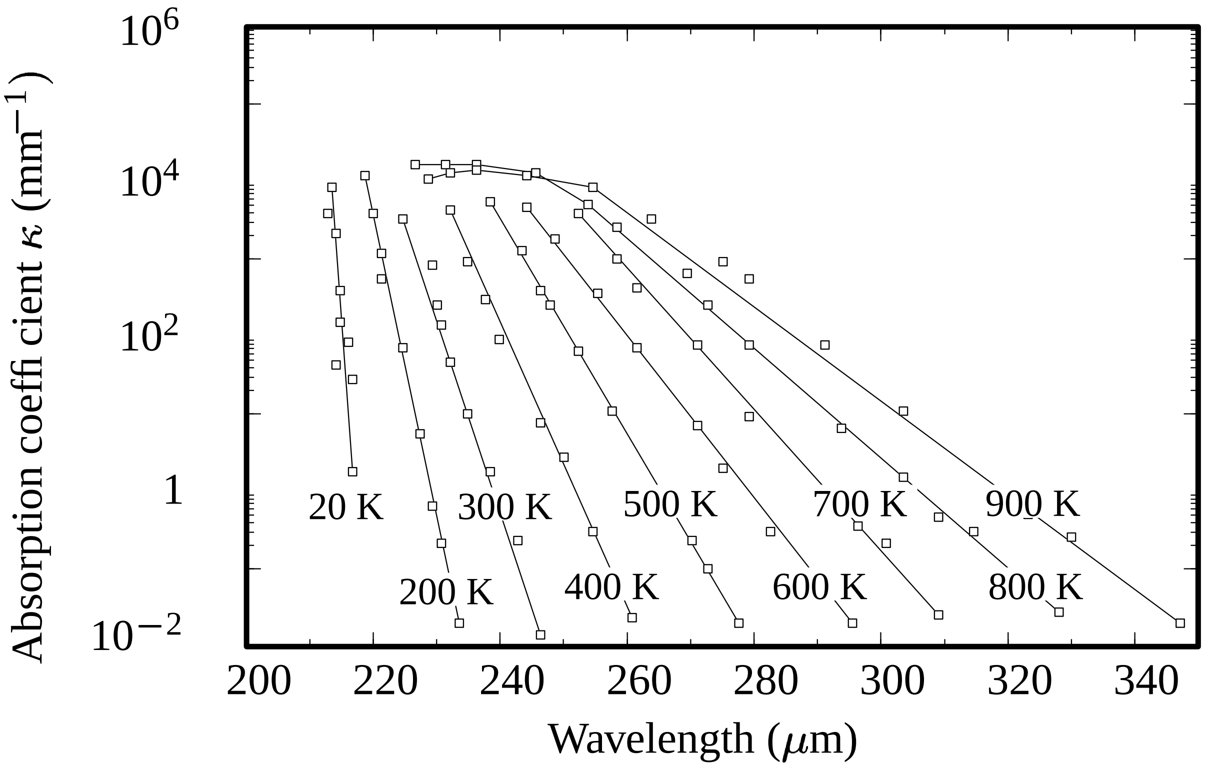
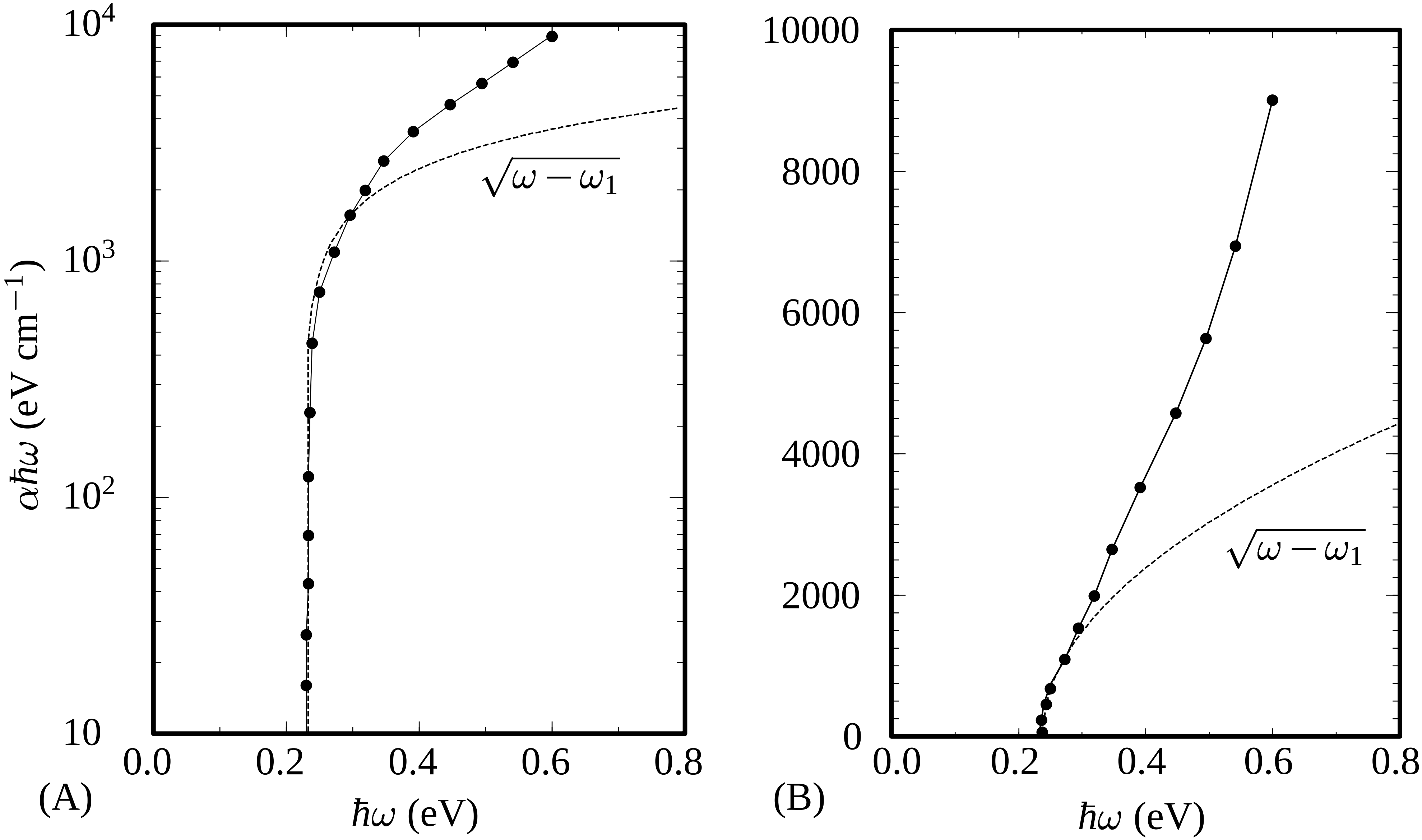


Figure 12: Urbach tails [Haupt (1959)]

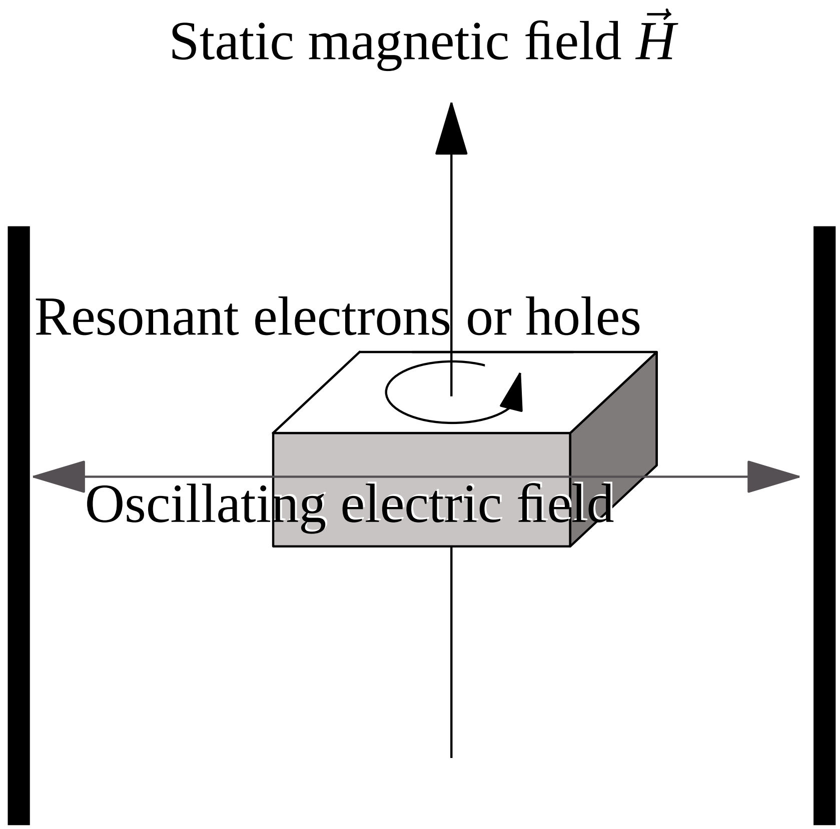
$$\alpha \propto \exp\left[-\frac{(\mathcal{E}_g - \hbar\omega)}{k_B T}\right]. \qquad \text{(L76)}$$


10^4
10^3
10^2
10
$\alpha\hbar\omega$ (eV cm^{-1})
0.0
0.2
0.4
0.6
0.8
$\hbar\omega$ (eV)
$\sqrt{\omega-\omega_1}$
(A)
10000
8000
6000
4000
2000
0
0.0
0.2
0.4
0.6
0.8
$\hbar\omega$ (eV)
$\sqrt{\omega-\omega_1}$
(B)

Definitions

- Cyclotron Resonance
- Direct and Indirect Optical Transitions
- Excitons
- Optoelectronics
- Lasers

Cyclotron Resonance



Setting centripetal force equal to Lorenz force gives

$$\frac{m^\star v^2}{R} = ? \qquad ? \tag{L1}$$

$$\omega_c = \frac{v}{R} = \frac{eB}{m^\star c} = 17.6\,\frac{m}{m^\star}\left[\frac{B}{\text{kG}}\right]\text{GHz.} \tag{L2}$$

Cyclotron Resonance

$$\dot{\vec{v}} + \frac{\vec{v}}{\tau} = -\frac{e\vec{E}}{m^\star} - \frac{e}{m^\star c}\vec{v} \times \vec{B}. \tag{L3}$$

$$\left(-i\omega + \frac{1}{\tau}\right)\vec{v} = -\frac{e\vec{E}}{m^\star} - \omega_c(\hat{x}v_y - \hat{y}v_x) \tag{L4}$$

$$\Rightarrow \left(-i\omega + \frac{1}{\tau}\right)\vec{v} = -\frac{e\vec{E}}{m^\star} - \omega_c \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \vec{v}. \tag{L5}$$

$$\vec{j} = -ne\vec{v} \equiv \sigma\vec{E}, \tag{L6}$$

$$\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix} \tag{L7}$$

$$\sigma_{xx} = \frac{\sigma_0(1 - i\omega\tau)}{(1 - i\omega\tau)^2 + \omega_c^2\tau^2} \tag{L8a}$$

$$\sigma_{xy} = -\frac{\sigma_0 \tau \omega_c}{(1 - i\omega\tau)^2 + \omega_c^2 \tau^2} \tag{L8b}$$

and

$$\sigma_{zz} = \frac{\sigma_0}{1 - i\omega\tau}, \tag{L8c}$$

with

$$\sigma_0 = \frac{ne^2\tau}{m^\star}. \tag{L8d}$$

$$\mathrm{Re}[\sigma_{xx}] = \sigma_0 \frac{\omega_c^2\tau^2 + \omega^2\tau^2 + 1}{(\omega_c^2\tau^2 - \omega^2\tau^2 + 1)^2 + 4\omega^2\tau^2}. \tag{L9}$$

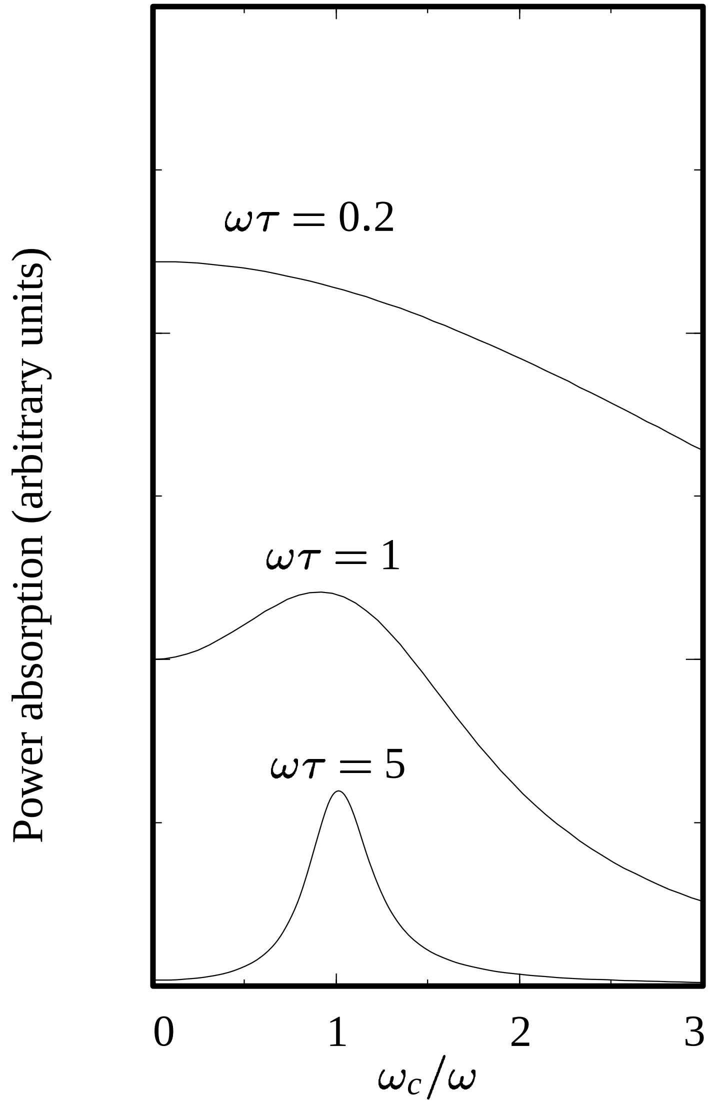


Figure 1: Cyclotron theory

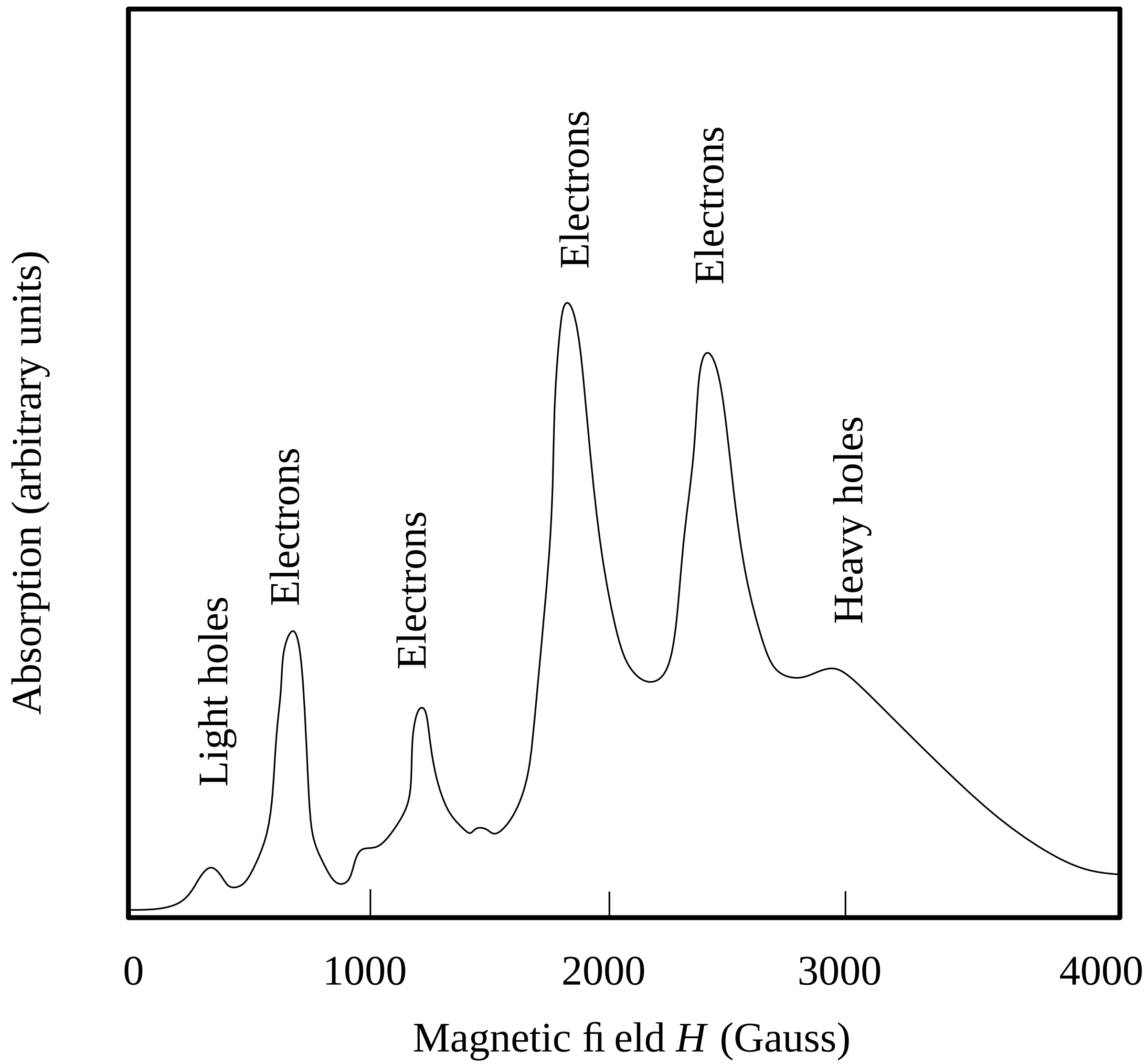


Figure 2: Cyclotron resonance in germanium. The magnetic field is oriented at 10° from the (110) plane and 30° from the [100] direction. [Source: Dexter et al. (1956)]

$$\mathcal{E} = \frac{\hbar^2}{2}\left[\frac{k_1^2}{m_1^\star} + \frac{k_2^2}{m_2^\star} + \frac{k_3^2}{m_3^\star}\right] \tag{L10}$$

$$0 = i\omega\vec{v} - \frac{e}{c}\begin{pmatrix} \frac{1}{m_1^\star} & 0 & 0 \\ 0 & \frac{1}{m_2^\star} & 0 \\ 0 & 0 & \frac{1}{m_1^\star} \end{pmatrix}\begin{pmatrix} 0 & B_3 & -B_2 \\ -B_3 & 0 & B_1 \\ B_2 & -B_1 & 0 \end{pmatrix}\vec{v} \tag{L11}$$

$$\Rightarrow \omega = \frac{e}{c}\sqrt{\sum_{\alpha=1}^{3} \frac{B_\alpha^2 m_\alpha^\star}{m_1^\star m_2^\star m_3^\star}}. \tag{L12}$$

Theory for absorption across energy gap

$$\mathrm{Im}[\epsilon_{\alpha\beta}] = \frac{4e^2\pi^2}{m^2\omega^2\mathcal{V}} \sum_{ll'} (f_l - f_{l'}) \langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle \delta(\mathcal{E}_{l'} - \mathcal{E}_l - \hbar\omega) \tag{L13}$$

$$= \left(\frac{2\pi e}{m\omega}\right)^2 \frac{1}{\mathcal{V}} \sum_{\vec{k}n_1n_2} \langle\vec{k}n_1|\hat{P}_\alpha|\vec{k}n_2\rangle\langle\vec{k}n_2|\hat{P}_\beta|\vec{k}n_1\rangle \delta(\mathcal{E}_{n_2\vec{k}} - \mathcal{E}_{n_1\vec{k}} - \hbar\omega) \tag{L14}$$

$$= \left(\frac{2\pi e}{m\omega}\right)^2 |P_{\alpha\beta}(\omega)|^2 D_{\mathrm{j}}(\hbar\omega), \tag{L15}$$

where

$$|P_{\alpha\beta}(\omega)|^2 \equiv \frac{\sum_{n_1n_2\vec{k}} \langle\vec{k}n_1|\hat{P}_\alpha|\vec{k}n_2\rangle\langle\vec{k}n_2|\hat{P}_\beta|\vec{k}n_1\rangle \delta(\mathcal{E}_{n_2\vec{k}} - \mathcal{E}_{n_1\vec{k}} - \hbar\omega)}{\sum_{n_1n_2\vec{k}} \delta(\mathcal{E}_{n_2\vec{k}} - \mathcal{E}_{n_1\vec{k}} - \hbar\omega)} \tag{L16}$$

and

$$D_{\mathrm{j}}(\hbar\omega) \equiv \frac{1}{\mathcal{V}} \sum_{n_1n_2\vec{k}} \delta(\mathcal{E}_{n_2\vec{k}} - \mathcal{E}_{n_1\vec{k}} - \hbar\omega). \tag{L17}$$

Direct Transitions

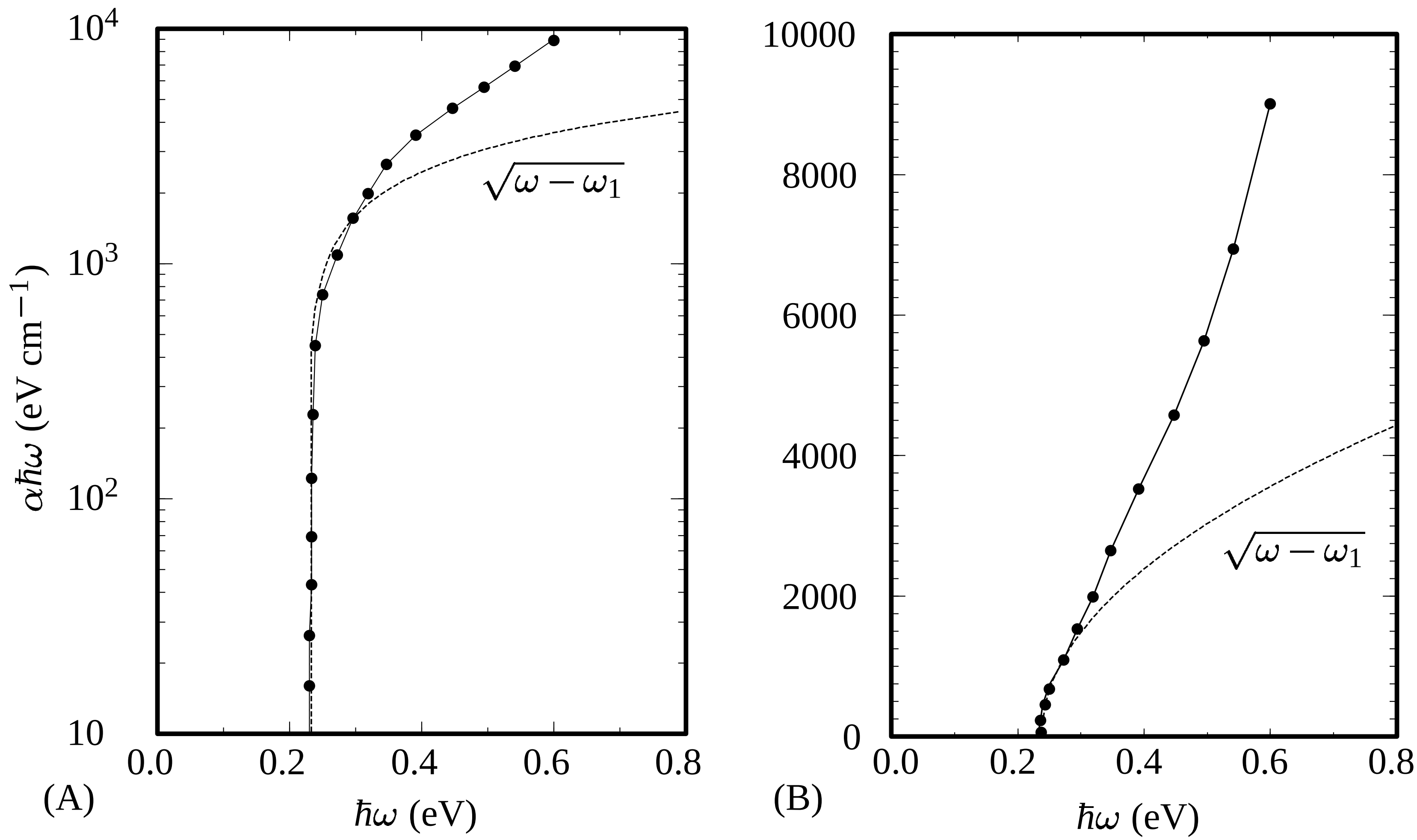


Figure 3: Measurement of absorption coefficient α times $\hbar\omega$, showing a van Hove singularity at onset of optical absorption in the direct gap semiconductor InSb. Data of Goebli and Fan and reported by Johnson (1967).

Direct Transitions

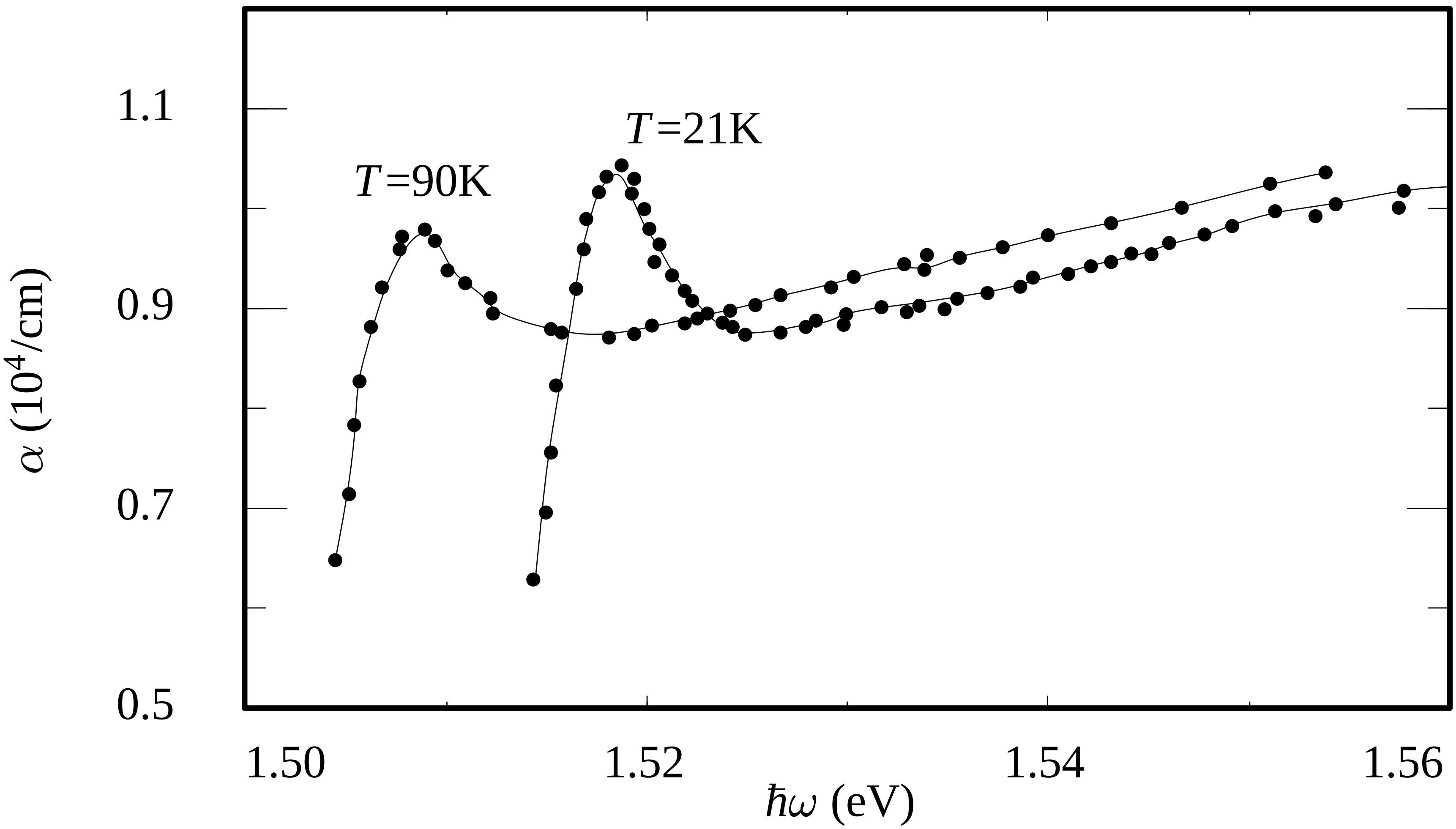


Figure 4: Absorption coefficient α in gallium arsenide, showing absorption due to excitons. [Source: Sturge (1962), p. 771.]

Indirect Transitions

$$\hbar\omega = \mathcal{E}_c - \mathcal{E}_v \pm \hbar\omega_{\text{ph}}(\vec{\delta k}). \tag{L18}$$

$$\kappa \propto \sum_{\vec{k}_c \vec{k}_v} \delta\left(\mathcal{E}_c(\vec{k}_c) - \mathcal{E}_v(\vec{k}_v) - \hbar\omega \pm \hbar\omega_{\text{ph}}(\vec{\delta k})\right) \tag{L19}$$

$$= \int d\mathcal{E}_c \int d\mathcal{E}_v \, D_{\text{c}}(\mathcal{E}_c) D_v(\mathcal{E}_v) \delta\left(\mathcal{E}_c - \mathcal{E}_v - \hbar\omega \pm \hbar\omega_{\text{ph}}\right) \tag{L20}$$

$$\propto \int_{\mathcal{E}_g} d\mathcal{E}_c \int^0 d\mathcal{E}_v \sqrt{\mathcal{E}_c - \mathcal{E}_g}\sqrt{-\mathcal{E}_v}\, \delta\left(\mathcal{E}_c - \mathcal{E}_v - \hbar\omega \pm \hbar\omega_{\text{ph}}\right) \tag{L21}$$

$$= \int_{\mathcal{E}_g}^{\hbar\omega \mp \hbar\omega_{\text{ph}}} d\mathcal{E}_c \sqrt{\mathcal{E}_c - \mathcal{E}_g}\sqrt{\hbar\omega - \mathcal{E}_c \mp \hbar\omega_{\text{ph}}} \tag{L22}$$

$$= (\hbar\omega \mp \hbar\omega_{\text{ph}} - \mathcal{E}_g)^2 \int_0^1 dy \sqrt{y}\sqrt{1-y}. \tag{L23}$$

Indirect Transitions

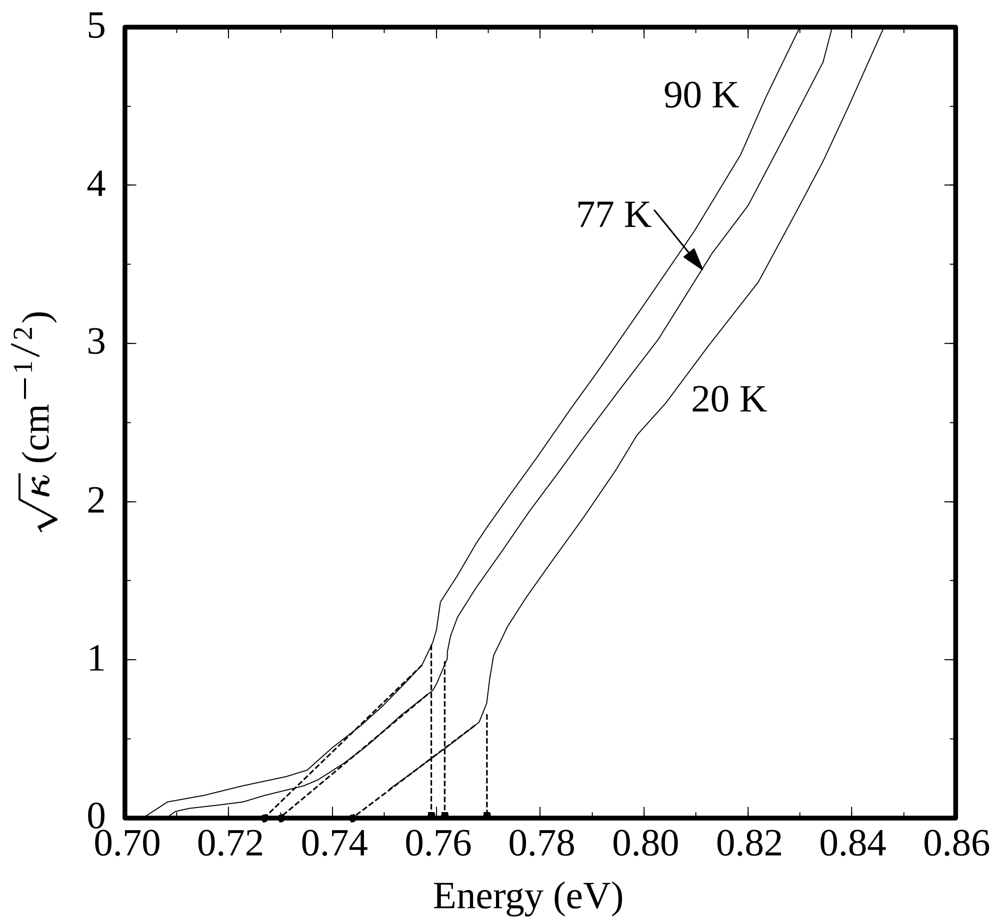


Figure 5: Onset of optical absorption in germanium.. [Source: Macfarlane et al. (1957)]

Excitons

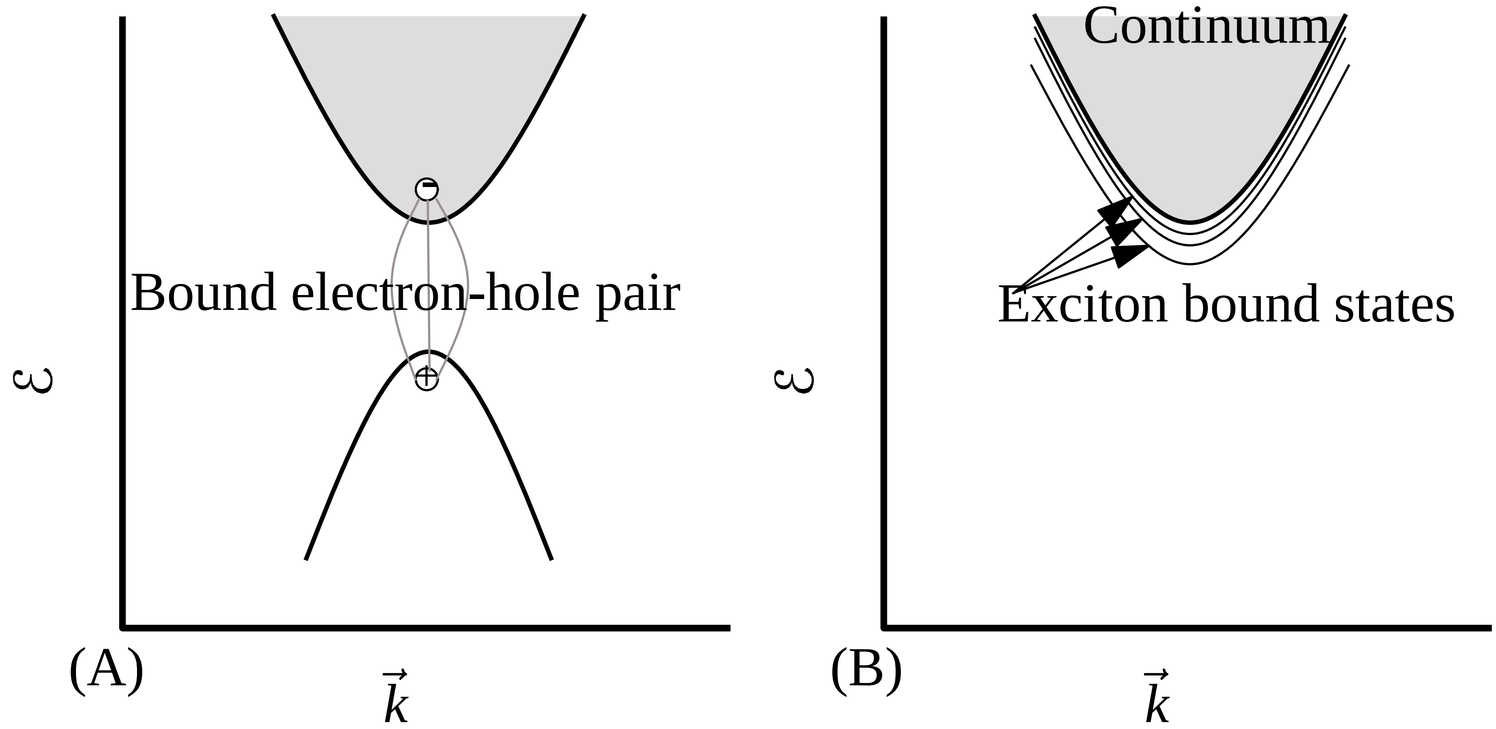


Figure 6: Schematic view of energy levels resulting from exciton formation.

$$\left[\frac{-\hbar^2}{2m_n^\star}\nabla^2_{\vec{r}_n} + \frac{-\hbar^2}{2m_p^\star}\nabla^2_{\vec{r}_p} - \frac{e^2}{\epsilon^0|\vec{r}_n - \vec{r}_n|} - \mathcal{E}\right]\Psi(\vec{r}_n, \vec{r}_p) = 0. \quad \text{(L24)}$$

$$\vec{R} = \frac{m_n^\star \vec{r}_n + m_p^\star \vec{r}_p}{m_n^\star + m_p^\star} \quad \text{(L25)}$$

$$\vec{r} = \vec{r}_n - \vec{r}_p \quad \text{(L26)}$$

to give

$$0 = \left[\frac{-\hbar^2}{2(m_n^\star + m_p^\star)}\nabla^2_{\vec{R}} - \mathcal{E}_{\text{cm}}\right]\Psi_{\text{cm}}(\vec{R}) \quad \text{(L27)}$$

$$0 = \left[\frac{-\hbar^2}{2\mu}\nabla^2_{\vec{r}} - \frac{e^2}{\epsilon^0 r} - \mathcal{E}_{\text{b}}\right]\Psi_{\text{b}}(\vec{r}), \quad \text{(L28)}$$

with the reduced mass μ given by

$$\mu = \frac{m_n^\star m_p^\star}{m_n^\star + m_p^\star}. \quad \text{(L29)}$$

$$\mathcal{E}_l = -\frac{\mu e^4}{2\hbar^2 {\epsilon^0}^2 l^2} = -\frac{\mu}{m{\epsilon^0}^2 l^2} \cdot 13.6\,\text{eV} \tag{L30}$$

$$a_0^* = \frac{\epsilon^0 \hbar^2}{e^2 \mu} = \frac{m\epsilon^0}{\mu} \cdot 0.529\,\text{Å}. \tag{L31}$$

Mott–Wannier Excitons

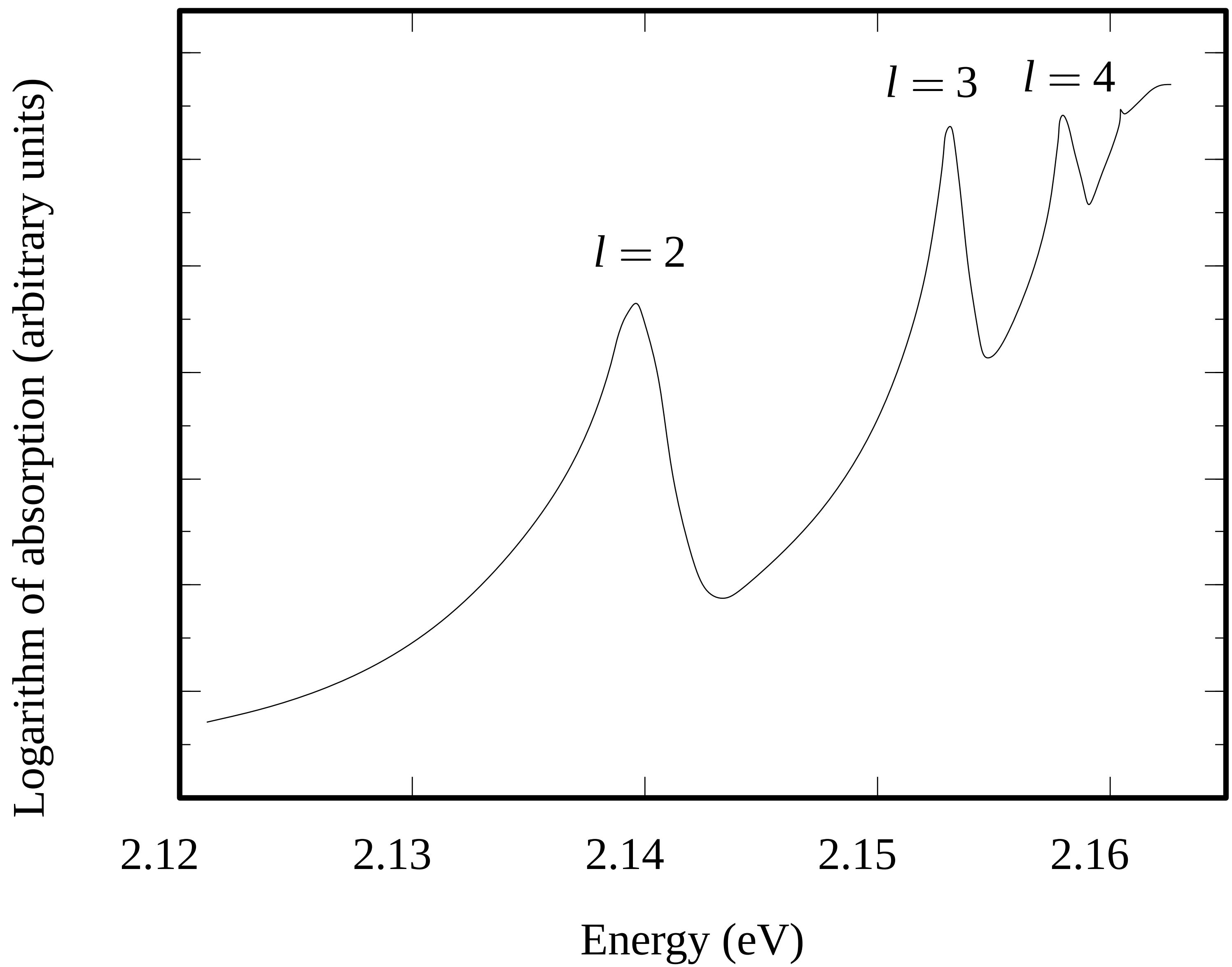


Figure 7: Absorption in Cu_2O. [Experiments of Baumeister (1961), p 361.]

$$j = -I\mathcal{G}(L_p + L_n) \tag{L32}$$

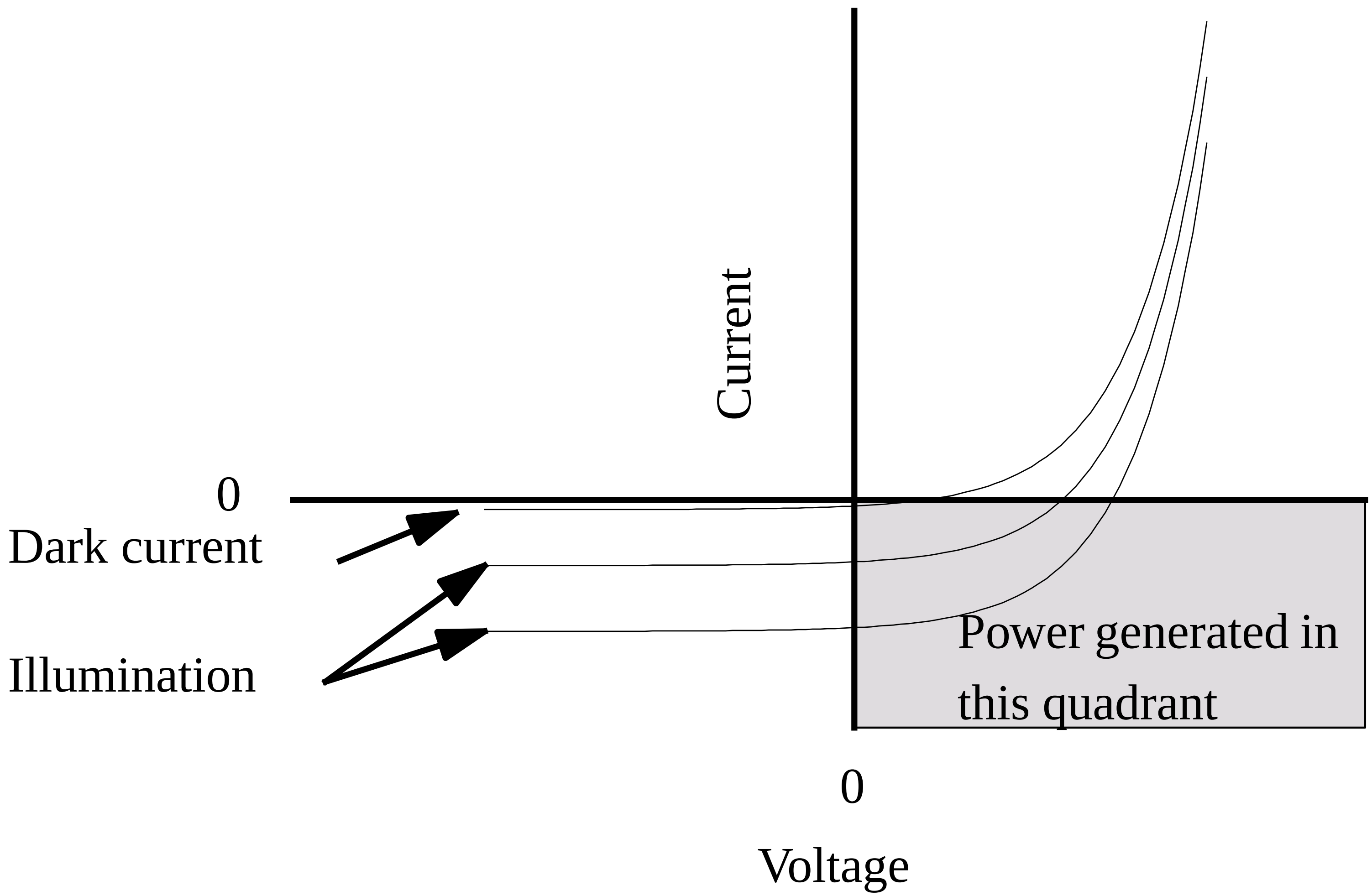


Figure 8: The current–voltage characteristic for a solar cell

$$R_{\text{sp}} = A_{21} f_2 (1 - f_1) \tag{L33}$$

$$R_{12} = B_{12} f_1 (1 - f_2) N_{\mathcal{E}_{12}} D_{\text{ph}}(\mathcal{E}_{12}) \tag{L34}$$

$$R_{21} = B_{21} f_2 (1 - f_1) N_{\mathcal{E}_{12}} D_{\text{ph}}(\mathcal{E}_{12}) + A_{21} f_2 (1 - f_1). \tag{L35}$$

$$\frac{f_2(1 - f_1)}{f_1(1 - f_2)} = e^{-\beta \mathcal{E}_{12}}, \tag{L36}$$

$$R_{12} = R_{21} \tag{L37}$$

$$\Rightarrow B_{12} N_{\mathcal{E}_{12}} D_{\text{ph}}(\mathcal{E}_{12}) = e^{-\beta \mathcal{E}_{12}} \left[B_{21} N_{\mathcal{E}_{12}} D_{\text{ph}}(\mathcal{E}_{12}) + A_{21} \right] \tag{L38}$$

$$\Rightarrow D_{\text{ph}}(\mathcal{E}_{12}) B_{12} - A_{21} = e^{-\beta \mathcal{E}_{12}} \left[D_{\text{ph}}(\mathcal{E}_{12}) B_{21} - A_{21} \right] \tag{L39}$$

$$\Rightarrow B_{12} \quad = \quad B_{21} \;\text{ and }\; A_{21} = D_{\text{ph}}(\mathcal{E}_{12})B_{21}. \tag{L40}$$

$$R_{21} = B_{21} f_2(1 - f_1)(N_{\mathcal{E}_{12}} + 1)D_{\text{ph}}(\mathcal{E}_{12}). \tag{L41}$$

$$R_{12} - R_{21} \quad = \quad B_{21}[(f_1 - f_2)N_{\mathcal{E}_{12}} - f_2(1 - f_1)]D_{\text{ph}}(\mathcal{E}_{12}). \tag{L42}$$

$$\text{Re}[\sigma_{\alpha\beta}(\omega)] = \frac{e^2\pi}{\hbar\omega m^2\mathcal{V}}(f_1 - f_2)F_{12}(\omega)\langle 1|\hat{P}_\alpha|2\rangle\langle 2|\hat{P}_\beta|1\rangle. \tag{L43}$$

$$g(\omega) = \frac{N}{\mathcal{V}}\frac{4\pi^2c^2}{\omega\bar{n}}\left(\frac{e^2}{\hbar c}\right)F_{12}(\omega)(f_2 - f_1)\frac{\sum_\beta |\langle 1|\hat{P}_\beta|2\rangle|^2}{3m^2c^2}. \tag{L44}$$

$$D_{\text{ph}}(\omega) = \frac{\bar{n}^3\omega^2}{\pi^2 c^3}. \tag{L45}$$

$$R_{21} - R_{12} = \frac{\partial}{\partial t} N_{\mathcal{E}_{12}} = -N \frac{\mathcal{E}_{12}}{\hbar} \bar{n} \left(\frac{e^2}{\hbar c}\right) 4(f_1 - f_2) \sum_{\beta} \frac{|\langle 1|\hat{P}_{\beta}|2\rangle|^2}{3m^2c^2} N_{\mathcal{E}_{12}}. \tag{L46}$$

$$\Re \exp[x(g-\alpha)] > 1. \tag{L47}$$

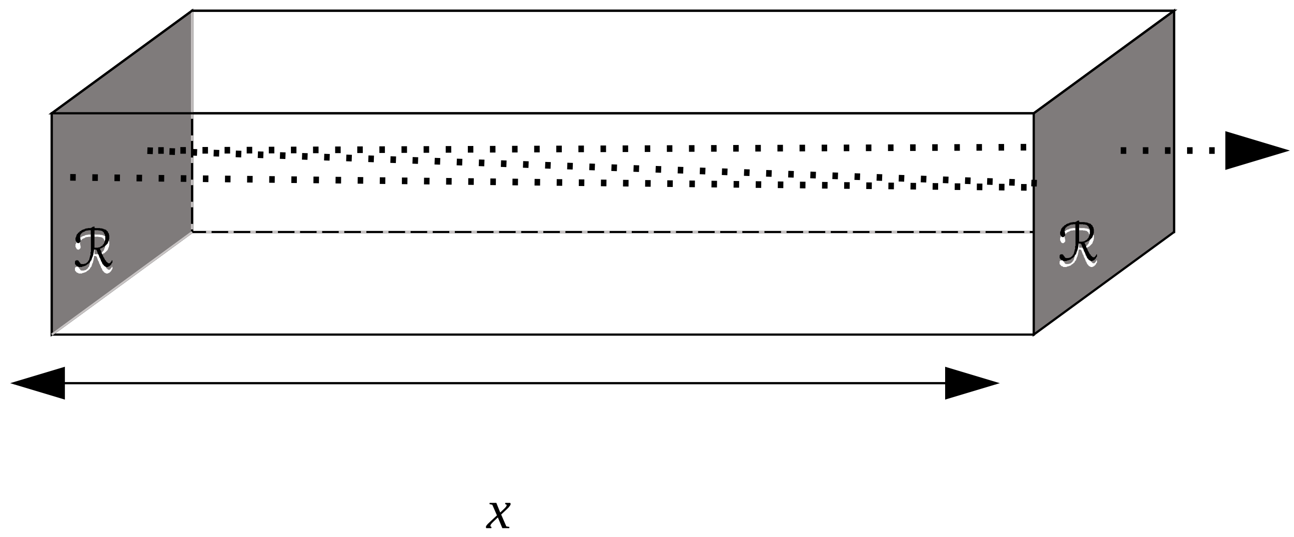


Figure 9: Light in a laser cavity reflects several times back and forth from mirrored ends of reflection coefficient $\mathcal{R}$ so as to stimulate more light emission before exiting.

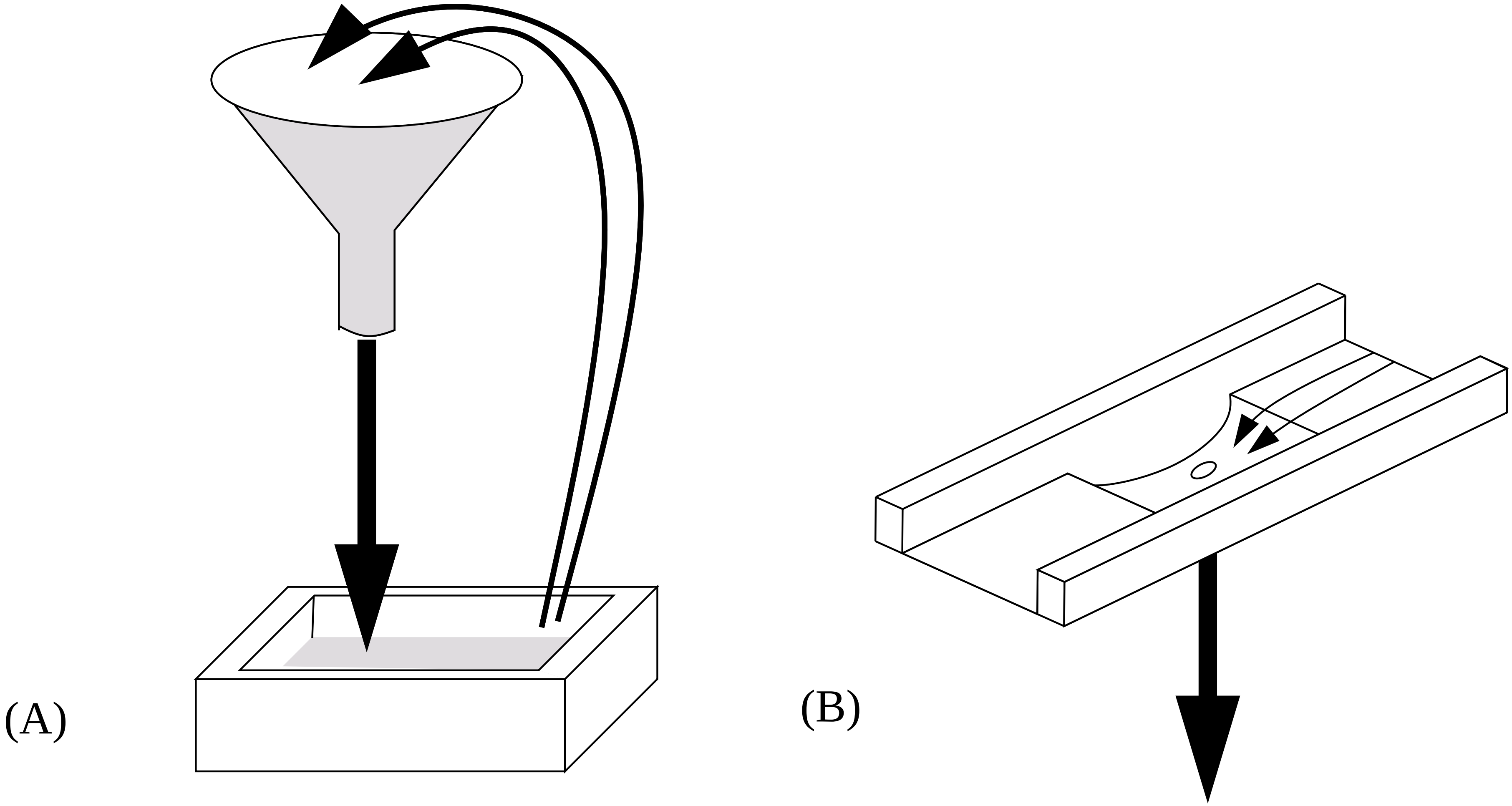


Figure 10:

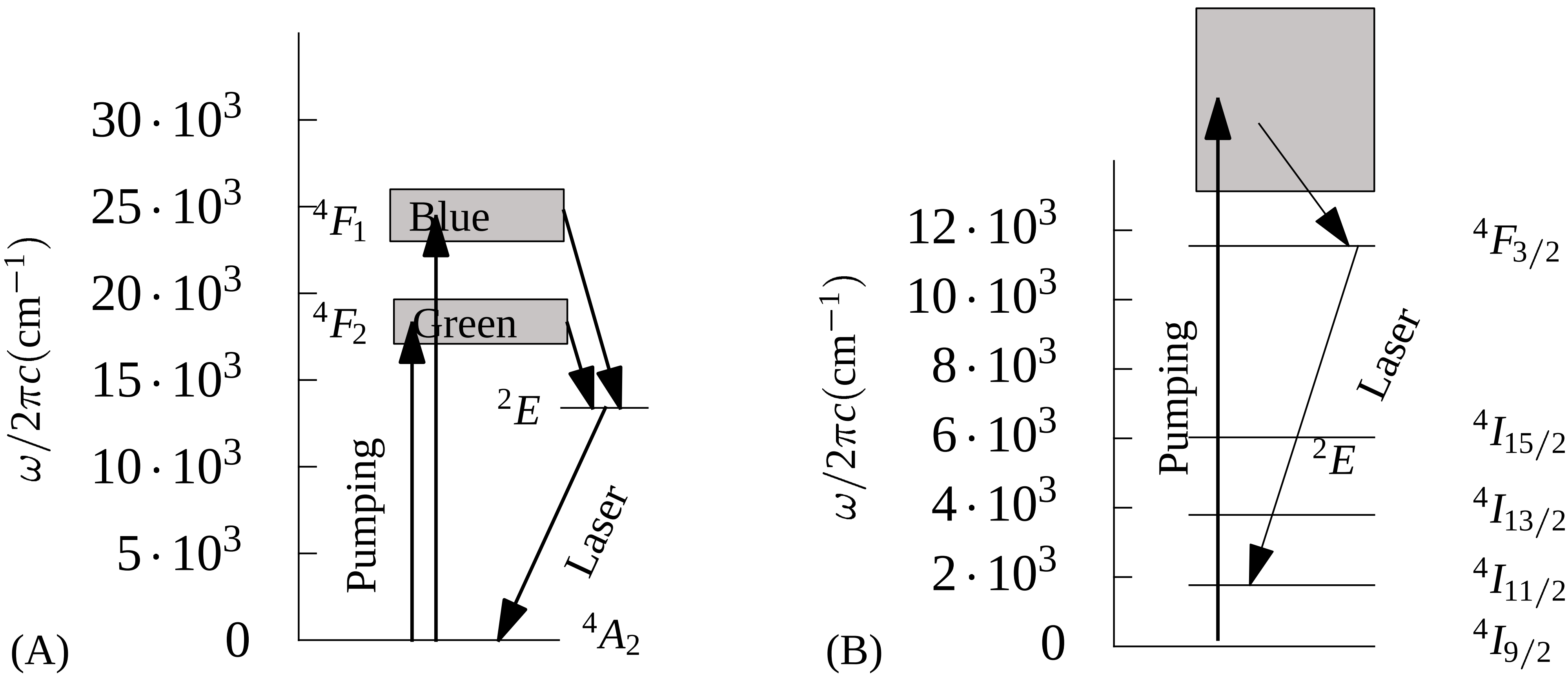


Figure 11: (A) Energy levels of $Cr^{3}+$ in Al_2O_3 (ruby). (B) Energy levels of Nd in $Y_3Al_5O_{12}$ (Nd:YAG).

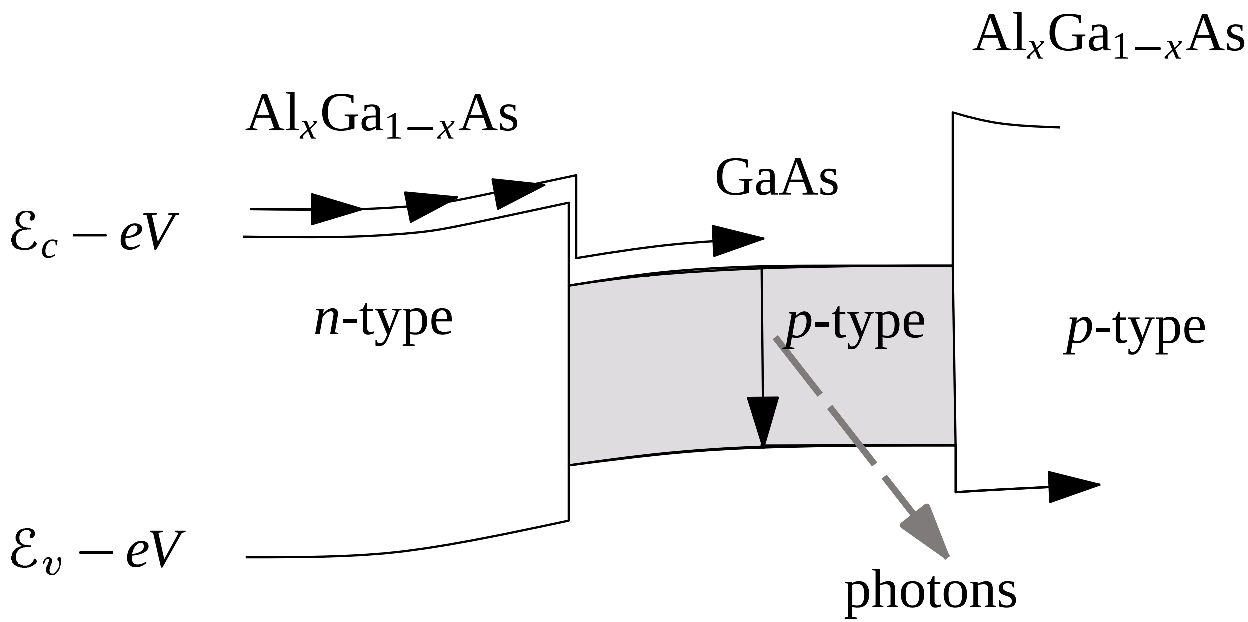


Figure 12: Double heterojunction structure

Active Areas

- ☞ Porous Silicon
- ☞ Negative μ dielectrics
- ☞ Materials to manipulate light as semiconductors manipulate electrons.

Optical Properties: Phenomenological Theory

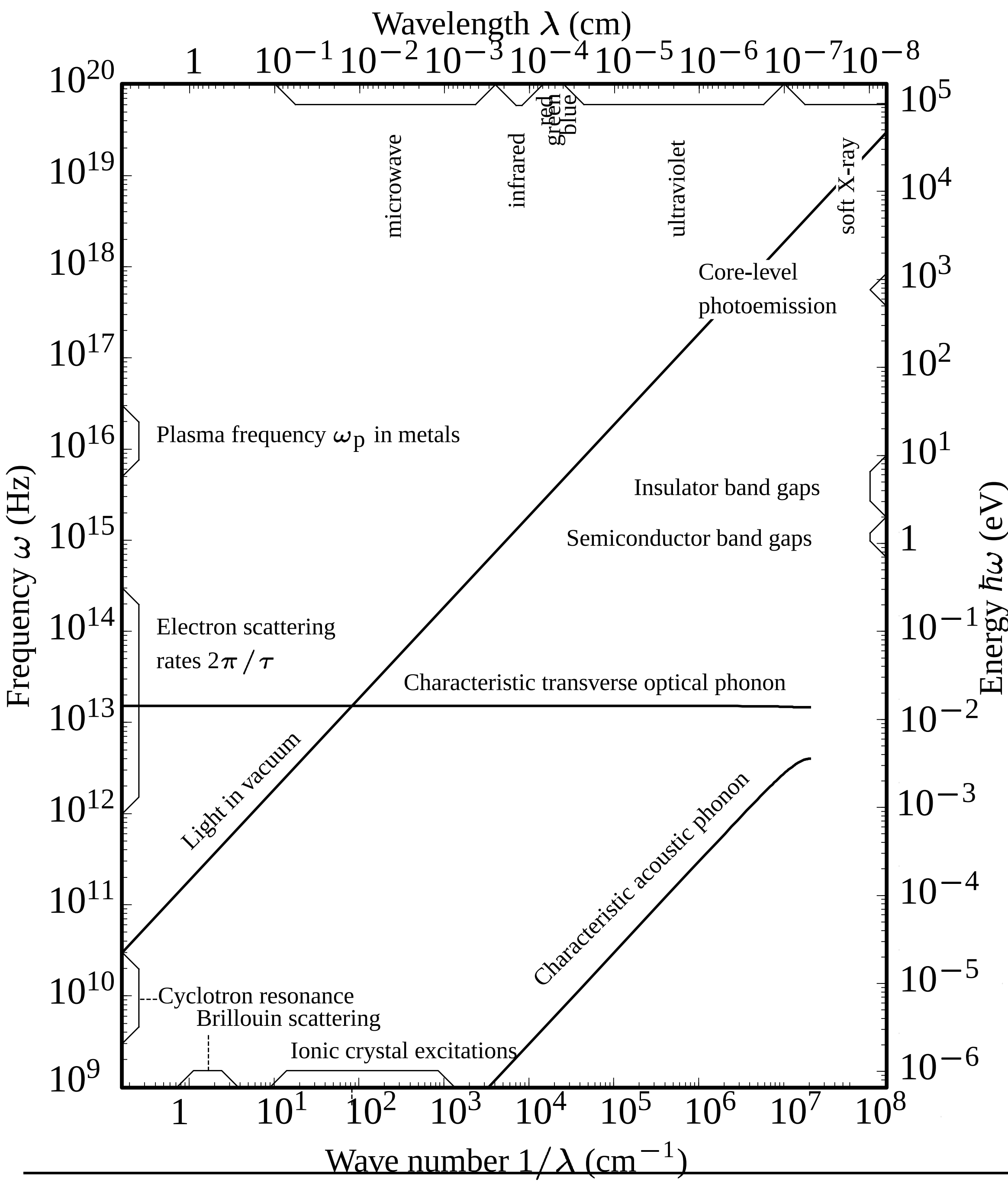

Wavelength λ (cm)
1 10^{-1} 10^{-2} 10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8}
microwave
infrared
red
green
blue
ultraviolet
soft X-ray
Core-level photoemission
Plasma frequency ω_p in metals
Insulator band gaps
Semiconductor band gaps
Electron scattering rates $2\pi/\tau$
Characteristic transverse optical phonon
Light in vacuum
Characteristic acoustic phonon
Cyclotron resonance
Brillouin scattering
Ionic crystal excitations
Frequency ω (Hz)
10^{9} 10^{10} 10^{11} 10^{12} 10^{13} 10^{14} 10^{15} 10^{16} 10^{17} 10^{18} 10^{19} 10^{20}
Energy $\hbar\omega$ (eV)
10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 1 10^{1} 10^{2} 10^{3} 10^{4} 10^{5}
1 10^{1} 10^{2} 10^{3} 10^{4} 10^{5} 10^{6} 10^{7} 10^{8}
Wave number $1/\lambda$ (cm^{-1})

Figure 1:

Definitions

- ☞ Maxwell's Equations
- ☞ Dielectric Functions
- ☞ Kramers–Kronig Relations
- ☞ Sum Rules
- ☞ Kubo–Greenwood Formula

Return of the Drude Model

$$m\dot{\vec{v}} = -e\vec{E} - m\frac{\vec{v}}{\tau}, \tag{L1}$$

$$-i\omega m\vec{v} = -e\vec{E} - m\frac{\vec{v}}{\tau} \tag{L2}$$

$$\Rightarrow \vec{j} = -ne\vec{v} = ? \qquad ? \tag{L3}$$

$$\Rightarrow \sigma(\omega) = ? \qquad ? \tag{L4}$$

Maxwell's Equations

$$\vec{\nabla}\cdot\vec{E} = -4\pi en \qquad \vec{\nabla}\cdot\vec{B}=0 \tag{L5a}$$

$$\vec{\nabla}\times\vec{E} = -\frac{1}{c}\frac{\partial\vec{B}}{\partial t} \qquad \vec{\nabla}\times\vec{B}=\frac{4\pi\vec{j}}{c}+\frac{1}{c}\frac{\partial\vec{E}}{\partial t}. \tag{L5b}$$

$$\vec{P}=\int^{t} dt'\,\vec{j}_{\text{int}}(t'). \tag{L6}$$

$$-e\frac{\partial n_{\text{int}}}{\partial t} = -\vec{\nabla}\cdot\vec{j}_{\text{int}} \tag{L7}$$

$$\Rightarrow en_{\text{int}} = \vec{\nabla}\cdot\vec{P}, \tag{L8}$$

$$\vec{D} = \vec{E}+4\pi\vec{P}. \tag{L9}$$

$$\vec{\nabla}\cdot\vec{D} = -4\pi en_{\text{ext}} \qquad \vec{\nabla}\cdot\vec{B}=0 \tag{L10a}$$

$$\vec{\nabla} \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t} \qquad \vec{\nabla} \times \vec{B} = \frac{4\pi \vec{j}_{\rm ext}}{c} + \frac{1}{c}\frac{\partial \vec{D}}{\partial t}. \tag{L10b}$$

$$\vec{j}(\vec{r},t) = \int dt' d\vec{r}' \sigma(\vec{r}-\vec{r}', t-t')\vec{E}(\vec{r}',t') \tag{L11a}$$

$$\equiv \sigma * \vec{E}(\vec{r},t). \tag{L11b}$$

$$\vec{j}(\vec{q},\omega) = \sigma(\vec{q},\omega)\vec{E}(\vec{q},\omega). \tag{L12}$$

$$\vec{D}(\vec{r},t) = \epsilon * \vec{E}(\vec{r},t) \Rightarrow \vec{D}(\vec{q},\omega) = \epsilon(\vec{q},\omega)\vec{E}(\vec{q},\omega). \tag{L13}$$

$$\epsilon(\vec{q},\omega) = 1 + \frac{4\pi i}{\omega}\sigma(\vec{q},\omega). \tag{L14}$$

$$\vec{\nabla}\times\vec{\nabla}\times\vec{E} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{\nabla}\times\vec{B} = -\frac{1}{c^2}\frac{\partial^2\epsilon*\vec{E}}{\partial t^2} \quad \text{(L15)}$$

$$\Rightarrow q^2\vec{E}-\vec{q}(\vec{q}\cdot\vec{E}) = \epsilon(\vec{q},\omega)\frac{\omega^2}{c^2}\vec{E}. \quad \text{(L16)}$$

$$q^2\vec{E} = \epsilon(\vec{q},\omega)\frac{\omega^2}{c^2}\vec{E} \quad \text{(L17)}$$

$$\Rightarrow q = \omega\tilde{n}/c; \quad \tilde{n}(\vec{q},\omega) = \sqrt{\epsilon(\vec{q},\omega)}, \quad \text{(L18)}$$

$$\vec{E}_0 e^{i\omega[\tilde{n}x/c-t]}. \quad \text{(L19)}$$

$$\epsilon_1 = \bar{n}^2-\kappa^2 \quad \text{(L20a)}$$

$$\epsilon_2 = 4\pi\mathrm{Re}[\sigma]/\omega = 2\bar{n}\kappa. \quad \text{(L20b)}$$

$$\alpha = \frac{2\omega}{c}\kappa = \frac{\omega\epsilon_2}{\bar{n}c}. \quad \text{(L21)}$$

$$\epsilon(\vec{q},\omega)\frac{\omega^2}{c^2}\vec{E} = 0 \quad \text{(L22)}$$

$$\Rightarrow \epsilon(\vec{q},\omega) = 0. \quad \text{(L23)}$$

Mechanical Oscillators as Dielectric Function

$$\vec{E}(\vec{r},t) = \vec{E}e^{-i\omega t}, \tag{L24}$$

$$m_l\ddot{\vec{r}} = -m_l\omega_l^2\vec{r} - m_l\dot{\vec{r}}/\tau_l - e\vec{E}(\vec{r},t) \tag{L25}$$

$$\Rightarrow \vec{r}(\omega) = -\frac{e\vec{E}}{m_l(\omega_l^2 - i\omega/\tau_l - \omega^2)} \tag{L26}$$

$$\vec{j}(\omega) = \frac{-i\omega n_l e^2\vec{E}}{m_l(\omega_l^2 - i\omega/\tau_l - \omega^2)}, \tag{L27}$$

$$\sigma(\omega) = \frac{-i\omega n_l e^2}{m_l(\omega_l^2 - i\omega/\tau_l - \omega^2)}. \tag{L28}$$

$$\epsilon(\omega) = 1 + \sum_l \frac{4\pi n_l e^2/m_l}{\omega_l^2 - \omega^2 - i\omega/\tau_l}. \tag{L29}$$

$$\sigma(\omega) = \frac{ne^2\tau}{m(1 - i\omega\tau)} \tag{L30}$$

Mechanical Oscillators as Dielectric Function

$$\epsilon(\omega) = 1 - \frac{\omega_{\mathrm{p}}^2}{\omega(\omega + i/\tau)}, \quad \text{(L31)}$$

Plasma frequency ω_{p}:

$$\omega_{\mathrm{p}} = \sqrt{\frac{4\pi n e^2}{m}}. \quad \text{(L32)}$$

$$\epsilon_1(\omega) = \mathrm{Re}[\epsilon(\omega)] = 1 + \sum_l \frac{4\pi n_l e^2 (\omega_l^2 - \omega^2)/m_l}{(\omega_l^2 - \omega^2)^2 + (\omega/\tau_l)^2} \quad \text{(L33a)}$$

$$\epsilon_2(\omega) = \mathrm{Im}[\epsilon(\omega)] = \sum_l \frac{4\pi n_l e^2 \omega/(\tau_l m_l)}{(\omega_l^2 - \omega^2)^2 + (\omega/\tau_l)^2}, \quad \text{(L33b)}$$

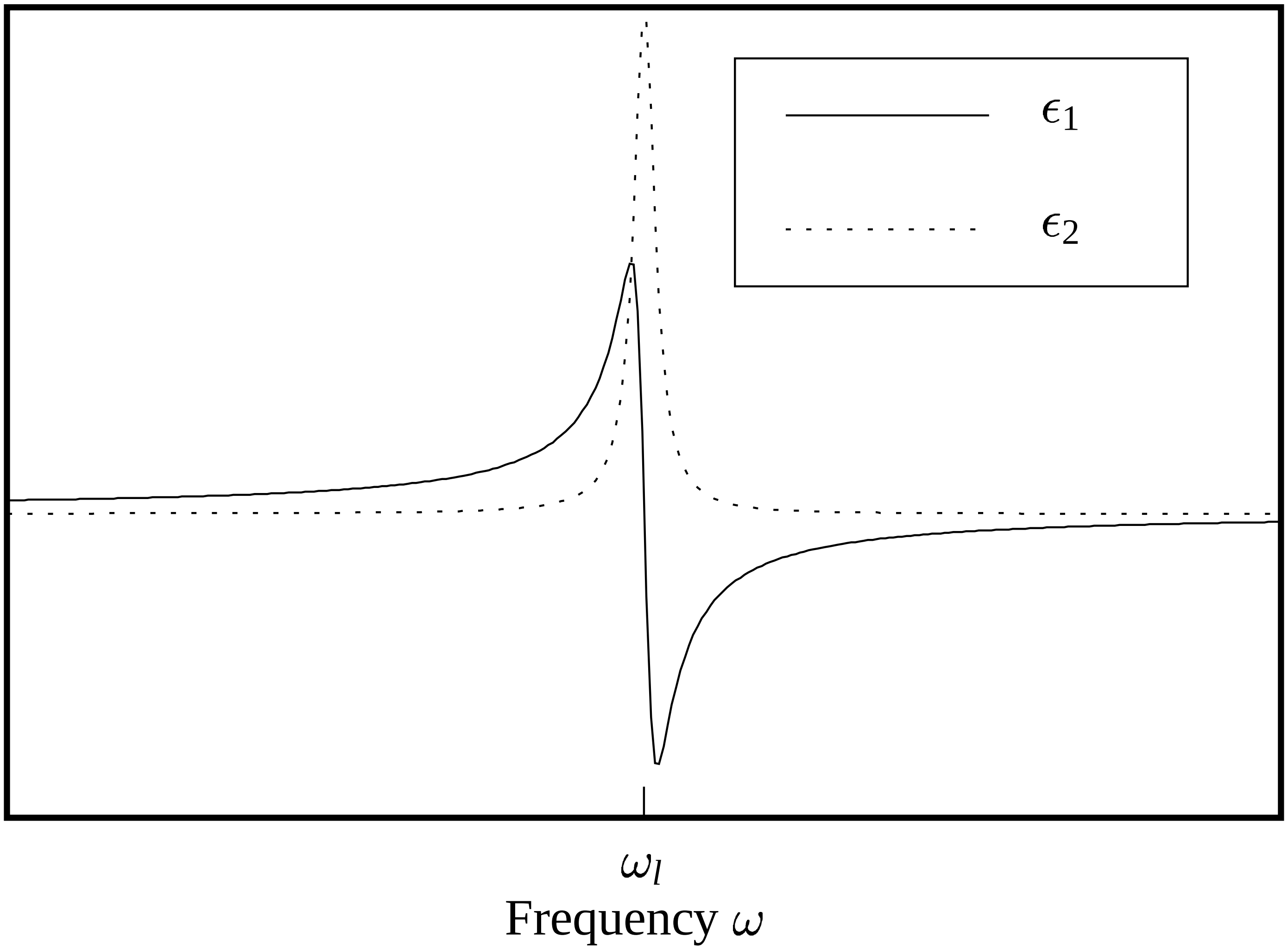


Figure 2: Characteristic shapes of the real and imaginary parts of the dielectric function described in Eq. (L33).

Kramers–Kronig Relations

$$\vec{D}(\omega) = \epsilon(\omega)\vec{E}(\omega) \Rightarrow \vec{D}(t) = \int dt'\,\epsilon(t')\vec{E}(t-t'). \tag{L34}$$

$$\vec{D}(t) = \epsilon(t)t_0\vec{E}_0. \tag{L35}$$

$$\epsilon(t) = 0 \ \text{ for } t < 0. \tag{L36}$$

$$\epsilon(\omega) = \int_0^\infty dt\, e^{i\omega t}\epsilon(t). \tag{L37}$$

$$\epsilon(\omega) = \oint \frac{d\omega'}{2\pi i}\frac{\epsilon(\omega')}{\omega'-\omega-i\eta}. \tag{L38}$$

$$\epsilon(\omega) - \epsilon^\infty = \oint \frac{d\omega'}{2\pi i}\frac{\epsilon(\omega')-\epsilon^\infty}{\omega'-\omega-i\eta}. \tag{L39}$$

Kramers–Kronig Relations

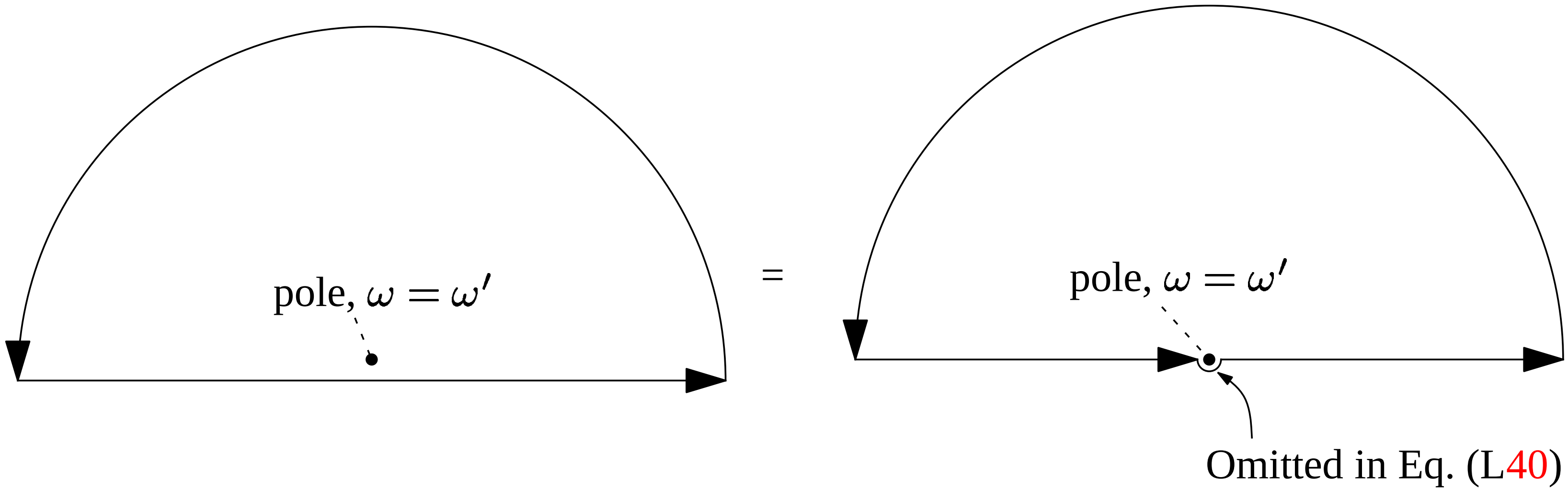


Figure 3: Contours for Kramers Kronig integrals

$$\epsilon(\omega) - \epsilon^{\infty} = \mathcal{P}\int \frac{d\omega'}{\pi i}\frac{\epsilon(\omega') - \epsilon^{\infty}}{\omega' - \omega} \tag{L40}$$

$$\mathrm{Re}[\epsilon(\omega) - \epsilon^{\infty}] = \mathcal{P}\int \frac{d\omega'}{\pi}\frac{\mathrm{Im}[\epsilon(\omega') - \epsilon^{\infty}]}{\omega' - \omega} \tag{L41a}$$

$$\mathrm{Im}[\epsilon(\omega) - \epsilon^{\infty}] = -\mathcal{P}\int \frac{d\omega'}{\pi}\frac{\mathrm{Re}[\epsilon(\omega') - \epsilon^{\infty}]}{\omega' - \omega}. \tag{L41b}$$

$$\epsilon_1(\omega) - \epsilon^{\infty} = \mathcal{P}\int_0^{\infty} \frac{2\omega' d\omega'}{\pi} \frac{\epsilon_2(\omega')}{\omega'^2 - \omega^2} \quad \text{(L42a)}$$

$$\epsilon_2(\omega) = -\mathcal{P}\int_0^{\infty} \frac{2\omega d\omega'}{\pi} \frac{\epsilon_1(\omega') - \epsilon^{\infty}}{\omega'^2 - \omega^2}. \quad \text{(L42b)}$$

Application to Optical Experiments

$$\tilde{r} = \frac{\tilde{n}-1}{\tilde{n}+1} \equiv \rho e^{i\theta}. \tag{L43}$$

$$\ln(\frac{\tilde{r}(\omega)}{\tilde{r}(0)}) = \ln(\rho(\omega)/\rho(0)) + i(\theta(\omega)-\theta(0)), \tag{L44}$$

$$\theta(\omega)-\theta(0) = -\frac{1}{\pi}\mathcal{P}\int d\omega' \ln\left[\frac{\rho(\omega')}{\rho(0)}\right][\frac{1}{\omega'-\omega}-\frac{1}{\omega'}] \tag{L45}$$

$$\Rightarrow \theta(\omega) = -\frac{2\omega}{\pi}\mathcal{P}\int_0^\infty d\omega' \frac{\ln\rho(\omega')}{\omega'^2-\omega^2}. \tag{L46}$$

$$\epsilon_1(0)-1 = \frac{2}{\pi}\int_0^\infty d\omega' \frac{\epsilon_2(\omega')}{\omega'}. \tag{L47}$$

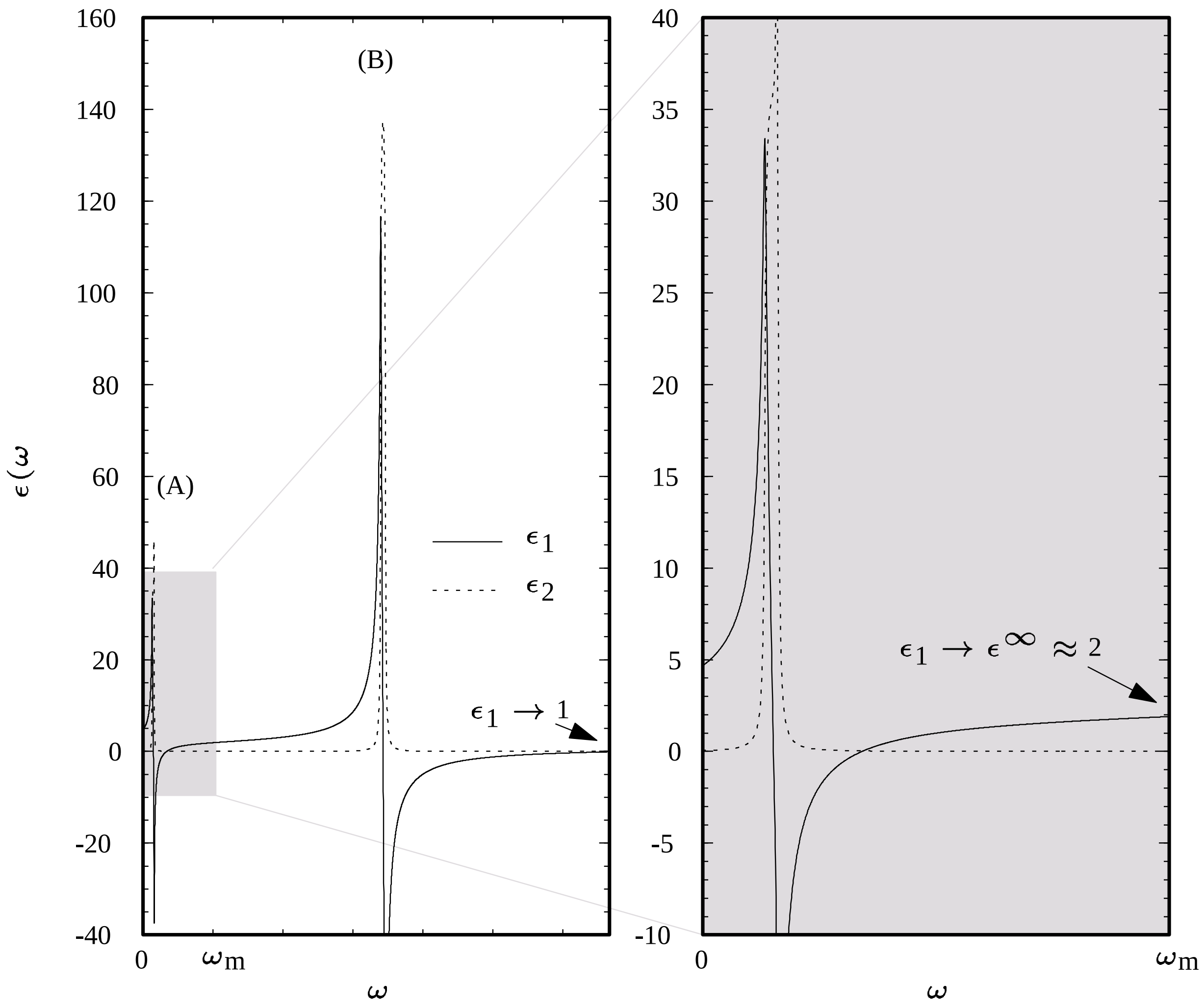


Figure 4: Dielectric functions from widely separated sets of modes.

$$\mathrm{Re}[\epsilon(\omega)] = 1 - \frac{2}{\pi\omega^2}\int_0^{\omega_\mathrm{m}} d\omega'\,\omega'\epsilon_2(\omega') + \frac{2}{\pi}\int_{\omega_\mathrm{m}}^{\infty} d\omega'\,\frac{\epsilon_2(\omega')}{\omega'} \quad \text{(L48)}$$

$$= \epsilon^{\infty} - \frac{\omega_\mathrm{p}^2}{\omega^2}, \quad \text{(L49)}$$

where

$$\epsilon^{\infty} = 1 + \frac{2}{\pi}\int_{\omega_\mathrm{m}}^{\infty} d\omega'\,\frac{\epsilon_2(\omega')}{\omega'} \quad \text{(L50)}$$

and

$$\omega_\mathrm{p}^2 \equiv \frac{4\pi n e^2}{m_\mathrm{opt}} = \frac{2}{\pi}\int_0^{\omega_\mathrm{m}} d\omega'\,\omega'\,\epsilon_2(\omega') \quad \text{(L51)}$$

$$\Rightarrow \int_0^{\omega_\mathrm{m}} d\omega'\,\omega'\epsilon_2(\omega') = \frac{2\pi^2 n e^2}{m_\mathrm{opt}}. \quad \text{(L52)}$$

$$\mathcal{E}_l = \hbar\omega_l \tag{L53}$$

Born approximation:

$$|\tilde{l}(t)\rangle \approx \mathcal{N}\left[e^{-i\hat{\mathcal{H}}\frac{t}{\hbar}}|l\rangle + \int_{-\infty}^{t} dt' e^{-i\hat{\mathcal{H}}\frac{(t-t')}{\hbar}} \frac{\hat{U}(t')}{i\hbar} e^{-i\hat{\mathcal{H}}\frac{t'}{\hbar}}|l\rangle\right] \tag{L54}$$

$$= \mathcal{N}\left[e^{-i\omega_l t}|l\rangle + \sum_{l'} \int_{-\infty}^{t} dt' |l'\rangle e^{-i\omega_{l'}(t-t')} \frac{\langle l'|\hat{U}|l\rangle}{i\hbar} e^{-i\omega t' - i\omega_l t'}\right] \tag{L55}$$

$$= \left\{|l\rangle + \sum_{l' \neq l} |l'\rangle \frac{\langle l'|\hat{U}|l\rangle e^{-i\omega t}}{\hbar(\omega_l - \omega_{l'} + \omega)}\right\} e^{-i\omega_l t}. \tag{L56}$$

If, on the other hand, the time dependent potential were to have the form $U^* \exp[i\omega^* t]$, then one would have instead

$$|\tilde{l}(t)\rangle = \left\{|l\rangle + \sum_{l' \neq l} |l'\rangle \frac{\langle l'|\hat{U}^*|l\rangle e^{i\omega^* t}}{\hbar(\omega_l - \omega_{l'} - \omega^*)}\right\} e^{-i\omega_l t}. \tag{L57}$$

$$\vec{A} = \frac{c\vec{E}}{i\omega} e^{-i\omega t} + \text{c.c.}. \tag{L58}$$

$$\hat{j} = -\frac{e}{m}[\hat{P} + \frac{e}{c}\vec{A}], \tag{L59}$$

$$\hat{P} \to \hat{P} + \frac{e}{c}\vec{A}, \tag{L60}$$

$$\frac{(\hat{P} + \frac{e}{c}\vec{A})^2}{2m} \tag{L61}$$

$$= \quad \frac{\hat{P}^2}{2m} + \frac{e}{2mc}[\vec{A}\cdot\hat{P} + \hat{P}\cdot\vec{A}] + \dots \tag{L62}$$

$$= \quad \frac{\hat{P}^2}{2m} + \frac{e}{mc}[\vec{A}\cdot\hat{P}] + \dots. \tag{L63}$$

$$\hat{U}(t) = \frac{e}{mi\omega}[\vec{E}\cdot\hat{P}]e^{-i\omega t} - \frac{e}{mi\omega^*}[\vec{E}\cdot\hat{P}]e^{i\omega^* t}. \tag{L64}$$

$$\vec{J} = \mathcal{V}\vec{j} = -\frac{e}{m}\langle\tilde{l}|\hat{P}+\frac{e\vec{A}}{c}|\tilde{l}\rangle \tag{L65}$$

$$\begin{aligned}
&= -\frac{e}{m}\langle l|\hat{P}|l\rangle - [\frac{e^2\vec{E}}{im\omega}e^{-i\omega t}+\text{c.c.}] \\
&- \frac{e^2}{i\hbar m^2}\sum_{l'\neq l}\langle l|\hat{P}|l'\rangle\langle l'|\vec{E}\cdot\hat{P}|l\rangle\left\{\frac{e^{-i\omega t}}{\omega(\omega_l-\omega_{l'}+\omega)} - \frac{e^{i\omega^* t}}{\omega^*(\omega_l-\omega_{l'}-\omega^*)}\right\} \\
&- \frac{e^2}{i\hbar m^2}\sum_{l'\neq l}\langle l|\vec{E}\cdot\hat{P}|l'\rangle\langle l'|\hat{P}|l\rangle\left\{\frac{e^{-i\omega t}}{\omega(\omega_l^*-\omega_{l'}^*-\omega)} - \frac{e^{i\omega^* t}}{\omega^*(\omega_l^*-\omega_{l'}^*+\omega^*)}\right\}.
\end{aligned} \tag{L66}$$

$$\begin{aligned}
&\sigma_{\alpha\beta}(\omega) \\
&= \frac{-e^2}{im\omega\mathcal{V}}\sum_l\left[f_l\delta_{\alpha\beta}+\sum_{l'}\frac{f_l}{\hbar m}\left\{\frac{\langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle}{\omega_l-\omega_{l'}+\omega}+\frac{\langle l|\hat{P}_\beta|l'\rangle\langle l'|\hat{P}_\alpha|l\rangle}{\omega_l^*-\omega_{l'}^*-\omega}\right\}\right].
\end{aligned} \tag{L67}$$

The Kubo–Greenwood Formula

$$\sigma_{\alpha\beta}(\omega) = \frac{-e^2}{im\omega\mathcal{V}}\left[\sum_l f_l\delta_{\alpha\beta} + \sum_{l'} \frac{f_l - f_{l'}}{\hbar m}\frac{\langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle}{\omega_l - \omega_{l'} + \omega + i\eta}\right]. \tag{L68}$$

$$\mathrm{Re}\left[\sigma_{\alpha\beta}(\omega)\right] = -\mathrm{Im}\frac{e^2}{m\omega\mathcal{V}}\left[\sum_{ll'} \frac{f_l - f_{l'}}{\hbar m}\frac{\langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle}{\omega_l - \omega_{l'} + \omega + i\eta}\right] \tag{L69}$$

$$= \frac{\pi}{\omega\mathcal{V}}\sum_{ll'}(f_l - f_{l'})\langle l|\frac{e\hat{P}_\alpha}{m}|l'\rangle\langle l'|\frac{e\hat{P}_\beta}{m}|l\rangle\delta(\mathcal{E}_{l'} - \mathcal{E}_l - \hbar\omega). \tag{L70}$$

$$\mathrm{Re}\left[\sigma_{\alpha\beta}(\omega)\right] = \frac{e^2}{m\omega\mathcal{V}}\sum_{\substack{l \text{ occupied} \\ l' \text{ unoccupied}}} \frac{\gamma_{l'}}{\hbar m}\frac{\langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle}{[\omega - (\omega_{l'} - \omega_l)]^2 + \gamma_{l'}^2}. \tag{L71}$$

The Kubo–Greenwood Formula

$$\mathrm{Re}\left[\sigma_{\alpha\beta}(\omega)\right] = \frac{e^2\pi}{\hbar\omega m^2\mathcal{V}}\sum_{ll'}(f_l - f_{l'})\langle l|\hat{P}_\alpha|l'\rangle\langle l'|\hat{P}_\beta|l\rangle F_{ll'}(\omega), \qquad \text{(L72)}$$

Susceptibility

$$U(\vec{q},\omega)e^{i\vec{q}\cdot\vec{r}-i\omega t}+\text{c.c.} \tag{L73}$$

$$n(\vec{r},t)=\sum_{l} f_l\langle\tilde{l}(t)|\vec{r}\rangle\langle\vec{r}|\tilde{l}(t)\rangle. \tag{L74}$$

$$U(\vec{q},\omega)=-eV(\vec{q},\omega), \tag{L75}$$

$$-en(\vec{q},\omega)=\chi_{\text{c}}(\vec{q},\omega)V(\vec{q},\omega) \tag{L76}$$

$$\chi_{\text{c}}(\vec{q},\omega)=e^2\sum_{\vec{k}\sigma}\frac{1}{\hbar\mathcal{V}}\frac{\left(f_{\vec{k}+\vec{q}}-f_{\vec{k}}\right)}{\omega_{\vec{k}+\vec{q}}-\omega_{\vec{k}}-\omega}. \tag{L77}$$

$$\begin{aligned}
\nabla^2 V &= \nabla^2 V_{\text{ext}}+4\pi en=4\pi en_{\text{ext}}+4\pi en && \text{(L78)}\\
\Rightarrow \nabla^2 V &= -\vec{\nabla}\cdot\vec{D}+4\pi en && \text{(L79)}\\
\Rightarrow -q^2V(\vec{q},\omega) &= -i\vec{q}\cdot\vec{D}+4\pi en(\vec{q},\omega) && \text{(L80)}
\end{aligned}$$

$$\Rightarrow -q^2 V(\vec{q},\omega) = -i\vec{q}\cdot\vec{D} - 4\pi\chi_c(\vec{q},\omega)V(\vec{q},\omega) \quad \text{(L81)}$$

$$\Rightarrow (4\pi\chi_c - q^2)V(\vec{q},\omega) = -i\vec{q}\cdot\vec{D} \quad \text{(L82)}$$

$$\Rightarrow (q^2 - 4\pi\chi_c)\vec{E} = \vec{q}(\vec{q}\cdot\vec{D}) \quad \text{(L83)}$$

Dynamic Lindhard dielectric function

$$\epsilon(\vec{q},\omega) = 1 - \frac{4\pi\chi_c}{q^2} \quad \text{(L84)}$$

Many-Body Green Functions

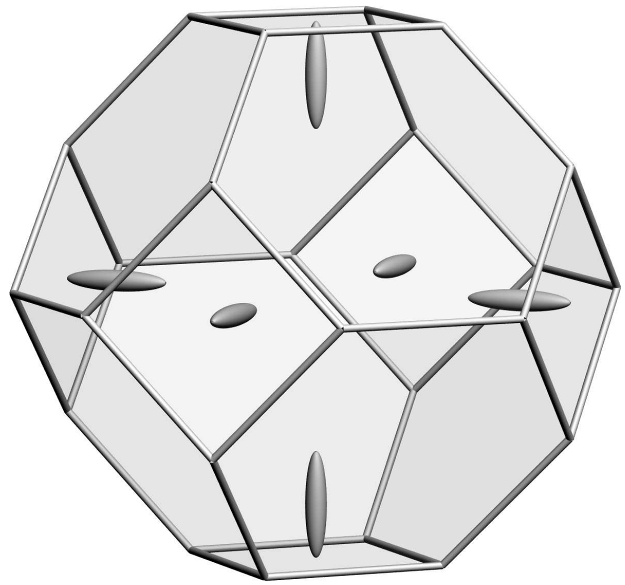
Classics....

☞ Kadanoff and Baym (1962)

☞ Abrikosov, Gor'kov, and Dzyaloshinskii (1965)

☞ Fetter and Walecka (1971)

Electronics



Definitions

- ☞ Work Functions
- ☞ Schottky Barrier
- ☞ Intrinsic Semiconductors
- ☞ Doping
- ☞ Semiconductor Junctions
- ☞ Rectification
- ☞ Diodes and Transitors
- ☞ Heterostructures
- ☞ Two-Dimensional Electron Gas (2DEG)
- ☞ Quantum Point Contact
- ☞ Quantum Dot

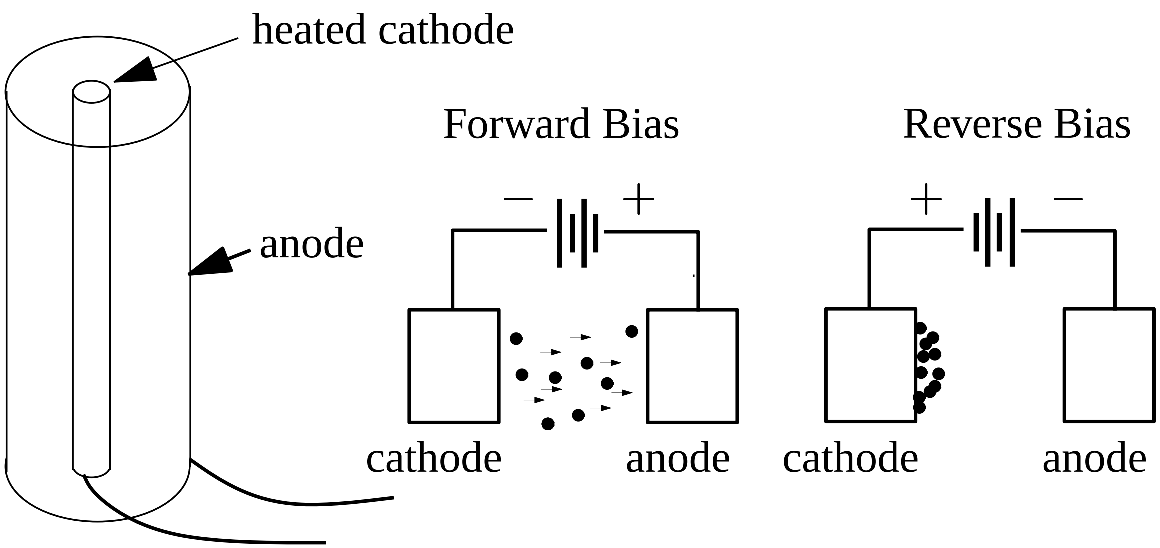


Figure 1: Operation of a diode.

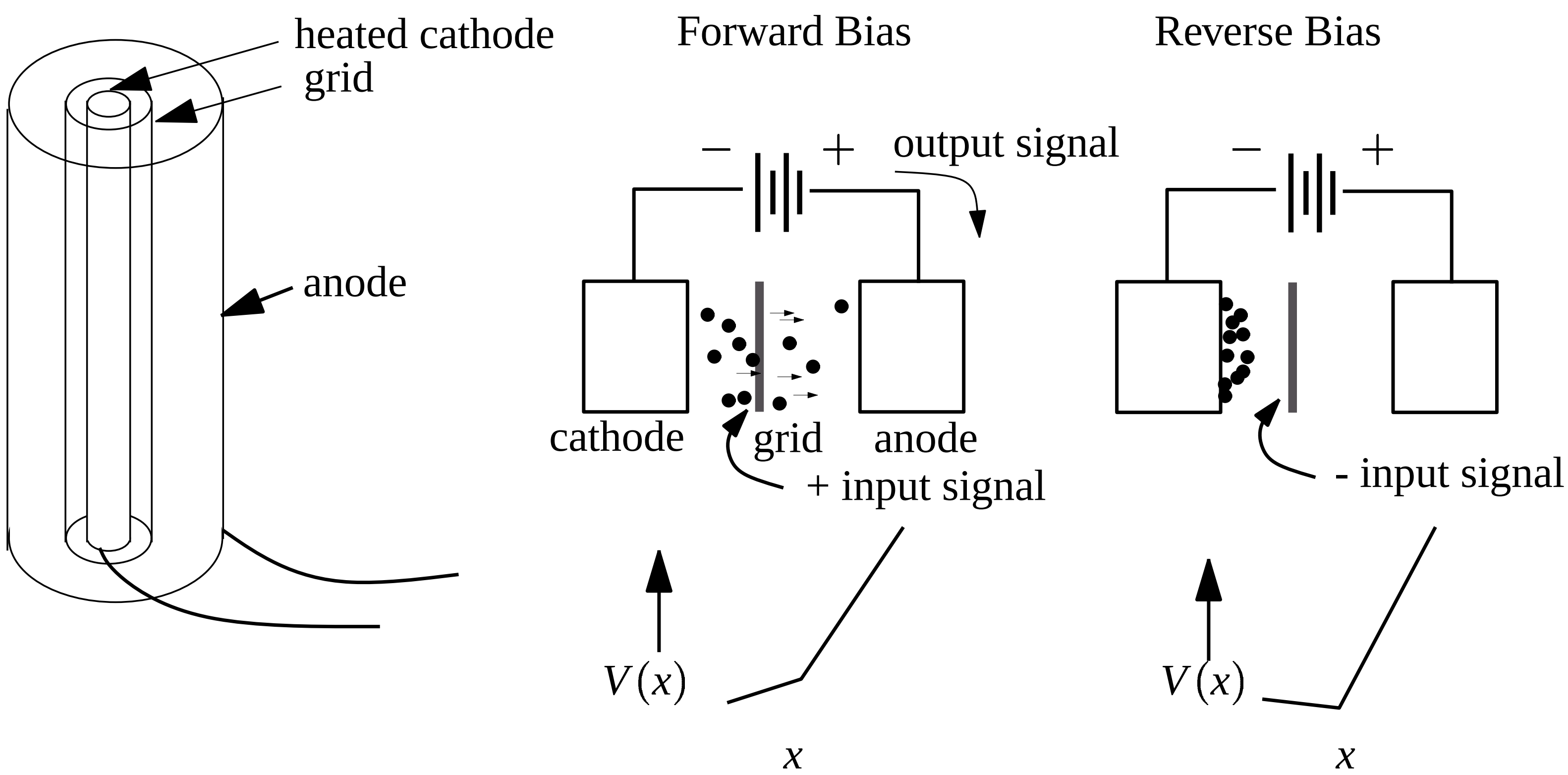


Figure 2: Operation of a triode.

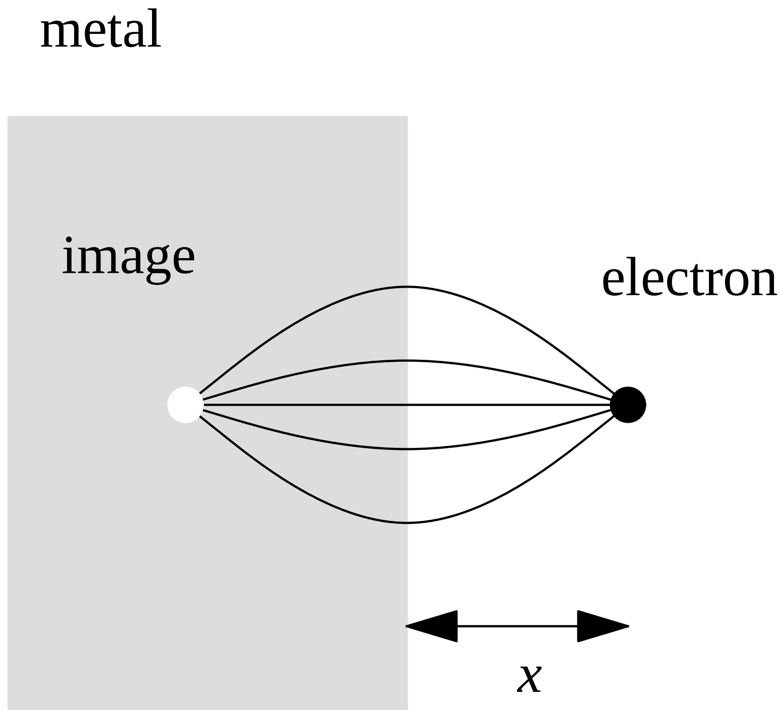


Figure 3: An electron attracted to metal surface.

$$F = \frac{e^2}{(2x)^2}, \tag{L1}$$

$$U(x) = -\frac{e^2}{4x} = -\frac{1}{x} 3.6 \cdot 10^{-4} \mu\mathrm{m\,eV}. \tag{L2}$$

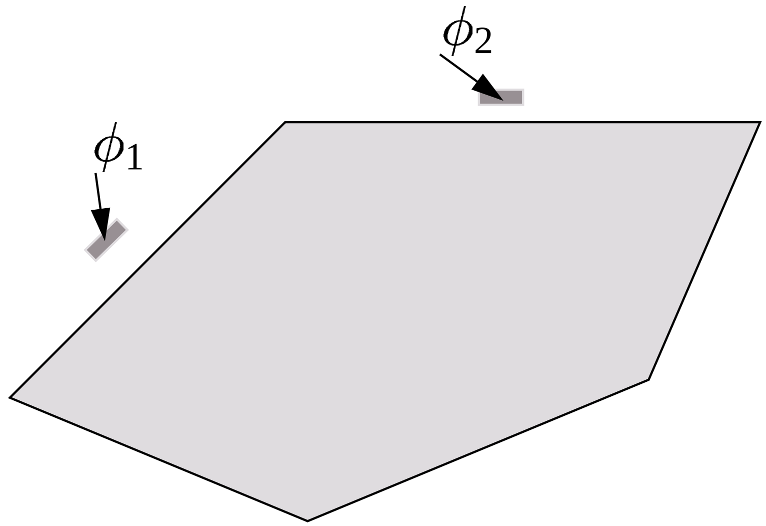


Figure 4: Work function.

Schottky Barrier

$$U(x) = -\frac{e^2}{4x} - e|E|x, \tag{L3}$$

$$x_0 = \sqrt{\frac{e}{4|E|}} \Rightarrow U(x_0) = -e\sqrt{e|E|}. \tag{L4}$$

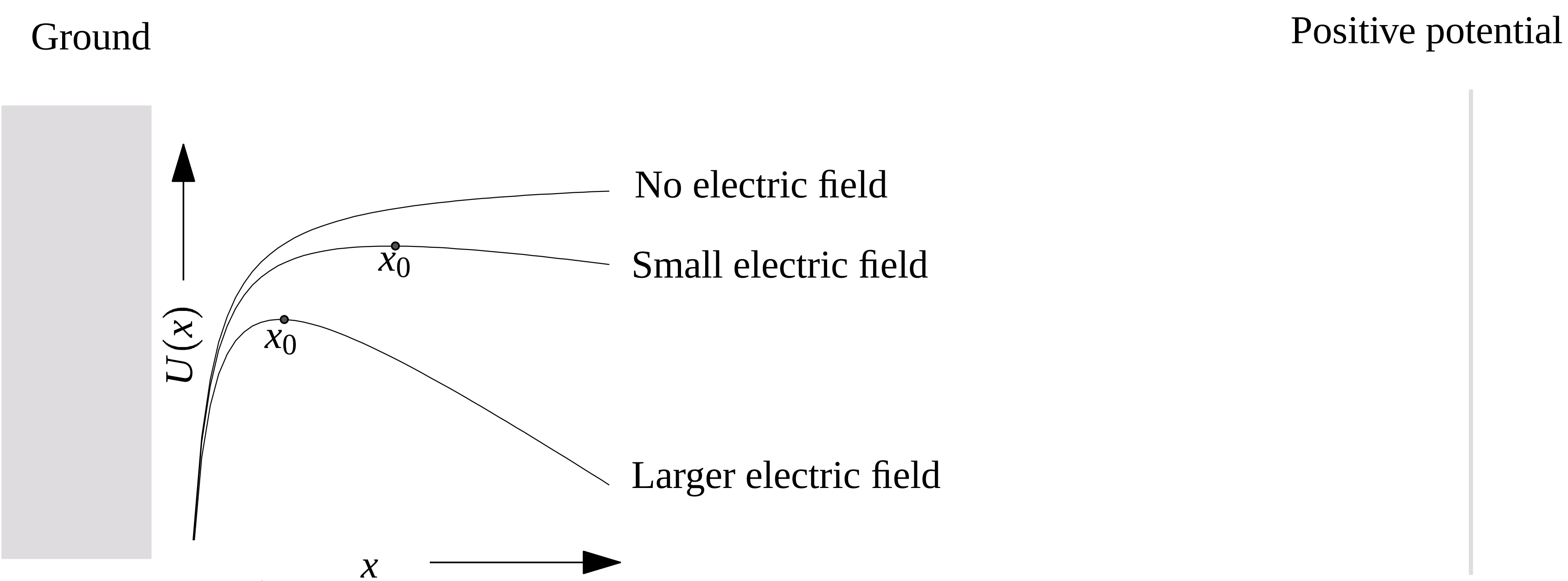


Figure 5: Schottky barrier

$$f_{x\vec{k}} = \frac{1}{e^{\beta(\mathcal{E}^0_{\vec{k}}+U(x)-\mu)}+1}. \tag{L5}$$

$$f_{x\vec{k}} \approx e^{-\beta(\mathcal{E}^0_{\vec{k}}+U(x)+\phi)}. \tag{L6}$$

$$\begin{aligned} j &= -e\exp\{-\beta[\phi+U(x_0)]\}\int[d\vec{k}]\,\frac{\hbar k_x}{m}\theta(k_x)e^{-\beta\hbar^2k^2/2m} && \text{(L7)}\\ &= -\mathcal{A}T^2\exp\left\{-\beta\left[\phi-e\sqrt{e|E|}\right]\right\}, && \text{(L8)}\end{aligned}$$

where

$$\mathcal{A} = \frac{em}{2\pi^2\hbar^3}k_B^2 = 120.2\,\mathrm{A\,cm^{-2}\,K^{-2}}. \tag{L9}$$

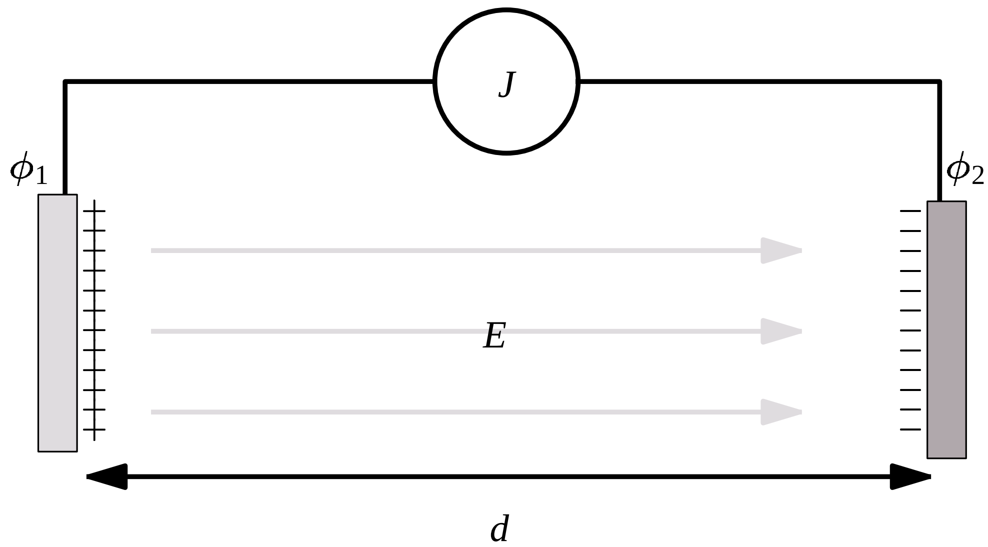


Figure 6: Contact potential of two metals

$$V = Ed = 4\pi\sigma d, \tag{L10}$$

$$\phi_2 - \phi_1 = 4\pi e\sigma d. \tag{L11}$$

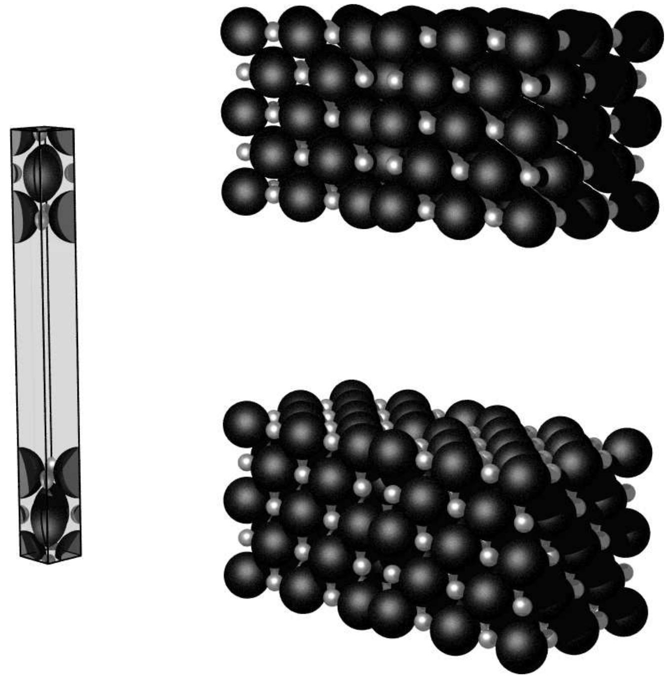


Figure 7: Periodic unit cell that produces surfaces

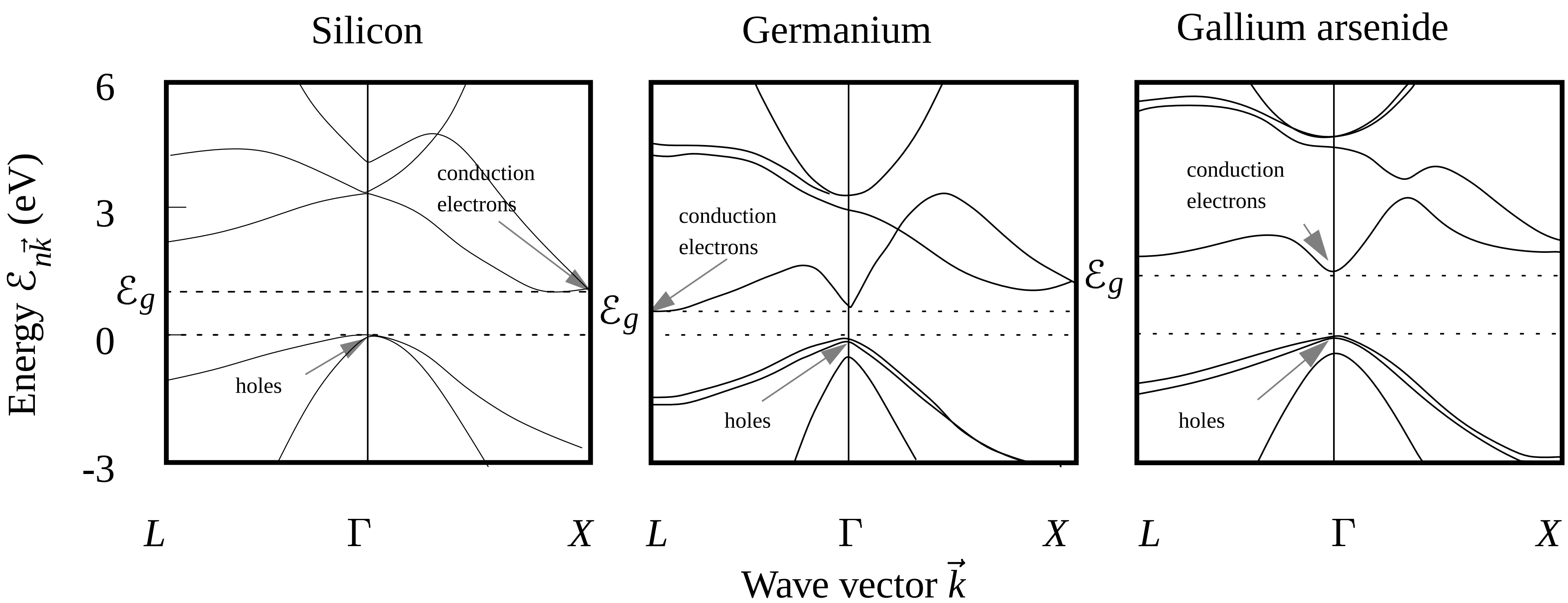


Figure 8: Essential features of band structures of silicon, germanium, and gallium arsenide.

$$e^{-\beta\mathcal{E}_g/2} \sim 10^{-9}. \tag{L12}$$

Pure Semiconductors

Com-pound		$\mathcal{E}_g$ (eV)	$d\mathcal{E}_g/dT$ (eV/K)	n_i (cm^{-3})	ϵ^0	$m_n^\star$ (m)	$m_{ph}^\star$ (m)	$m_{pl}^\star$ (m)	μ_n (cm^2/V s)	μ_p (cm^2/V s)
Si	i	1.11	$-9.0 \cdot 10^{-5}$	$1.02 \cdot 10^{10}$	11.9	1.18	0.54	0.15	1350	480
Ge	i	0.74	$-3.7 \cdot 10^{-4}$	$2.33 \cdot 10^{13}$	16.5	0.55	0.3	0.04	3900	1800
GaAs	d	1.43	$-3.9 \cdot 10^{-4}$	$2 \cdot 10^{6}$	12.5	0.067	0.50	0.07	7900	450
SiC	i	2.2	$-5.8 \cdot 10^{-4}$		9.7	0.82	1		900	50
AlAs	i	2.14	$-4 \cdot 10^{-4}$	$2 \cdot 10^{17}$	10.0	0.5	0.5	0.26	294	
AlSb	i	1.63	$-4 \cdot 10^{-4}$		12.0	0.3	1	0.5	200	400
GaN	d	3.44	$-6.7 \cdot 10^{-4}$	$2 \cdot 10^{17}$	12.0	0.3	1		440	
GaSb	d	0.7	$-3.7 \cdot 10^{-4}$	10^{14}	15.7	0.05	0.3	0.04	7700	1600
InP	d	1.34	$-2.9 \cdot 10^{-4}$	$1.2 \cdot 10^{8}$	15.2	0.073	0.6	0.12	5400	150
InAs	d	0.36	$-3.5 \cdot 10^{-4}$	$1.3 \cdot 10^{15}$	15.2	0.027	0.4	0.03	30 000	450
InSb	d	0.18	$-2.8 \cdot 10^{-4}$	$2.0 \cdot 10^{16}$	16.8	0.013	0.4	0.02	77 000	850

$$\mathcal{E}_{\vec{k}} = \mathcal{E}_c + \frac{\hbar^2}{2}\vec{k}^*\mathbf{M}^{-1}\vec{k} \quad \text{(L13a)}$$

$$\mathcal{E}_{\vec{k}} = \mathcal{E}_v - \frac{\hbar^2}{2}\vec{k}^*\mathbf{M}^{-1}\vec{k}, \quad \text{(L13b)}$$

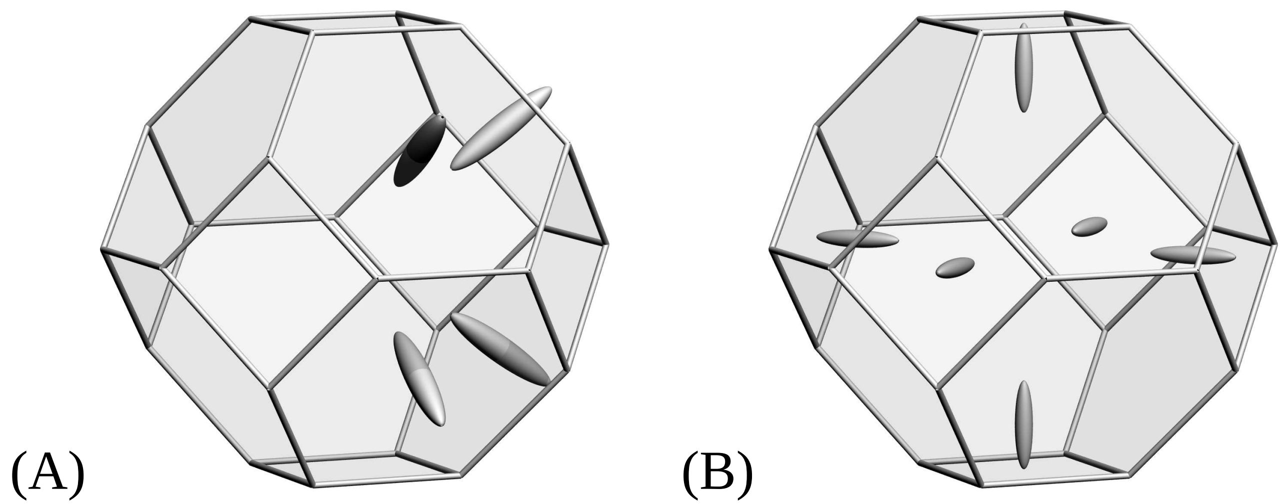


Figure 9: Semiconductor conduction band energy surfaces

$$n = \int_{\mathcal{E}_c}^{\infty} d\mathcal{E}\, D(\mathcal{E}) \frac{1}{e^{\beta(\mathcal{E}-\mu)}+1}, \tag{L14}$$

$$\begin{aligned} p &= \int_{-\infty}^{\mathcal{E}_v} d\mathcal{E}\, D(\mathcal{E}) \left\{1 - \frac{1}{e^{\beta(\mathcal{E}-\mu)}+1}\right\} && \text{(L15a)} \\ &= \int_{-\infty}^{\mathcal{E}_v} d\mathcal{E}\, D(\mathcal{E}) \frac{1}{e^{-\beta(\mathcal{E}-\mu)}+1}. && \text{(L15b)} \end{aligned}$$

$$\mathcal{E}_c - \mu \gg k_B T \quad \text{and} \quad \mu - \mathcal{E}_v \gg k_B T. \tag{L16}$$

$$n = \mathcal{N}_c e^{-\beta(\mathcal{E}_c-\mu)}, \quad p = \mathcal{N}_v e^{-\beta(\mu-\mathcal{E}_v)} \tag{L17}$$

$$\begin{aligned} \mathcal{N}_c &= \int_{\mathcal{E}_c}^{\infty} d\mathcal{E}\, D(\mathcal{E}) e^{-\beta(\mathcal{E}-\mathcal{E}_c)} && \text{(L18a)} \\ \mathcal{N}_v &= \int_{-\infty}^{\mathcal{E}_v} d\mathcal{E}\, D(\mathcal{E}) e^{-\beta(\mathcal{E}_v-\mathcal{E})}. && \text{(L18b)} \end{aligned}$$

Semiconductor in Equilibrium

$$D(\mathcal{E}) = \int [d\vec{k}]\,\delta\Big(\mathcal{E}-\mathcal{E}_c-\frac{1}{2}\hbar^2\vec{k}^*\mathbf{M}^{-1}\vec{k}\Big) \quad \text{(L19)}$$

$$= \int [d\vec{k}]\,\delta\Big(\mathcal{E}-\mathcal{E}_c-\frac{1}{2}\hbar^2\sum_l k_l^2/m_l\Big). \quad \text{(L20)}$$

$$m_n^\star = [m_1 m_2 m_3]^{1/3} \quad \text{and} \quad \vec{q} = (k_1/\sqrt{m_1}, k_2/\sqrt{m_2}, k_3/\sqrt{m_3}) \quad \text{(L21)}$$

$$D(\mathcal{E}) = 2\int m_n^{\star 3/2}\frac{d\vec{q}}{(2\pi)^3}\delta\Big(\mathcal{E}-\mathcal{E}_c-\frac{1}{2}\hbar^2 q^2\Big) = \sqrt{2(\mathcal{E}-\mathcal{E}_c)}\frac{m_n^{\star 3/2}}{\hbar^3\pi^2}\mathcal{M}_c. \quad \text{(L22)}$$

$$\mathcal{N}_c = \frac{1}{4}\left(\frac{2m_n^\star k_B T}{\pi\hbar^2}\right)^{3/2}\mathcal{M}_c \quad \text{(L23)}$$

$$\mathcal{N}_v = \frac{1}{4}\left(\frac{2m_p^\star k_B T}{\pi\hbar^2}\right)^{3/2}. \quad \text{(L24)}$$

Mass action: $np =$? ?. (L25)

$$a_* = \frac{\epsilon \hbar^2}{m^\star e^2} \quad \text{and} \quad \mathcal{E}_b = \frac{e^2}{2\epsilon a_*} = \frac{m^\star}{m}\frac{1}{\epsilon^2} \cdot 13.6\,\text{eV}. \qquad \text{(L26)}$$

Group V donors, $\mathcal{E}_c - \mathcal{E}_d$ (meV)										
Host	Eq. (L26)	N	P	As	Sb	Bi				
Si	113	140	45	53.7	42.7	70.6				
Ge	28		12.9	14.2	10.3	12.8				
Group III acceptors, $\mathcal{E}_a - \mathcal{E}_v$ (meV)										
Host	Eq. (L26)	B	In	Ga	Al	Tl				
Si	48	45	155	74	67	25				
Ge	15	9.73	12.0	11.3	10.8	13.5				
Donors, $\mathcal{E}_c - \mathcal{E}_d$ (meV)										
Host	Eq. (L26)	Pb	Se	Si	S	Ge	C			
GaAs	5.8	5.8	5.8	5.8	5.9	5.9	5.9			
Acceptors, $\mathcal{E}_a - \mathcal{E}_v$ (meV)										
Host	Eq. (L26)	Be	Mg	Zn	Cd	C	Si	Ge	Sn	Mn
GaAs	23	28	29	31	35	27	35	40	167	113
InP	21	31	31	46	57	41		210		270

$$n_i = \sqrt{\mathcal{N}_c \mathcal{N}_v} ? \qquad ? \qquad \text{(L27a)}$$

$$= 2.510 \cdot 10^{19}\text{cm}^{-3} \left(\frac{m_n^\star m_p^\star}{m^2}\right)^{3/4} \mathcal{M}_c^{1/2} \left(\frac{T}{300\,\text{K}}\right)^{3/2} ? \qquad ?. \qquad \text{(L27b)}$$

$$\mu_i = k_B T \ln \frac{n_i}{\mathcal{N}_c} + \mathcal{E}_c = \mathcal{E}_v + \frac{\mathcal{E}_g}{2} + \frac{3}{4} k_B T \ln(m_p^\star / m_n^\star) - \frac{1}{2} k_B T \ln \mathcal{M}_c. \tag{L28}$$

$$np = n_i^2 \tag{L29}$$

$$n = n_i e^{-\beta(\mu_i - \mu)}, \quad p = n_i e^{-\beta(\mu - \mu_i)}. \tag{L30}$$

Extrinsic Semiconductor

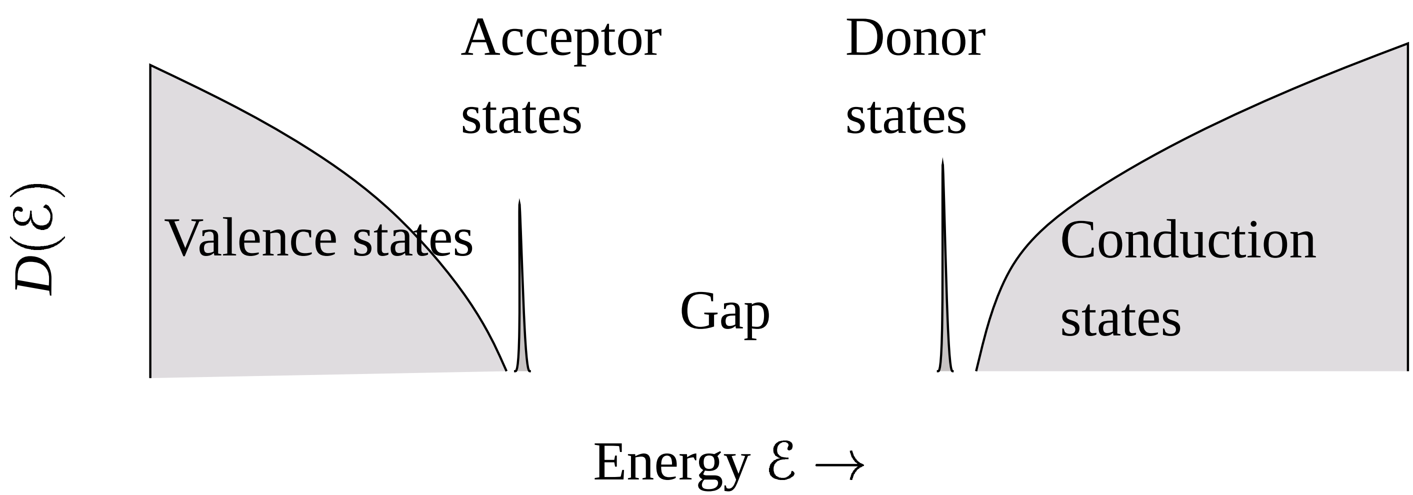


Figure 10: Densities of states with doping

$$f_d = \frac{0 \times 1 + 1 \times 2 \times e^{-\beta(\mathcal{E}_d - \mu)}}{1 + 2 \times e^{-\beta(\mathcal{E}_d - \mu)}} \tag{L31}$$

$$= \frac{1}{1 + \frac{1}{2} e^{\beta(\mathcal{E}_d - \mu)}} \ll 1.. \tag{L32}$$

$$f_a = \frac{1}{\frac{1}{4} e^{\beta(\mu - \mathcal{E}_a)} + 1} \ll 1. \tag{L33}$$

Extrinsic Semiconductor

$$n_{\mathrm{t}} + \mathcal{N}_d = \int_{\mathcal{E}_c} d\mathcal{E}\, D(\mathcal{E}) \frac{1}{1+e^{\beta(\mathcal{E}-\mu)}} + \int^{\mathcal{E}_v} d\mathcal{E}\, D(\mathcal{E}) \frac{1}{1+e^{\beta(\mathcal{E}-\mu)}} + \mathcal{N}_d f_d. \quad \text{(L34)}$$

$$\mathcal{N}_d = \int_{\mathcal{E}_c} d\mathcal{E}\, D(\mathcal{E}) \frac{1}{1+e^{\beta(\mathcal{E}-\mu)}} - \int^{\mathcal{E}_v} d\mathcal{E}\, D(\mathcal{E}) \frac{1}{1+e^{-\beta(\mathcal{E}-\mu)}} \quad \text{(L35)}$$

$$\Rightarrow \mathcal{N}_d = n - p = n_i e^{-\beta(\mu_i-\mu)} - n_i e^{-\beta(\mu-\mu_i)}. \quad \text{(L36)}$$

$$n - p = \mathcal{N}_d - \mathcal{N}_a. \quad \text{(L37)}$$

$$n = \frac{1}{2}[\mathcal{N}_d - \mathcal{N}_a] + \frac{1}{2}\left[(\mathcal{N}_d - \mathcal{N}_a)^2 + 4n_i^2\right]^{1/2} \quad \text{(L38a)}$$

$$p = \frac{1}{2}[\mathcal{N}_a - \mathcal{N}_d] + \frac{1}{2}\left[(\mathcal{N}_d - \mathcal{N}_a)^2 + 4n_i^2\right]^{1/2}. \quad \text{(L38b)}$$

$$n - p = 2n_i \sinh \beta(\mu - \mu_i) \Rightarrow \mu = \mu_i + k_B T \sinh^{-1}\left([\mathcal{N}_d - \mathcal{N}_a]/2n_i\right). \quad \text{(L39)}$$

$$n \approx ? \quad ? \tag{L40a}$$

$$p \approx ? \quad ?. \tag{L40b}$$

$$p \approx ? \quad ? \tag{L41a}$$

$$n \approx ? \quad ?. \tag{L41b}$$

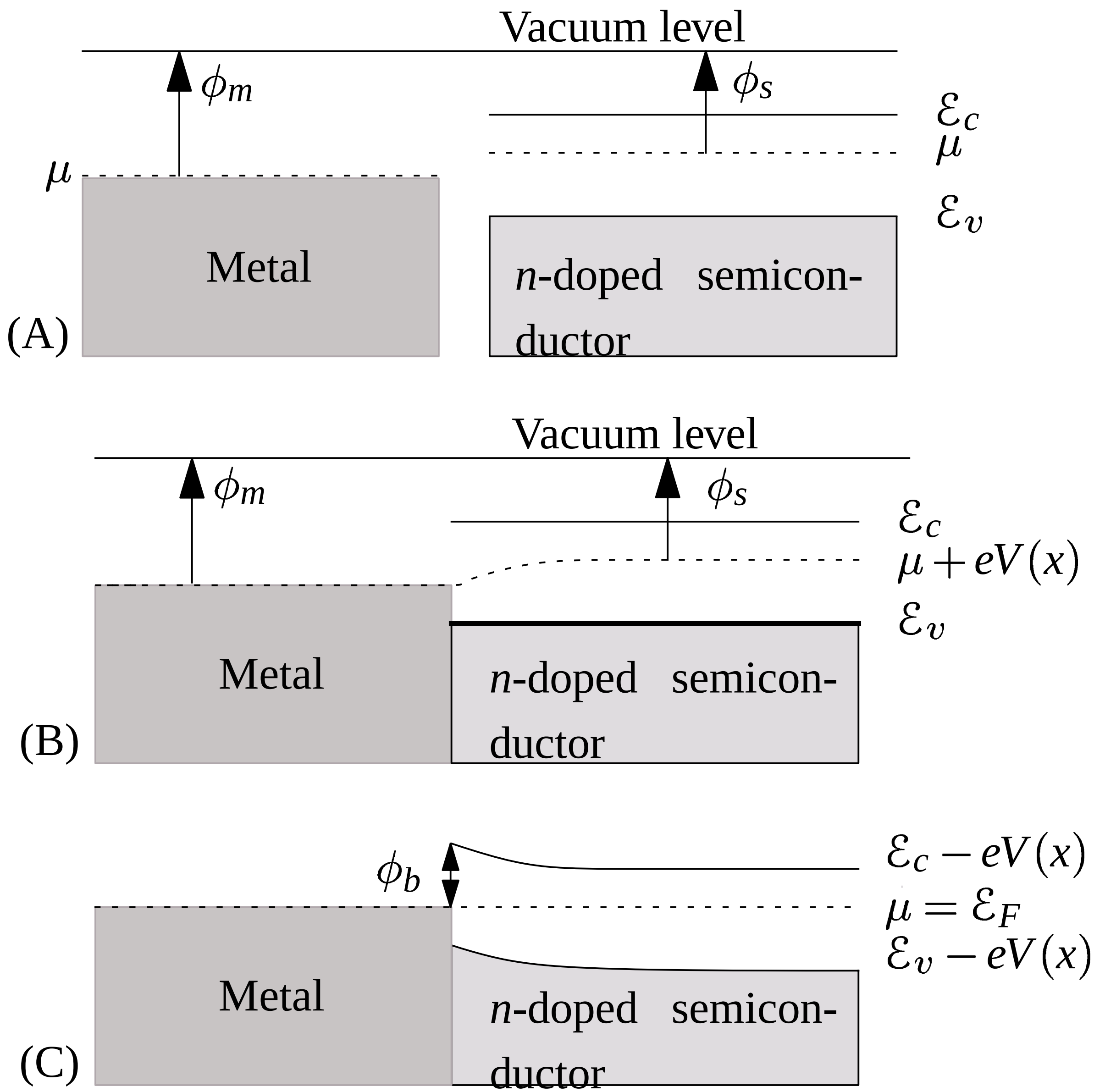


Figure 11: Schottky diode

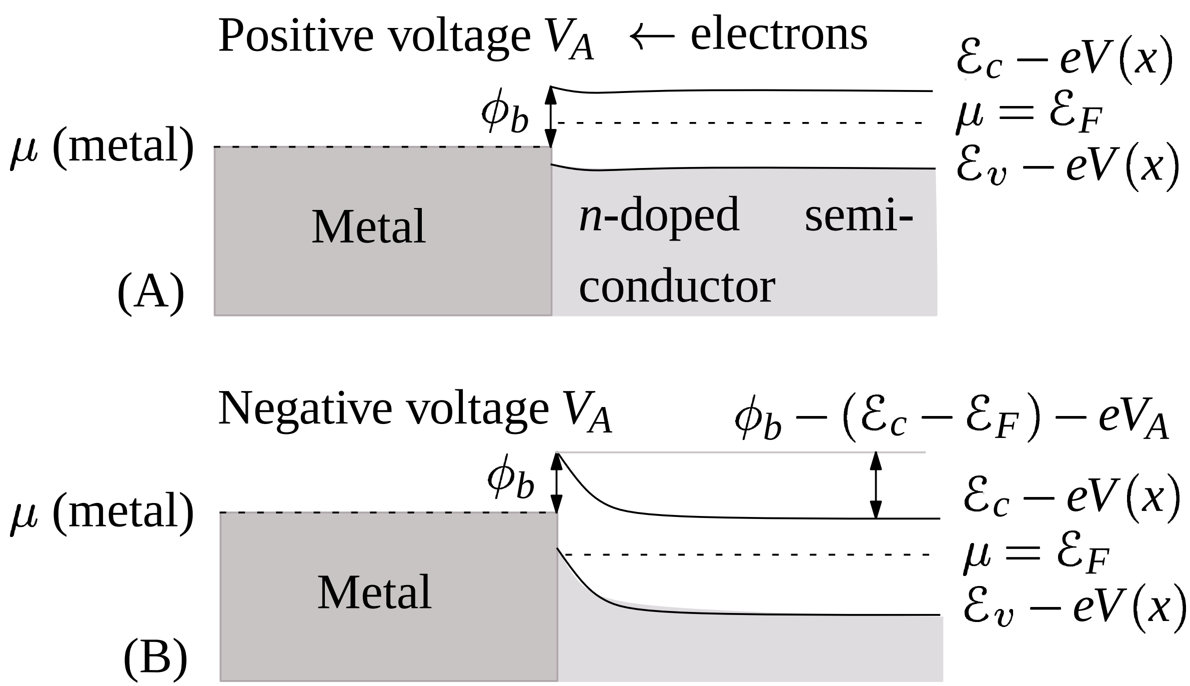


Figure 12: Biased Schottky diode

$$\frac{\hbar^2 k_x^2}{2m_n^\star} > \phi_b - (\mathcal{E}_c - \mu) - eV_A. \tag{L42}$$

$$j_{s\to m} = \int [d\vec{k}]\,\theta\left(\frac{\hbar^2 k_x^2}{2m_n^\star} - [\phi_b - (\mathcal{E}_c - \mu) - eV_A]\right)\frac{e\hbar k_x}{m_n^\star}\,e^{-\beta(\hbar^2 k^2/2m_n^\star + \mathcal{E}_c - \mu)} \tag{L43}$$

$$= \quad \frac{2}{(2\pi)^3}\frac{2m_n^\star \pi k_B T}{\hbar^2}\frac{e}{\hbar}\int_{\phi_b-\mathcal{E}_c+\mu-eV_A}^{\infty} d\left(\frac{\hbar^2 k_x^2}{2m_n^\star}\right) e^{-\beta(\hbar^2 k_x^2/2m_n^\star+\mathcal{E}_c-\mu)} \qquad \text{(L44)}$$

$$= \quad \frac{m_n^\star}{m}\mathcal{A}T^2 \exp\{-\beta[\phi_b - eV_A]\}. \qquad \text{(L45)}$$

$$j = \frac{m_n^\star}{m}\mathcal{A}T^2 \left[\exp\{-\beta[\phi_b - eV_A]\} - \exp\{-\beta\phi_b\}\right]. \qquad \text{(L46)}$$

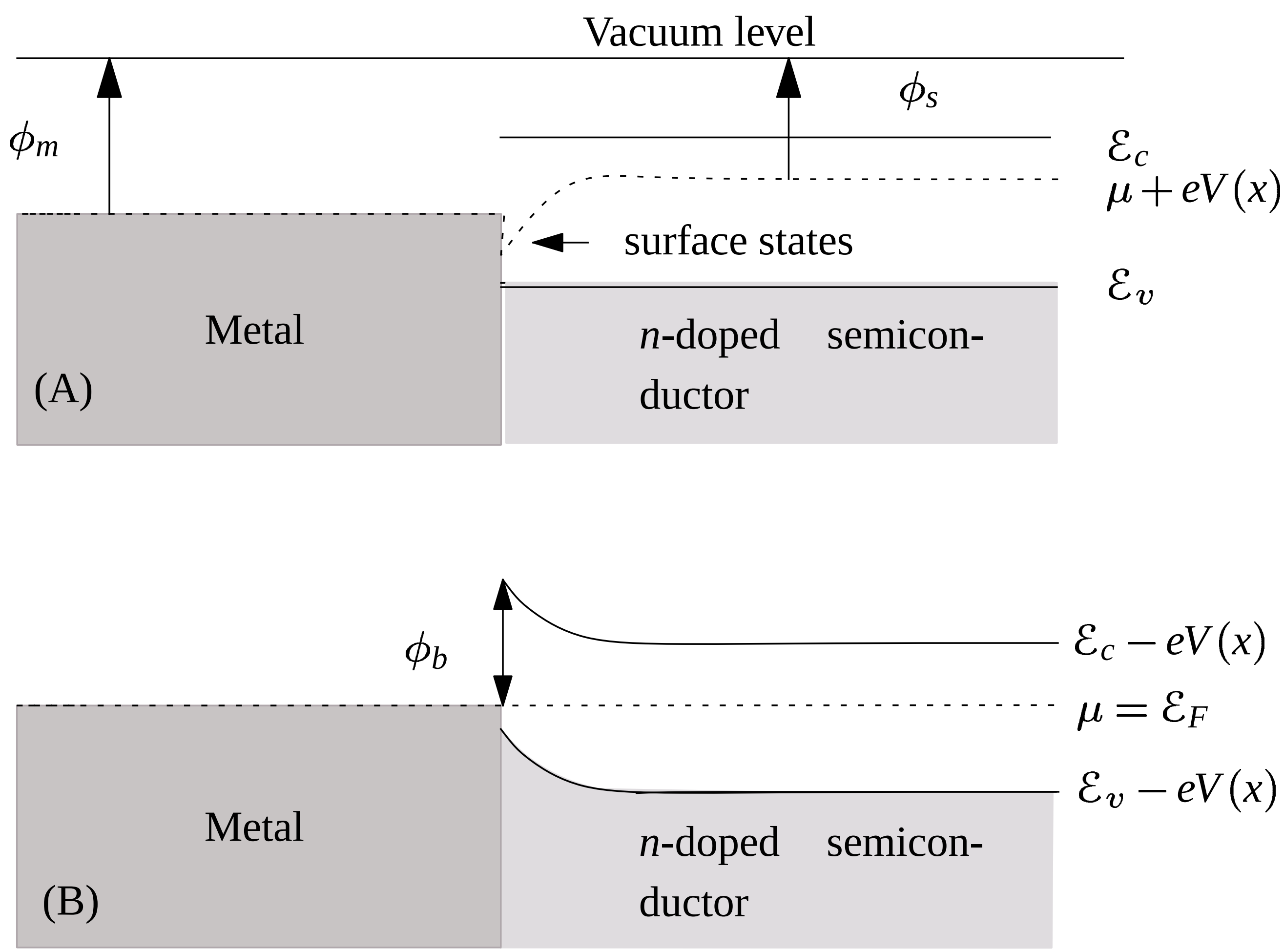


Figure 13: Effect of surface states on metal–semiconductor junction.

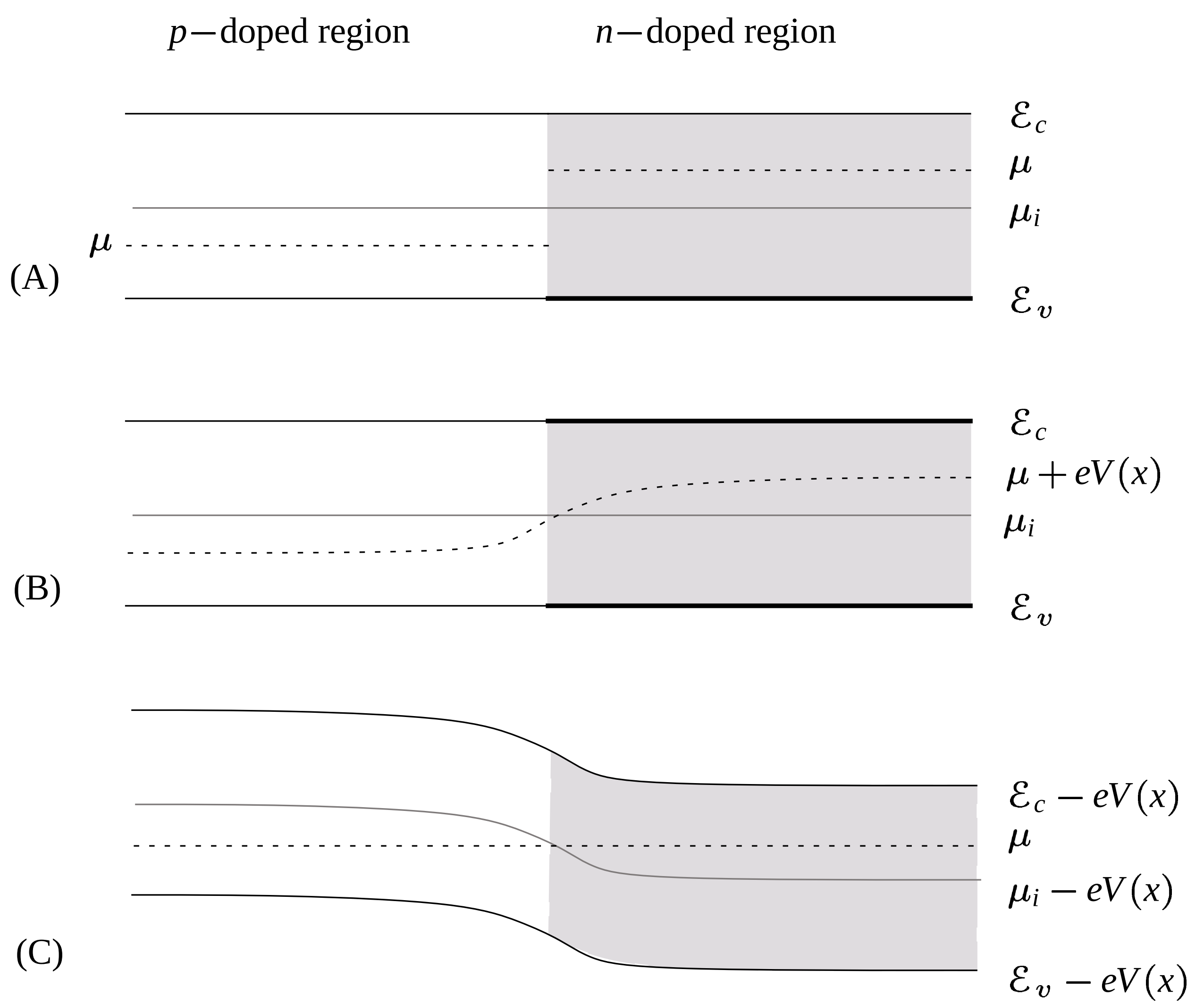


Figure 14: Band bending across semiconductor junction

Semiconductor Junctions

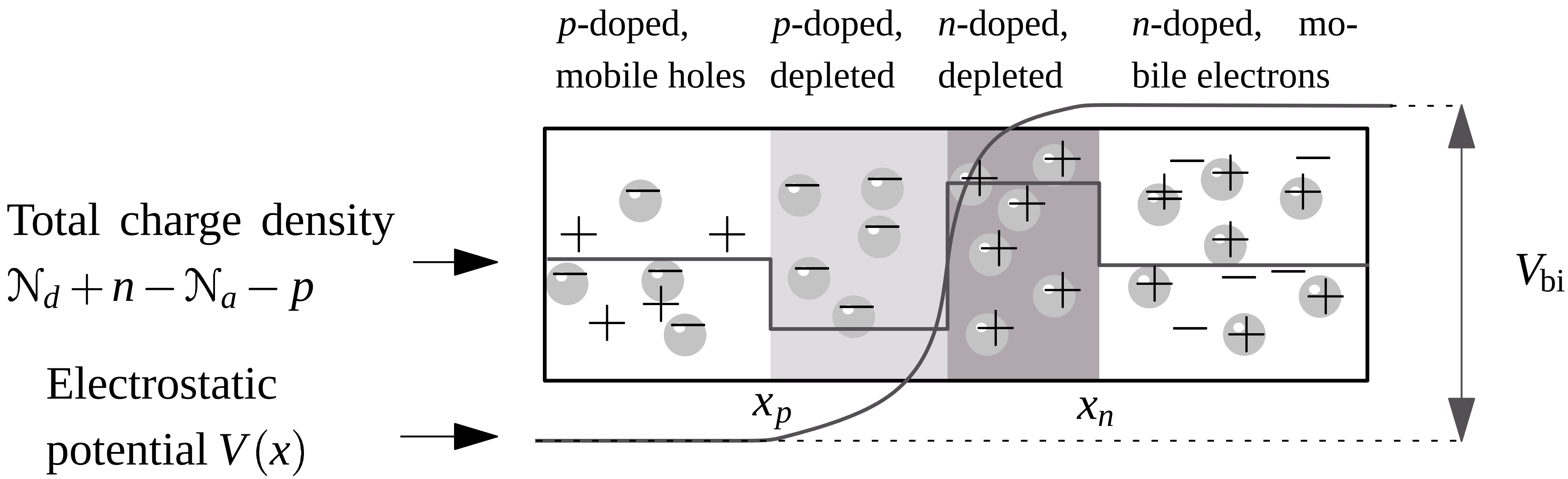


Figure 15: Illustration of the redistribution of mobile charges near a *p*–*n* junction.

$$n(x) = n_i e^{\beta(\mu + eV(x) - \mu_i)} \quad \text{(L47a)}$$

$$p(x) = n_i e^{\beta(\mu_i - eV(x) - \mu)}. \quad \text{(L47b)}$$

$$n(\infty)p(-\infty) = \mathcal{N}_d\mathcal{N}_a = n_i^2 e^{\beta(eV(\infty) - eV(-\infty))} \quad \text{(L48)}$$

$$\Rightarrow eV_{\rm bi} \equiv e[V(\infty) - V(-\infty)] \quad \text{(L49)}$$

$$= \quad k_B T \ln \frac{\mathcal{N}_d \mathcal{N}_a}{n_i^2} = \mathcal{E}_g + k_B T \ln [\frac{\mathcal{N}_d \mathcal{N}_a}{\mathcal{N}_c \mathcal{N}_v}], \tag{L50}$$

$$e n_{\text{ions}} = e[\mathcal{N}_d(x) - \mathcal{N}_a(x)]. \tag{L51}$$

$$\frac{\partial^2 V}{\partial x^2} = -4\pi e [\mathcal{N}_d(x) - n(x) - \mathcal{N}_a(x) + p(x)]/\epsilon^0, \tag{L52}$$

$$\mathcal{N}_a(x) \quad = \quad \mathcal{N}_a \theta(-x) \tag{L53a}$$

$$\mathcal{N}_d(x) \quad = \quad \mathcal{N}_d \theta(x). \tag{L53b}$$

$$V(x) = \begin{cases} V(-\infty) & \text{for } x < x_p \\ V(-\infty) + 2\pi e \frac{\mathcal{N}_a}{\epsilon^0}(x - x_p)^2 & \text{for } 0 > x > x_p \\ V(\infty) \quad - 2\pi e \frac{\mathcal{N}_d}{\epsilon^0}(x - x_n)^2 & \text{for } 0 < x < x_n \\ V(\infty) & \text{for } x > x_n. \end{cases} \tag{L54}$$

$$V(-\infty) + 2\pi e \frac{\mathcal{N}_a}{\epsilon^0} x_p^2 = V(\infty) - 2\pi e \frac{\mathcal{N}_d}{\epsilon^0} x_n^2, \;\; \mathcal{N}_d x_n = -\mathcal{N}_a x_p. \tag{L55}$$

$$x_n = \sqrt{\frac{\epsilon^0 \mathcal{N}_a V_{\text{bi}}}{2\pi e \mathcal{N}_d [\mathcal{N}_a + \mathcal{N}_d]}} \tag{L56a}$$

$$x_p = -\sqrt{\frac{\epsilon^0 \mathcal{N}_d V_{\text{bi}}}{2\pi e \mathcal{N}_a [\mathcal{N}_a + \mathcal{N}_d]}}, \tag{L56b}$$

$$J \propto e^{\beta e V_A} - 1, \tag{L57}$$

$$\frac{\partial g}{\partial t} = -\frac{\partial}{\partial \vec{r}} \cdot \dot{\vec{r}} g - \frac{\partial}{\partial \vec{k}} \cdot \dot{\vec{k}} g + \frac{f-g}{\tau}. \qquad \text{(L58)}$$

$$n = \int [d\vec{k}]\, g_{\vec{r}\vec{k}}, \qquad \text{(L59)}$$

$$\frac{\partial n}{\partial t} = -\frac{\partial}{\partial \vec{r}} \cdot \langle \dot{\vec{r}} \rangle n + \frac{n^{(0)} - n}{\tau_n}, \qquad \text{(L60)}$$

$$\begin{aligned}
\langle \dot{\vec{r}} \rangle &= \frac{1}{n} \int [d\vec{k}]\, g_{\vec{r}\vec{k}} \vec{v}_{\vec{k}} && \text{(L61)}\\
&= \frac{1}{n} \int [d\vec{k}] \left[f - \tau \vec{v}_{\vec{k}} \cdot \left\{ e\vec{E} \frac{\partial f}{\partial \mu} + \frac{\partial f}{\partial \vec{r}} \right\} \right] \vec{v}_{\vec{k}} && \text{(L62)}\\
&\approx \frac{1}{n} \int [d\vec{k}] \left[-\tau \vec{v}_{\vec{k}} \cdot \left\{ e\vec{E} \beta g + \frac{\partial g}{\partial \vec{r}} \right\} \right] \vec{v}_{\vec{k}} && \text{(L63)}\\
&= -\mu_n \vec{E} - \frac{\mathcal{D}_n}{n} \frac{\partial n}{\partial \vec{r}} && \text{(L64)}\\
\mu_n &= \frac{e}{3} \beta \left\langle \tau v_{\vec{k}}^2 \right\rangle && \text{(L65)}
\end{aligned}$$

$$\mathcal{D}_n = \frac{1}{3}\left\langle \tau v_{\vec{k}}^2 \right\rangle = \frac{k_B T \mu_n}{e}. \tag{L66}$$

$$\vec{j}_n = e\mu_n n\vec{E} + e\mathcal{D}_n\vec{\nabla} n \tag{L67a}$$

$$\vec{j}_p = e\mu_p p\vec{E} - e\mathcal{D}_p\vec{\nabla} p, \tag{L67b}$$

$$\frac{\partial n}{\partial t} = \frac{1}{e}\vec{\nabla}\cdot\vec{j}_n + \frac{n^{(0)} - n}{\tau_n} \tag{L68a}$$

$$\frac{\partial p}{\partial t} = -\frac{1}{e}\vec{\nabla}\cdot\vec{j}_p + \frac{p^{(0)} - p}{\tau_p}, \tag{L68b}$$

$$\vec{\nabla}\cdot\vec{E} = \frac{4\pi e(p - n + n_{\text{ions}})}{\epsilon^0}. \tag{L69}$$

Detailed Theory of Rectification

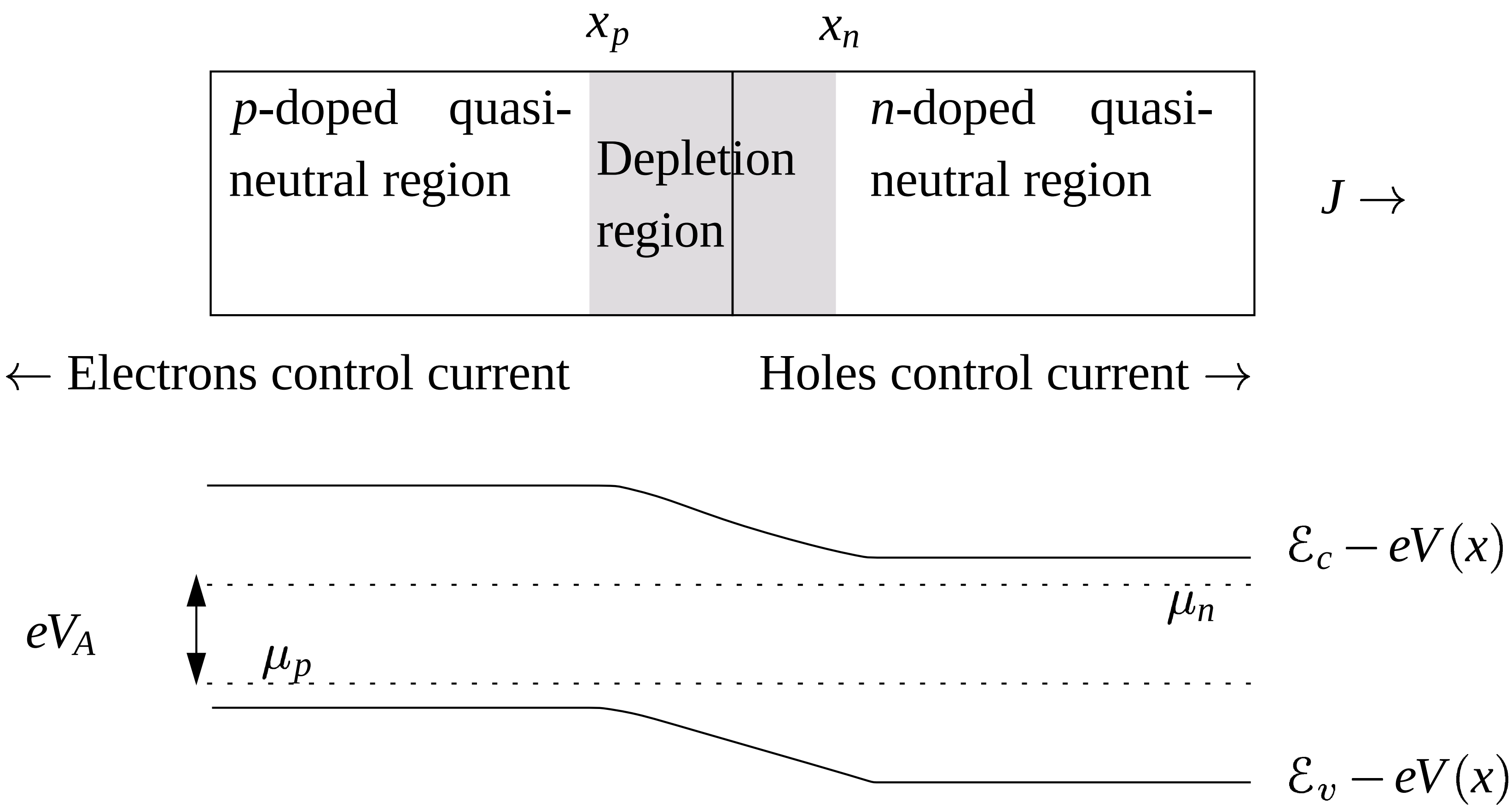


Figure 16: p–n junction in forward bias

$$j_n = e\mathcal{D}_n \vec{n}' \quad \text{(L70a)}$$

$$j_p = -e\mathcal{D}_p \vec{p}' \quad \text{(L70b)}$$

$$n(x) = \mathcal{N}_d e^{\beta e[V(x)-V(x_n)]}\left[1+\frac{j_n}{e\mathcal{N}_d\mathcal{D}_n}\int_{x_n}^{x} dx'\, e^{-\beta e[V(x')-V(x_n)]}\right] \tag{L71a}$$

$$p(x) = \mathcal{N}_a e^{-\beta e[V(x)-V(x_p)]}\left[1-\frac{j_p}{e\mathcal{N}_a\mathcal{D}_p}\int_{x_p}^{x} dx'\, e^{\beta e[V(x')-V(x_p)]}\right]. \tag{L71b}$$

$$\frac{n_i^2}{\mathcal{N}_a\mathcal{N}_d}\frac{x_p-x_n}{L_n}e^{\beta eV_A} \approx 10^{-10}e^{\beta eV_A}. \tag{L72}$$

$$n(x) = \mathcal{N}_d e^{\beta e[V(x)-V(x_n)]} \tag{L73a}$$

$$p(x) = \mathcal{N}_a e^{-\beta e[V(x)-V(x_p)]} \tag{L73b}$$

$$\Rightarrow n(x_p) = \mathcal{N}_d e^{\beta e[V_A-V_{\rm bi}]} = \frac{n_i^2}{\mathcal{N}_a}e^{\beta eV_A} \tag{L73c}$$

$$p(x_n) = \mathcal{N}_a e^{\beta e[V_A-V_{\rm bi}]} = \frac{n_i^2}{\mathcal{N}_d}e^{\beta eV_A}. \tag{L73d}$$

$$0 = \mathcal{D}_p \frac{d^2 p}{dx^2} - \frac{p - p^{(0)}}{\tau_p} \quad \text{(L74a)}$$

$$0 = \mathcal{D}_n \frac{d^2 n}{dx^2} - \frac{n - n^{(0)}}{\tau_n}, \quad \text{(L74b)}$$

$$p - p^{(0)} = [p(x_n) - p^{(0)}]e^{-(x-x_n)/L_p} \quad \text{(L75a)}$$

$$n - n^{(0)} = [n(x_p) - n^{(0)}]e^{(x-x_p)/L_n} \quad \text{(L75b)}$$

$$L_n = \sqrt{\mathcal{D}_n \tau_n} \quad \text{and} \quad L_p = \sqrt{\mathcal{D}_p \tau_p} \quad \text{(L76)}$$

$$j_n = e\frac{\mathcal{D}_n}{L_n}[n(x_p) - n^{(0)}] \quad \text{(L77a)}$$

$$= e\frac{\mathcal{D}_n}{L_n}\frac{n_i^2}{\mathcal{N}_a}[e^{\beta e V_A} - 1] \quad \text{(L77b)}$$

$$j_p = e\frac{\mathcal{D}_p}{L_p}[p(x_n) - p^{(0)}], \tag{L77c}$$

$$= e\frac{\mathcal{D}_p}{L_p}\frac{n_i^2}{\mathcal{N}_d}[e^{\beta eV_A} - 1], \tag{L77d}$$

$$j = en_i^2[e^{\beta eV_A} - 1]\left[\frac{\mathcal{D}_n}{L_n\mathcal{N}_a} + \frac{\mathcal{D}_p}{L_d\mathcal{N}_d}\right]. \tag{L78}$$

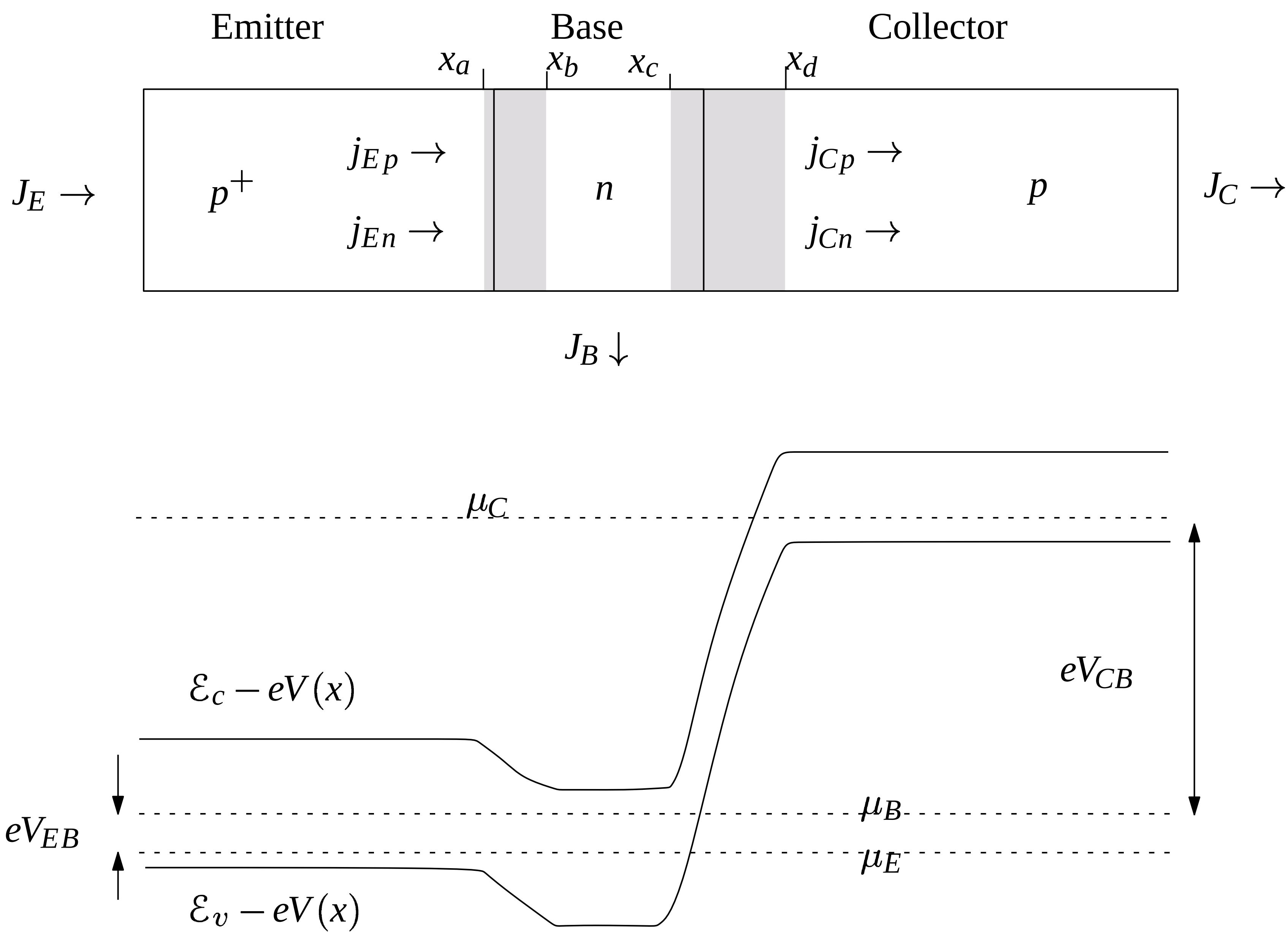


Figure 17: The binary junction transistor, made from two back-to-back p–n junctions.

$$n_E(x_a) = \frac{n_i^2}{\mathcal{N}_E} e^{\beta e V_{EB}} \tag{L79a}$$

$$p_B(x_b) = \frac{n_i^2}{\mathcal{N}_B} e^{\beta e V_{EB}} \tag{L79b}$$

$$p_B(x_c) = \frac{n_i^2}{\mathcal{N}_B} e^{\beta e V_{CB}} \tag{L79c}$$

$$n_C(x_d) = \frac{n_i^2}{\mathcal{N}_C} e^{\beta e V_{CB}}. \tag{L79d}$$

$$j_{En} = e\mathcal{D}_E n_E'(x_a) \tag{L80a}$$

$$j_{Ep} = -e\mathcal{D}_B p_B'(x_b) \tag{L80b}$$

$$j_{Cp} = -e\mathcal{D}_B p_B'(x_c) \tag{L80c}$$

$$j_{Cn} = e\mathcal{D}_C n_C'(x_d). \tag{L80d}$$

$$J_E = J_{\mathrm{FO}}(e^{\beta e V_{\mathrm{EB}}} - 1) - \alpha_{\mathrm{R}} J_{\mathrm{RO}}(e^{\beta e V_{\mathrm{CB}}} - 1) \tag{L81a}$$

$$J_C = \alpha_F J_{FO}(e^{\beta e V_{EB}} - 1) - J_{RO}(e^{\beta e V_{CB}} - 1) \tag{L81b}$$

with

$$J_{FO} = eA\left(\frac{\mathcal{D}_E}{L_E}\frac{n_i^2}{\mathcal{N}_E} + \frac{\mathcal{D}_B}{L_B}\frac{n_i^2}{\mathcal{N}_B}\coth(\frac{x_c - x_b}{L_B})\right) \tag{L81c}$$

$$J_{RO} = eA\left(\frac{\mathcal{D}_C}{L_C}\frac{n_i^2}{\mathcal{N}_C} + \frac{\mathcal{D}_B}{L_B}\frac{n_i^2}{\mathcal{N}_B}\coth(\frac{x_c - x_b}{L_B})\right) \tag{L81d}$$

$$\alpha_F J_{FO} = \alpha_R J_{RO} = eA\frac{\mathcal{D}_B}{L_B}\frac{n_i^2}{\mathcal{N}_B}\text{cosech}(\frac{x_c - x_b}{L_B}). \tag{L81e}$$

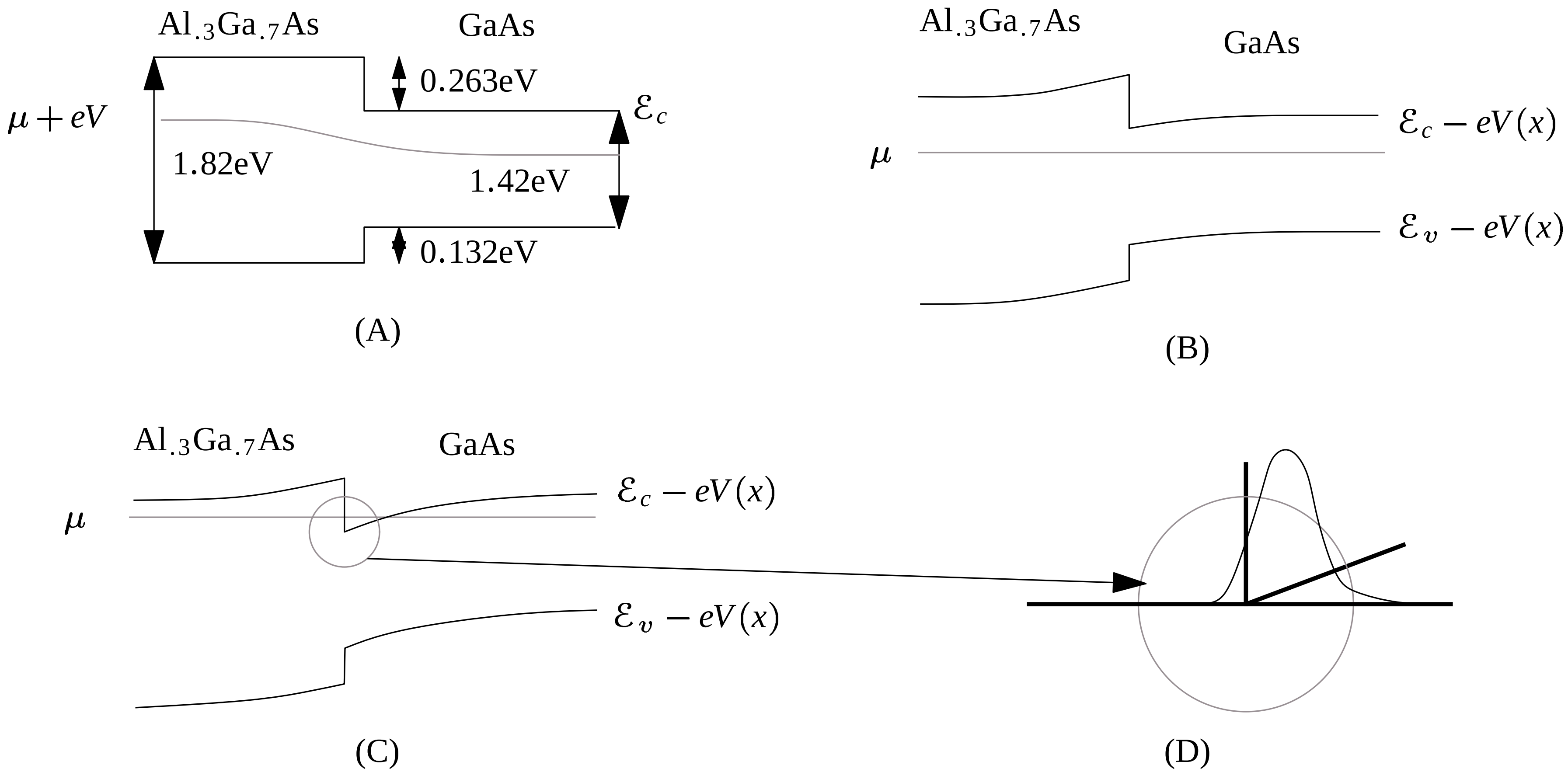


Figure 18: Junction between two semiconductors with different band gaps

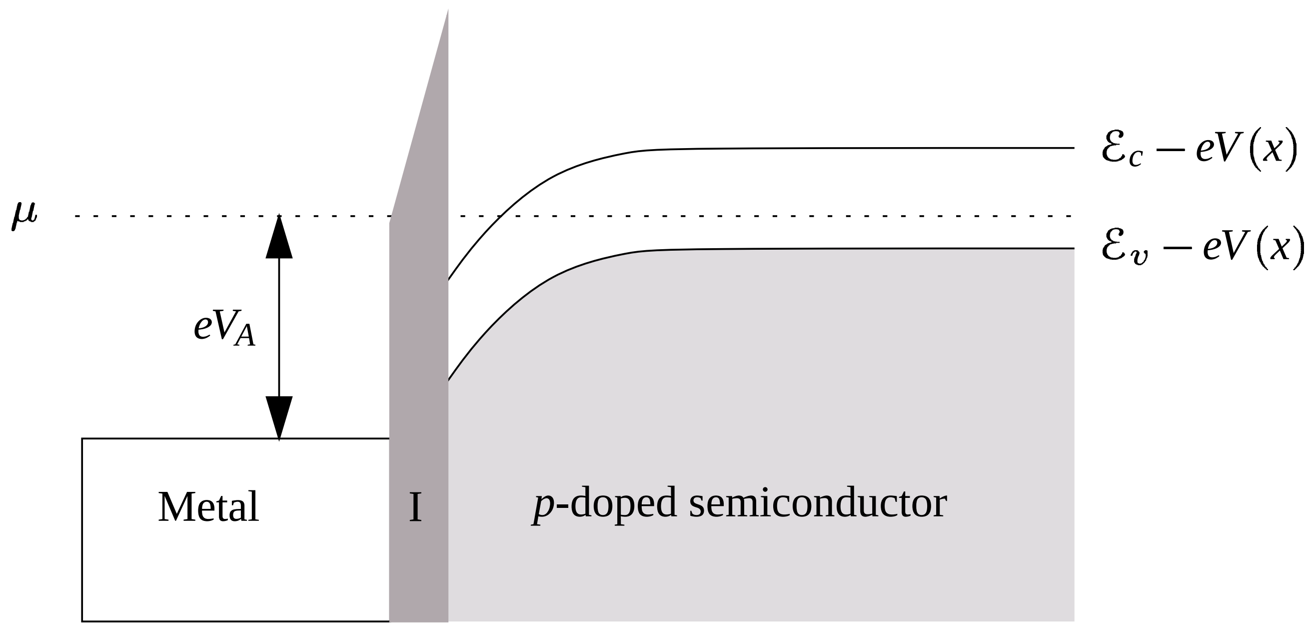


Figure 19: Metal–oxide–silicon junction

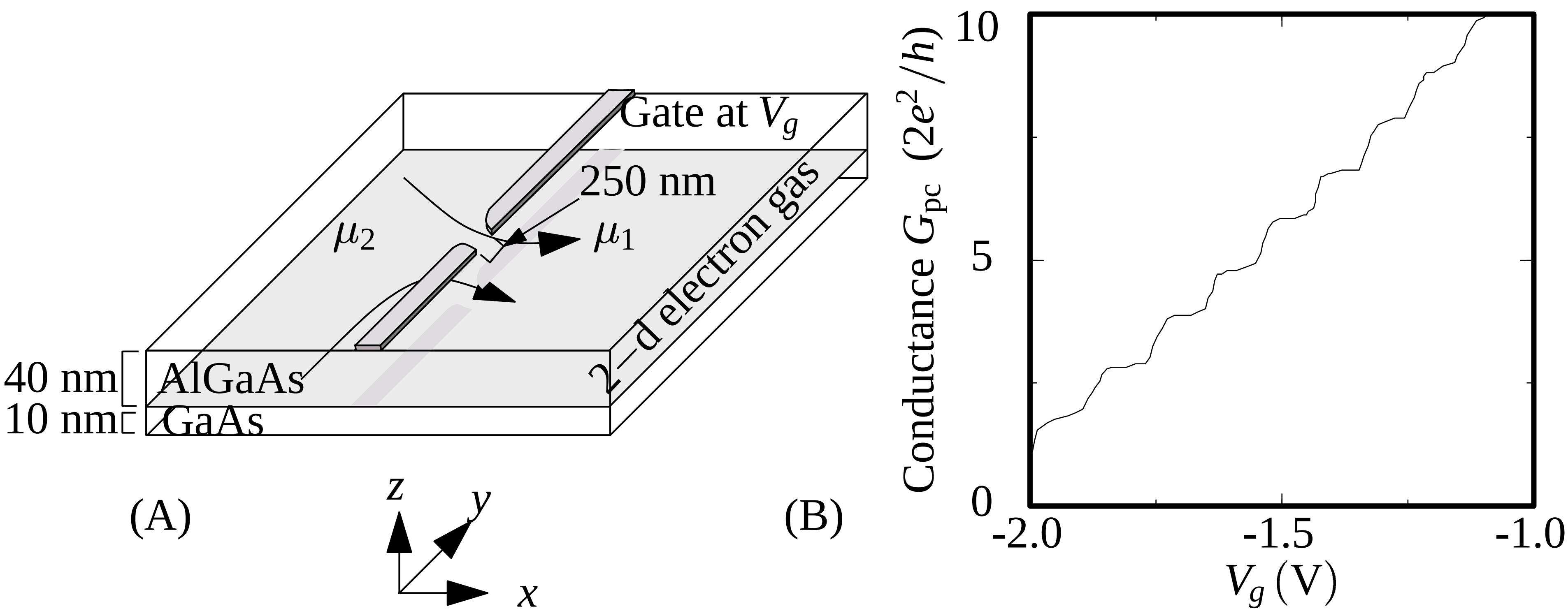


Figure 20: Quantum point contact. Data of van Wees et al. (1988)

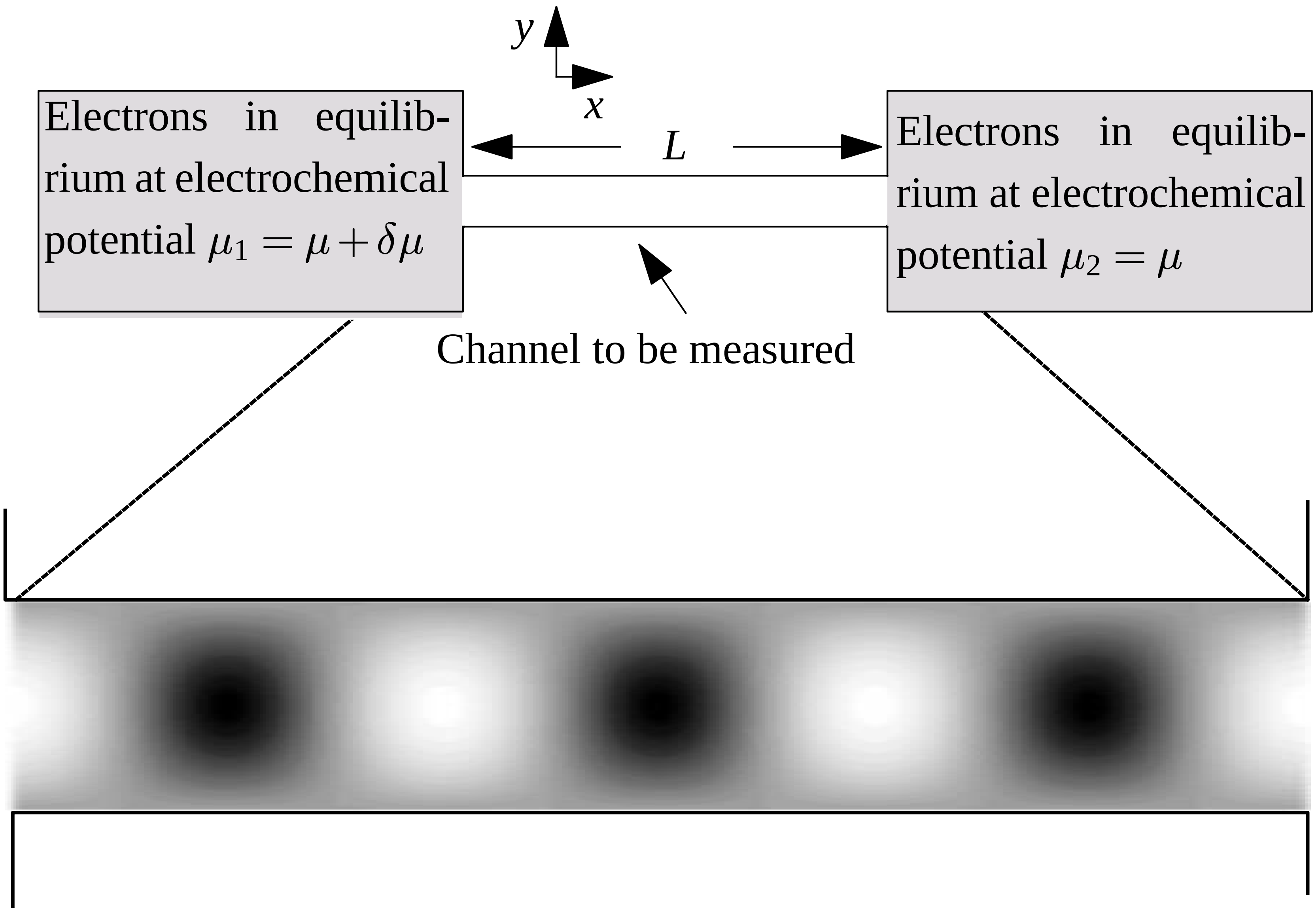


Figure 21: Setting for Landauer argument

$$\mathcal{E}_{lk_x} = \mathcal{E}^y_l + \frac{\hbar^2 k_x^2}{2m}. \tag{L82}$$

$$J = \frac{1}{L}\sum_{lk_x} -ev_{lk_x}[f_2(\mathcal{E}_{lk_x}) - f_1(\mathcal{E}_{lk_x})] \tag{L83}$$

$$= -e\sum_l \int dk_x D_{k_x} \frac{\partial \mathcal{E}_{lk_x}}{\partial \hbar k_x}[\theta(\mu+\delta\mu-\mathcal{E}_{lk_x}) - \theta(\mu-\mathcal{E}_{lk_x})] \tag{L84}$$

$$= -e\frac{2}{2\pi\hbar}\sum_l \int_{\mathcal{E}^y_l}^{\infty} d\mathcal{E}\,[\theta(\mu+\delta\mu-\mathcal{E}) - \theta(\mu-\mathcal{E})] \tag{L85}$$

$$= -e\frac{2}{2\pi\hbar}\delta\mu\sum_l \theta(\mu-\mathcal{E}^y_l) \tag{L86}$$

$$= \frac{2Ne^2}{h}V \tag{L87}$$

$$\Rightarrow G_{\text{pc}} = \frac{2Ne^2}{h}. \tag{L88}$$

$$V = J\left(R + \frac{1}{G_{\text{pc}}}\right) \tag{L89}$$

$$\Rightarrow G_{\text{pc}} = \frac{J}{V - JR}. \tag{L90}$$

Quantum Dot

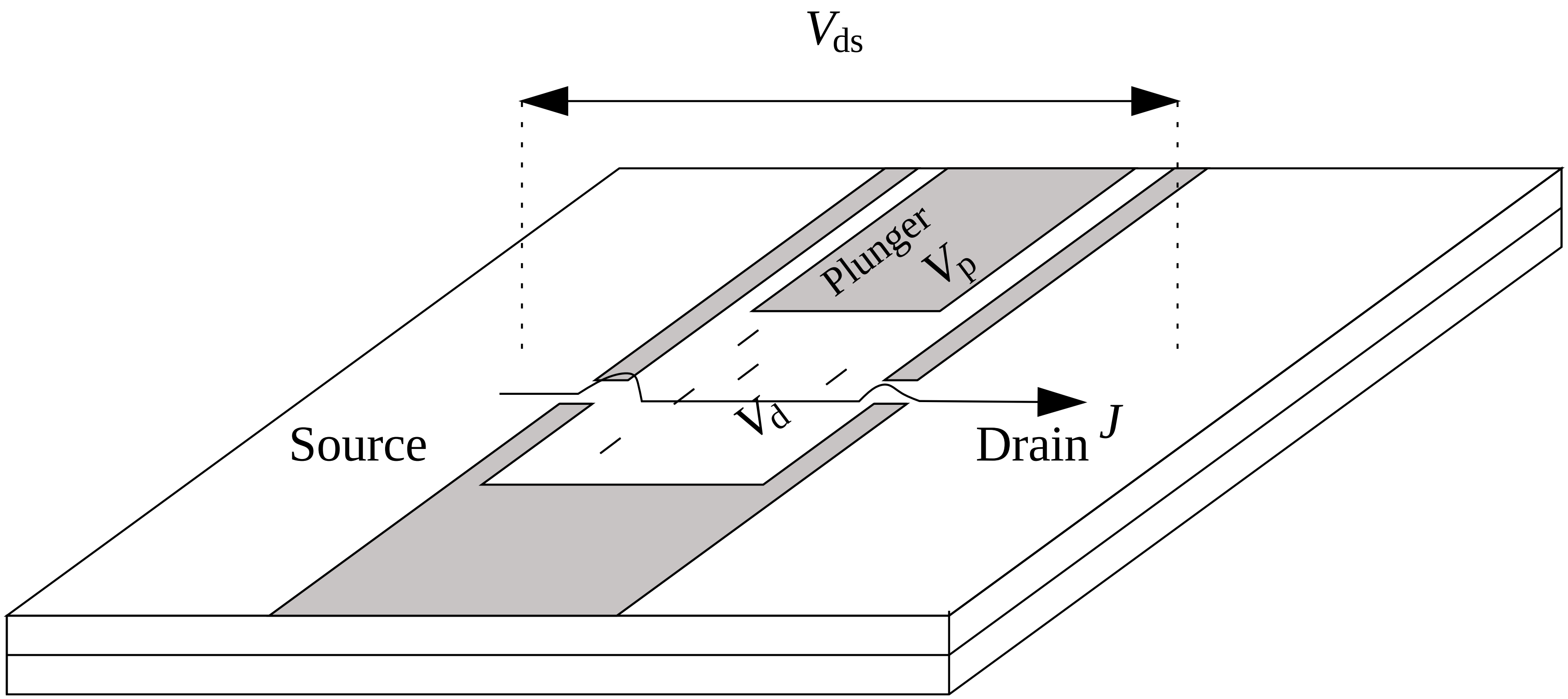


Figure 22: Quantum dot.

$$\frac{\hbar^2 k^2}{2m} = 1.5 \cdot 10^{-6} \frac{\text{eV}}{d^2/[\mu\text{m}]^2}. \tag{L91}$$

$$\frac{e^2}{d} = 1.4 \cdot 10^{-3} \frac{\text{eV}}{d/[\mu\text{m}]}. \tag{L92}$$

$$Q_{\rm d} = C_{\rm d}V_{\rm d} - C_{\rm dp}V_{\rm p}, \tag{L93}$$

$$Q_{\rm p} = -C_{\rm pd}V_{\rm d} + C_{\rm p}V_{\rm p}. \tag{L94}$$

$$C_{\rm d} = C_{\rm dp} = C_{\rm pd}. \tag{L95}$$

$$U_{\rm electrostatic} = \frac{1}{2}[Q_{\rm d}V_{\rm d} + Q_{\rm p}V_{\rm p}] + [Q_{\rm reservoir} - Q_{\rm p}]V_{\rm p}. \tag{L96}$$

$$= \frac{Q_{\rm d}^2}{2C_{\rm d}} + V_{\rm p}Q_{\rm d} + \ldots. \tag{L97}$$

$$N \equiv \frac{Q_{\rm d}}{-e} = \frac{C_{\rm d}V_{\rm p}}{e}. \tag{L98}$$

$$N = 0.625\frac{C_{\rm d}}{100\,\rm aF}\frac{V_{\rm p}}{10^{-3}\,\rm V}, \tag{L99}$$

$$V_{\rm p} = [N + 1/2]\frac{e}{C_{\rm d}}. \tag{L100}$$

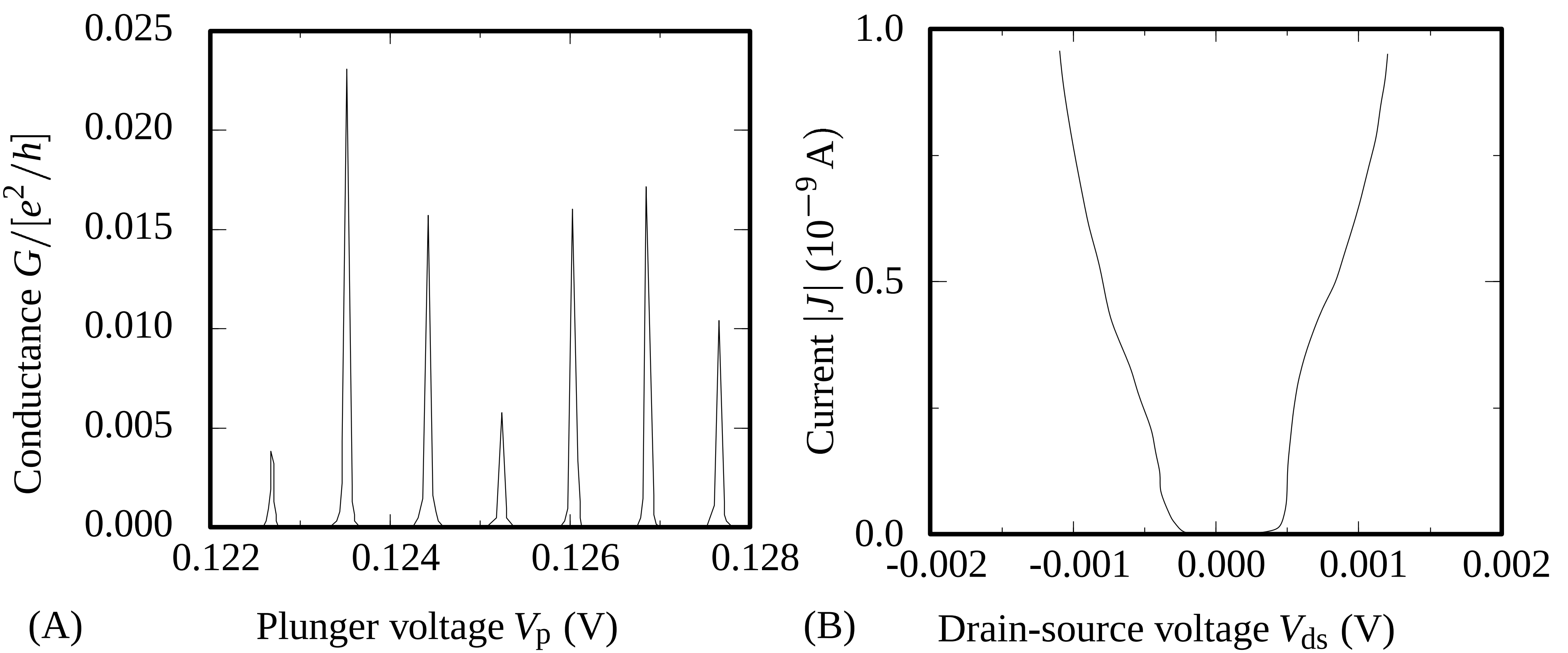
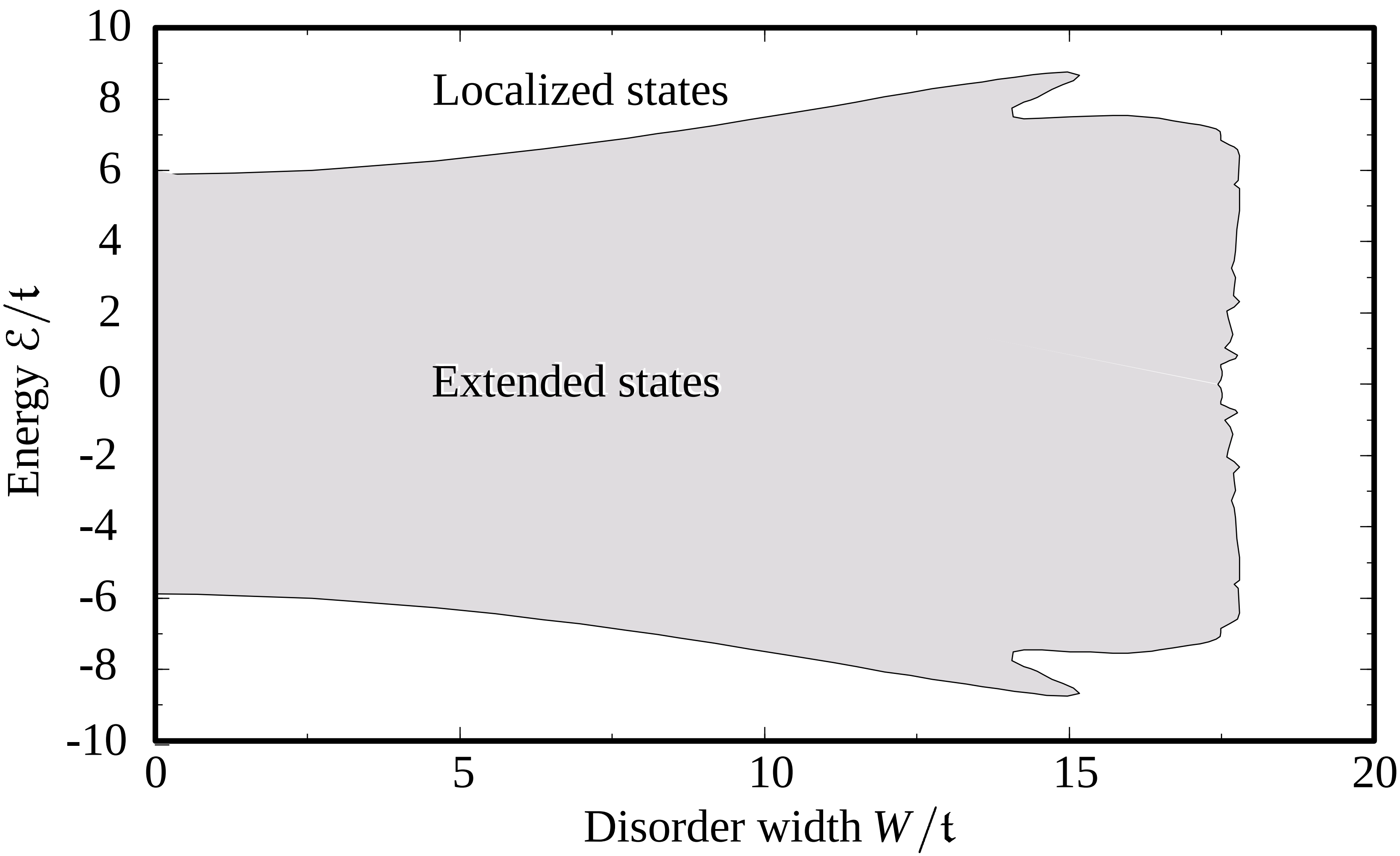


Figure 23: Conductance of quantum dot; Meirav and Foxman (1996)



Localized states
Extended states
10
8
6
4
2
0
-2
-4
-6
-8
-10
Energy $\mathcal{E}/t$
0
5
10
15
20
Disorder width W/t

Definitions

- Weak Scattering Theory
- Noise
- Metal–Insulator Transitions
- Green's Functions
- Effects of Impurities
- Anderson Localization
- Mobility Edge and Localization Length
- Scaling Theory

Problem: A perfect crystal is a perfect electrical conductor

General Formula for Relaxation Time

$$\mathcal{P}(\vec{k} \rightarrow \vec{k}', t) = g_{\vec{k}} \left[1 - g_{\vec{k}'}\right] \delta_{\sigma\sigma'} W_{\vec{k}\vec{k}'}. \tag{L1}$$

$$\left.\frac{dg}{dt}\right|_{\text{coll.}} = \frac{\mathcal{V}}{2} \int [d\vec{k}']\, g_{\vec{k}'}[1 - g_{\vec{k}}] W_{\vec{k}'\vec{k}} - g_{\vec{k}}[1 - g_{\vec{k}'}] W_{\vec{k}\vec{k}'}. \tag{L2}$$

$$W_{\vec{k}\vec{k}'} = \frac{2\pi}{\hbar} \delta(\mathcal{E}_{\vec{k}} - \mathcal{E}_{\vec{k}'}) |\langle \vec{k} | \hat{U}_{\text{tot}} | \vec{k}' \rangle|^2, \tag{L3}$$

where

$$U_{\text{tot}}(\vec{r}) = \sum_{\vec{R}} U(r - \vec{R}). \tag{L4}$$

$$W_{\vec{k}\vec{k}'} = W_{\vec{k}'\vec{k}}. \tag{L5}$$

$$g_{\vec{k}} = f_{\vec{k}} + \vec{\mathcal{C}} \cdot \vec{k}. \tag{L6}$$

$$\left.\frac{dg}{dt}\right|_{\text{coll.}} = -\vec{\mathcal{C}} \cdot \frac{1}{2}\mathcal{V}\int [d\vec{k}']\,(\vec{k}-\vec{k}')W_{\vec{k}\vec{k}'}, \tag{L7}$$

and so

$$\left.\frac{dg}{dt}\right|_{\text{coll.}} = -\frac{g-f}{\tau_{\mathcal{E}}}, \tag{L8}$$

with

$$\frac{1}{\tau_{\mathcal{E}}} = ? \qquad\qquad ?. \tag{L9}$$

Ziman's Expression for Resistivity

$$\vec{q} = \vec{k} - \vec{k}' \tag{L10}$$

$$(1 - \hat{k}\cdot\hat{k}') = 2\left(\frac{q}{2k_F}\right)^2 \tag{L11}$$

$$W_{\vec{k}\vec{k}'} = \frac{2\pi}{\hbar}\left|\int \frac{d\vec{r}}{\mathcal{V}} e^{i\vec{q}\cdot\vec{r}} \sum_{\vec{R}} U(\vec{r}-\vec{R})\right|^2 \delta(\mathcal{E}_F - \mathcal{E}(\vec{k}')). \tag{L12}$$

$$W_{\vec{k}\vec{k}'} = \frac{2\pi}{\hbar}\frac{1}{\mathcal{V}^2}\left|\sum_{\vec{R}} e^{i\vec{q}\cdot\vec{R}} \int d\vec{r}\, e^{i\vec{q}\cdot\vec{r}} U(\vec{r})\right|^2 \delta(\mathcal{E}_F - \mathcal{E}(\vec{k}')) \tag{L13}$$

$$= \frac{2\pi}{\hbar} S(q)|U(q)|^2 \frac{N_s}{\mathcal{V}^2} \delta(\mathcal{E}_F - \mathcal{E}(|\vec{k}-\vec{q}|)), \tag{L14}$$

$$\int_{-1}^{1} d(\cos\theta)\delta(\mathcal{E}_F - \mathcal{E}(\sqrt{k_F^2 + q^2 - 2k_F q\cos\theta})) = \frac{\theta(2k_F - q)}{q\partial\mathcal{E}/\partial k_F} \tag{L15}$$

Ziman's Expression for Resistivity

$$\frac{1}{\tau_{\mathcal{E}}} = \frac{1}{4\pi\hbar^2 k_F^2 v_F} \frac{N_s}{\mathcal{V}} \int_0^{2k_F} dq\, q^3 S(q) |U(q)|^2 \quad \text{(L16)}$$

$$\Rightarrow \rho = \frac{m}{ne^2\tau_{\mathcal{E}}} = \frac{3\pi}{e^2\hbar v_F^2} \left(\frac{N_s}{\mathcal{V}}\right) \frac{1}{4k_F^4} \int_0^{2k_F} dq\, q^3 S(q) |U(q)|^2. \quad \text{(L17)}$$

Evidence that Liquid Metal Scatter Weakly

Metal:	Li	Na	Cu	Ag	Au	Zn	Hg	Al	Ga	Sn	Pb	Sb	Bi	Fe
l_T (Å):	45	157	34	51	27	15	5	20	17	5	6	4	4	3

Phonon Resistivity

$$\sum_l e^{i\vec{q}\cdot(\vec{R}^l+\hat{u}^l)} = \sum_l e^{i\vec{q}\cdot\vec{R}^l}[1+i\vec{q}\cdot\hat{u}^l+\ldots] \tag{L18}$$

$$\rightarrow \quad \frac{1}{\sqrt{N}}\sum_{l\vec{k}} e^{i\vec{q}\cdot\vec{R}^l} i[\hat{u}_{\vec{k}}\cdot\vec{q}e^{i\vec{k}\cdot R^l}+\hat{u}^*_{\vec{k}}\cdot\vec{q}e^{-i\vec{k}\cdot R^l}] \tag{L19}$$

$$= \quad \frac{1}{\sqrt{N}}\sum_{l\vec{k}} i[\hat{u}_{\vec{k}}\cdot\vec{q}e^{i(\vec{k}+\vec{q})\cdot R^l}+\hat{u}^*_{\vec{k}}\cdot\vec{q}e^{i(\vec{q}-\vec{k})\cdot R^l}] \tag{L20}$$

$$= \quad \sqrt{N}\sum_{\vec{K}\vec{k}} i[\hat{u}_{\vec{k}}\cdot\vec{q}\delta_{\vec{K},\vec{q}+\vec{k}}+\hat{u}^*_{\vec{k}}\cdot\vec{q}\delta_{\vec{K},\vec{q}-\vec{k}}]. \tag{L21}$$

$$S(\vec{q}) = \frac{1}{N}\left\langle|\sum_l e^{i\vec{q}\cdot(\vec{R}^l+\hat{u}^l)}|^2\right\rangle \tag{L22}$$

$$\approx \left\langle|\hat{u}^*_{\vec{q}}\cdot\vec{q}|^2\right\rangle \tag{L23}$$

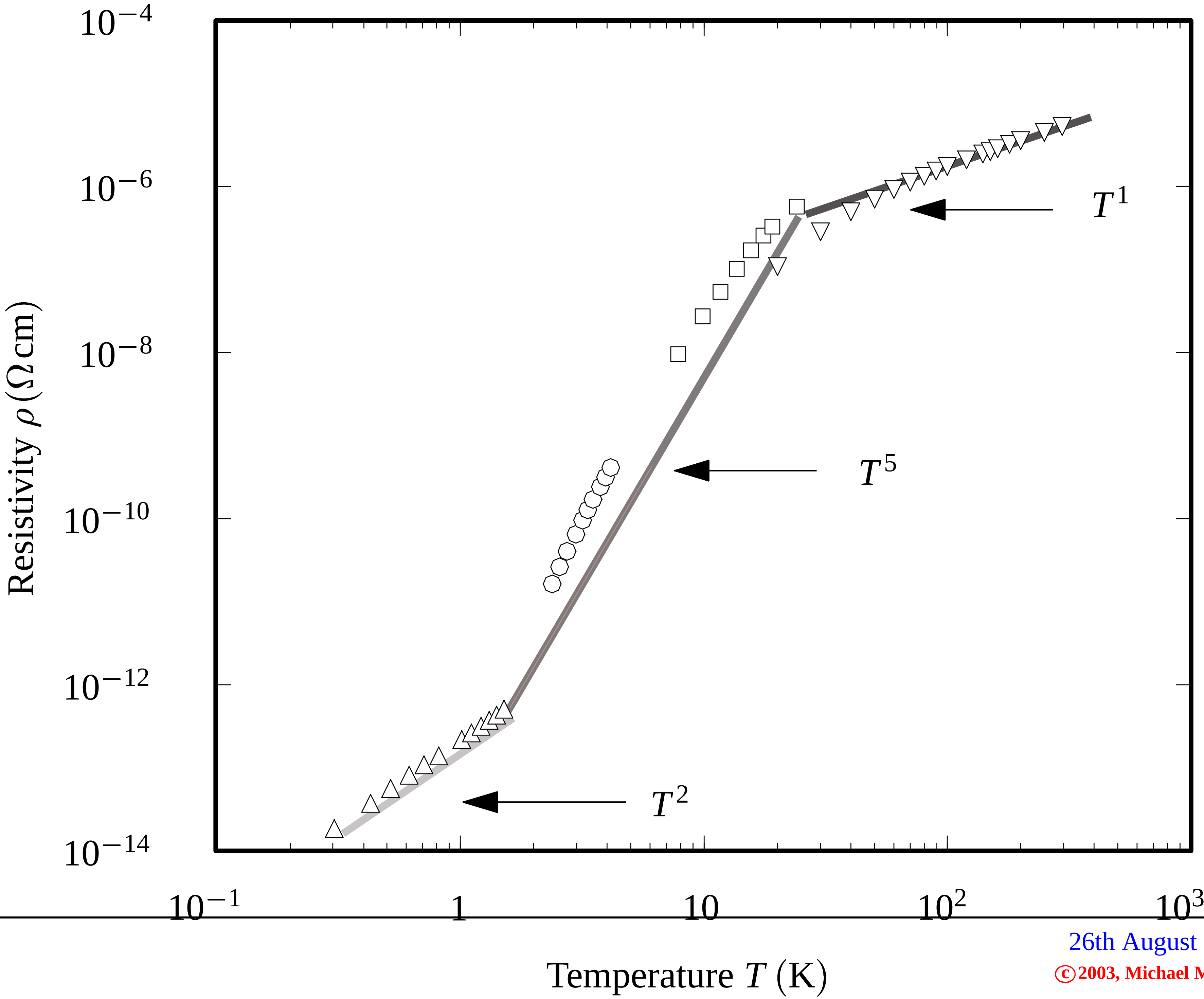
$$= \frac{\hbar}{2M\omega_{\vec{q}}}|\vec{\epsilon}\cdot\vec{q}|^2\left\langle\hat{a}_{\vec{k}}\hat{a}^*_{\vec{k}}+a^*_{\vec{k}}\hat{a}_{\vec{k}}\right\rangle \tag{L24}$$

$$= \frac{\hbar q^2}{2M\omega_{\vec{q}}}(2n_{\vec{q}}+1) \quad \text{(L25)}$$

$$\Rightarrow \rho = \frac{3\pi}{e^2\hbar v_F^2}\left(\frac{N_s}{\mathcal{V}}\right)\frac{1}{4k_F^4}\int_0^{2k_F} dq\, q^3 \frac{\hbar q^2}{2M\omega_{\vec{q}}}(2n_{\vec{q}}+1)|U(q)|^2, \quad \text{(L26)}$$

$$= \frac{3\pi}{e^2\hbar v_F^2}\left(\frac{N_s}{\mathcal{V}}\right)\frac{1}{4k_F^4}\frac{\hbar}{2Mc}\left(\frac{k_BT}{\hbar c}\right)^5\int_0^{2\Theta/T} dz\, z^4 \frac{e^z+1}{e^z-1}|U\left(\frac{k_F zT}{\Theta}\right)|^2, \quad \text{(L27)}$$

Phonon Resistivity



Matthiessen's Rule

When resistivity is small, add contributions from different sources.

Thermal noise

$$\langle \delta V^2 \rangle = 4k_B T R\, d\omega. \tag{L28}$$

Shot noise

$$\langle \delta J^2 \rangle = 2eJ\, d\omega. \tag{L29}$$

$1/f$ noise.

Non–compensated impurities

$$a_* = \frac{\epsilon\hbar^2}{m^\star e^2} \quad \text{and} \quad \mathcal{E}_b = \frac{e^2}{2\epsilon a_*} = \frac{m^\star}{m}\frac{1}{\epsilon^2}\cdot 13.6\,\text{eV}. \tag{L30}$$

$$\alpha = \frac{9}{2}{a_*}^3. \tag{L31}$$

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n_{\text{P}} \alpha \tag{L32}$$

$$\Rightarrow \epsilon = \frac{3 + 8\pi n_{\text{P}}\alpha}{3 - 4\pi n_{\text{P}}\alpha}, \tag{L33}$$

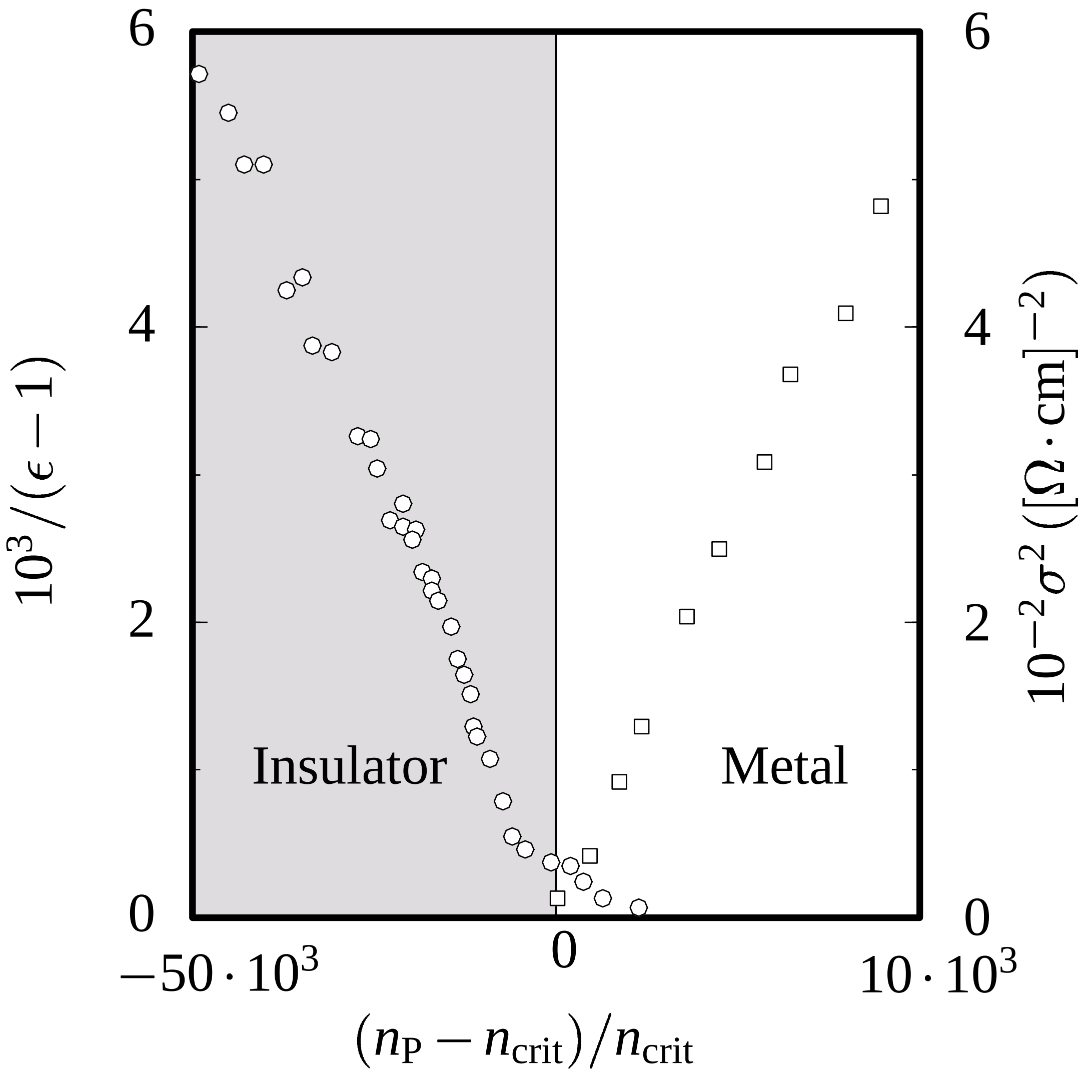


Figure 2: Metal–insulator transition in silicon doped with phosphorus. Rosenbaum (1985)

$$n_{\rm crit} = \frac{3}{4\pi\alpha} = \frac{0.053}{a_*^3} \quad \Rightarrow n_{\rm crit}^{1/3} a_* = 0.38, \tag{L34}$$

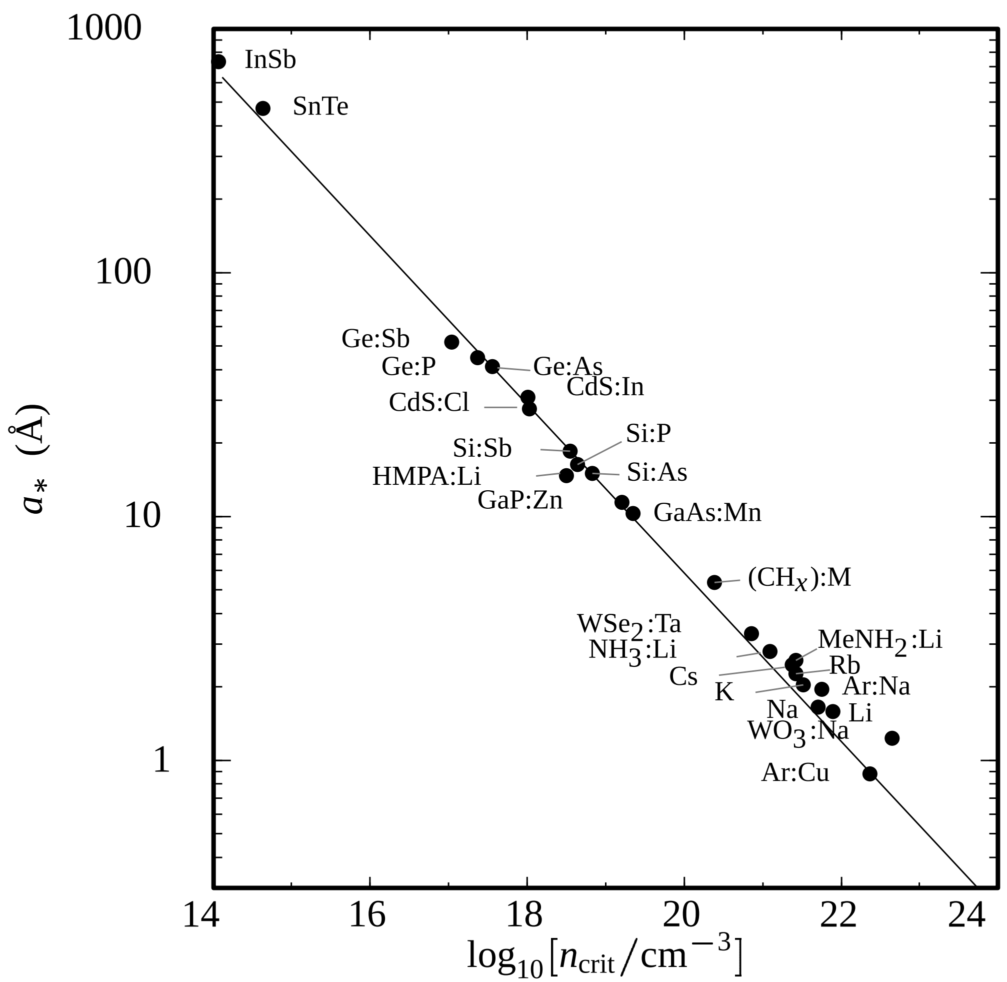


Figure 3: A host of different systems displays metal–insulator transitions when $a_* n^{1/3} = 0.26$, Edwards and Sienko (1982)

Compensated impurities

$$\hat{\mathcal{H}}_{\mathrm{TB}} = \sum_{\vec{R}} U_{\vec{R}} |\vec{R}\rangle\langle\vec{R}| + \sum_{\langle \vec{R}\vec{R}' \rangle} \mathfrak{t}|\vec{R}\rangle\langle\vec{R}'| + \mathfrak{t}|\vec{R}'\rangle\langle\vec{R}|, \tag{L35}$$

$$\hat{\mathcal{H}}_1 = U_0|0\rangle\langle 0|. \tag{L36}$$

$$\mathcal{E}|\psi\rangle = \left(\hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1\right)|\psi\rangle. \tag{L37}$$

$$\langle\vec{R}|\hat{G}(t)|0\rangle = \langle\vec{R}|e^{-i\hat{\mathcal{H}}t/\hbar}|0\rangle. \tag{L38}$$

$$\hat{G}(\mathcal{E}) = \frac{1}{i\hbar}\int_0^{\infty} dt\, e^{i\mathcal{E}t/\hbar}\hat{G}(t) \tag{L39}$$

$$\Rightarrow \hat{G}(\mathcal{E}) = (\mathcal{E}-\hat{\mathcal{H}})^{-1}. \tag{L40}$$

$$\hat{G}(\mathcal{E}) = \frac{i}{\hbar}\int_{-\infty}^{0} dt\, e^{i\mathcal{E}t/\hbar}\hat{G}(t), \tag{L41}$$

$$\hat{G} = (\mathcal{E}-\hat{\mathcal{H}})^{-1} = \sum_n (\mathcal{E}-\hat{\mathcal{H}})^{-1}|\mathcal{E}_n\rangle\langle\mathcal{E}_n| = \sum_n \frac{|\mathcal{E}_n\rangle\langle\mathcal{E}_n|}{\mathcal{E}-\mathcal{E}_n}. \tag{L42}$$

$$\hat{G}^{\pm}(\mathcal{E}) \sim \frac{|\mathcal{E}_n\rangle\langle\mathcal{E}_n|(\mathcal{E}_r-\mathcal{E}_n)}{(\mathcal{E}_r-\mathcal{E}_n)^2+\eta^2} \mp \frac{i\eta|\mathcal{E}_n\rangle\langle\mathcal{E}_n|}{(\mathcal{E}_r-\mathcal{E}_n)^2+\eta^2} \tag{L43}$$

$$= |\mathcal{E}_n\rangle\langle\mathcal{E}_n|\left\{\frac{1}{\mathcal{E}_r-\mathcal{E}_n} \mp i\pi\delta(\mathcal{E}_r-\mathcal{E}_n)\right\}. \tag{L44}$$

$$\mp \frac{1}{\pi}\,\mathrm{Im}[\langle\vec{R}|\hat{G}^{\pm}(\mathcal{E})|\vec{R}\rangle] = \sum_n \delta(\mathcal{E}_r - \mathcal{E}_n)|\langle\vec{R}|n\rangle|^2 \tag{L45}$$

$$\langle R|\hat{G}_0|R'\rangle = \sum_k \frac{\langle R|k\rangle\,\langle k|R'\rangle}{\mathcal{E}-\mathcal{E}_0(k)} \tag{L46}$$

$$= \sum_l \frac{1}{N}\frac{e^{2\pi i l(R-R')/N}}{\mathcal{E}-2\mathfrak{t}\cos(2\pi l/N)} \rightarrow \int_0^{2\pi}\frac{dk}{2\pi}\frac{e^{ik(R-R')}}{\mathcal{E}-2\mathfrak{t}\cos(k)}. \tag{L47}$$

$$z = e^{ik} \Rightarrow dk = \frac{e^{-ik}}{i}\,dz \tag{L48}$$

$$\oint \frac{dz}{2\pi i}\frac{z^{R-R'}}{z(\mathcal{E}-\mathfrak{t}(z+z^{-1}))} \tag{L49}$$

$$= \oint \frac{dz}{2\pi i}\frac{z^{R-R'}}{\mathcal{E}z-\mathfrak{t}z^2-\mathfrak{t}}. \tag{L50}$$

$$z = \frac{\mathcal{E} \pm \sqrt{\mathcal{E}^2 - 4\mathfrak{t}^2}}{2\mathfrak{t}} \equiv z_- \text{ or } z_+, \tag{L51}$$

$$\langle R|\hat{G}_0(\mathcal{E})|R'\rangle = \frac{\mathcal{E}}{|\mathcal{E}|}\frac{1}{\sqrt{\mathcal{E}^2 - 4\mathfrak{t}^2}}\left[\frac{\mathcal{E}}{2\mathfrak{t}} - \frac{\mathcal{E}}{|\mathcal{E}|}\sqrt{\left(\frac{\mathcal{E}}{2\mathfrak{t}}\right)^2 - 1}\right]^{|R-R'|}, \tag{L52}$$

$$\langle R|\hat{G}_0(\mathcal{E}_r \pm i\eta)|R\rangle = \frac{(-)\pm i}{\sqrt{4\mathfrak{t}^2 - \mathcal{E}_r^2}}\left[\left(\frac{\mathcal{E}_r}{2\mathfrak{t}}\right) \pm \frac{1}{i}\sqrt{1 - \left(\frac{\mathcal{E}_r}{2\mathfrak{t}}\right)^2}\right]^{|R-R'|}. \tag{L53}$$

$$\langle 0|\hat{G}_0(\mathcal{E})|0\rangle = \frac{1}{N}\sum_{k_1k_2}\frac{1}{\mathcal{E} - 2\mathfrak{t}[\cos 2\pi k_1/\sqrt{N} + \cos 2\pi k_2/\sqrt{N}]} \tag{L54}$$

$$= \frac{1}{(2\pi)^2}\int_0^{2\pi} dk_1 \int_0^{2\pi} dk_2 \, \frac{1}{\mathcal{E} - 2\mathfrak{t}[\cos k_1 + \cos k_2]} \tag{L55}$$

$$= \frac{1}{(2\pi)^2}\int dk_1 dk_2 \, \frac{1}{\delta\mathcal{E} - 4\mathfrak{t} - 2\mathfrak{t}[\cos k_1 + \cos k_2]} \tag{L56}$$

$$\sim \quad \frac{1}{(2\pi)} \int k dk \, \frac{1}{\delta\mathcal{E} - \mathfrak{t}k^2} \tag{L57}$$

$$\sim \quad \frac{\ln(-\delta\mathcal{E}/\mathfrak{t})}{4\pi\mathfrak{t}}. \tag{L58}$$

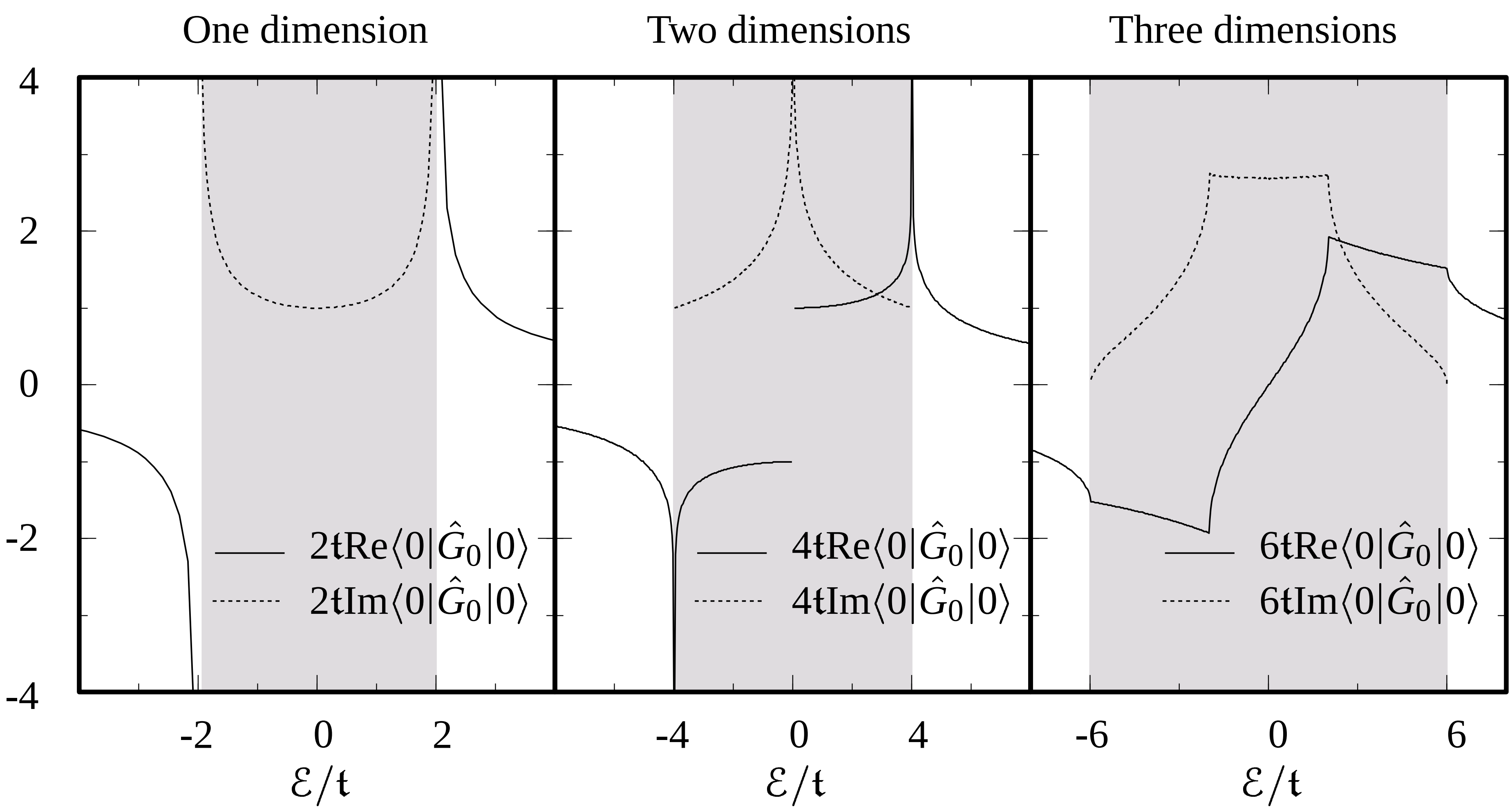


Figure 4: Green's functions for perfect square tight-binding lattice in one, two and three dimensions.

Adding Impurities

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{\mathcal{H}}_1, \tag{L59}$$

$$\hat{G}_0 = (\mathcal{E} - \hat{\mathcal{H}}_0)^{-1} \tag{L60}$$

$$\begin{aligned}
\hat{G} &= (\mathcal{E} - \hat{\mathcal{H}})^{-1} = (\mathcal{E} - \hat{\mathcal{H}}_0 - \hat{\mathcal{H}}_1)^{-1} && \text{(L61)}\\
&= ((\mathcal{E} - \hat{\mathcal{H}}_0)(1 - (\mathcal{E} - \hat{\mathcal{H}}_0)^{-1}\hat{\mathcal{H}}_1))^{-1} = (1 - \hat{G}_0\hat{\mathcal{H}}_1)^{-1}\hat{G}_0 && \text{(L62)}\\
&= \sum_{j=0}^{\infty} (\hat{G}_0\hat{\mathcal{H}}_1)^j \hat{G}_0 = \hat{G}_0 + \hat{G}_0\hat{\mathcal{H}}_1\hat{G}_0 + \hat{G}_0\hat{\mathcal{H}}_1\hat{G}_0\hat{\mathcal{H}}_1\hat{G}_0 + \dots && \text{(L63)}\\
&= \hat{G}_0 + \hat{G}_0\hat{\mathcal{H}}_1\hat{G} = \hat{G}_0 + \hat{G}\hat{\mathcal{H}}_1\hat{G}_0. && \text{(L64)}
\end{aligned}$$

$$\hat{G} \equiv \hat{G}_0 + \hat{G}_0\hat{T}\hat{G}_0. \tag{L65}$$

Single Impurity

$$
\begin{aligned}
\hat{G} &= \hat{G}_0 + \hat{G}_0|0\rangle U_0\langle 0|\hat{G}_0 + \hat{G}_0|0\rangle U_0\langle 0|\hat{G}_0|0\rangle U_0\langle 0|\hat{G}_0 + \ldots && \text{(L66)}\\
&= \hat{G}_0 + \hat{G}_0|0\rangle U_0\langle 0|\hat{G}_0 \sum_{p=0}^{\infty}\Big(U_0\langle 0|\hat{G}_0|0\rangle\Big)^p && \text{(L67)}\\
&= \hat{G}_0 + \frac{\hat{G}_0|0\rangle U_0\langle 0|\hat{G}_0}{1-U_0\langle 0|\hat{G}_0|0\rangle}. && \text{(L68)}
\end{aligned}
$$

$$
\begin{aligned}
\hat{G}_0 &\sim \frac{|\mathcal{E}_{n0}\rangle\langle\mathcal{E}_{n0}|}{\mathcal{E}-\mathcal{E}_{n0}} && \text{(L69)}\\
\Rightarrow \hat{G} &\sim \frac{|\mathcal{E}_{n0}\rangle\langle\mathcal{E}_{n0}|}{\mathcal{E}-\mathcal{E}_{n0}} - \frac{|\mathcal{E}_{n0}\rangle\,\langle\mathcal{E}_{n0}|0\rangle\,\langle 0|\mathcal{E}_{n0}\rangle\,\langle\mathcal{E}_{n0}|}{(\mathcal{E}-\mathcal{E}_{n0})\,\langle 0|\mathcal{E}_{n0}\rangle\,\langle\mathcal{E}_{n0}|0\rangle}, && \text{(L70)}
\end{aligned}
$$

$$
1-U_0\langle 0|\hat{G}_0(\mathcal{E})|0\rangle = 0. \qquad \text{(L71)}
$$

$$
1 \quad - \quad U_0\langle 0|\hat{G}_0(\mathcal{E})|0\rangle \approx -U_0\langle 0|\hat{G}_0'(\mathcal{E}_n)|0\rangle(\mathcal{E}-\mathcal{E}_n) \qquad \text{(L72)}
$$

with

$$\hat{G}_0' = \frac{\partial \hat{G}_0}{\partial \mathcal{E}}, \tag{L73}$$

$$\Rightarrow \frac{|\mathcal{E}_n\rangle\langle\mathcal{E}_n|}{\mathcal{E}-\mathcal{E}_n} \sim \frac{\hat{G}_0(\mathcal{E}_n)|0\rangle\langle 0|\hat{G}_0(\mathcal{E}_n)}{-\langle 0|\hat{G}_0'(\mathcal{E}_n)|0\rangle}\frac{1}{\mathcal{E}-\mathcal{E}_n} \tag{L74}$$

$$\Rightarrow |\mathcal{E}_n\rangle = \frac{\hat{G}_0(\mathcal{E}_n)|0\rangle}{\sqrt{-\langle 0|\hat{G}_0'(\mathcal{E}_n)|0\rangle}}. \tag{L75}$$

$$\mathcal{E} = \pm\sqrt{4\mathfrak{t}^2 + U_0^2}. \tag{L76}$$

$$\mathcal{E} = -4\mathfrak{t} - \mathfrak{t}e^{-4\pi\mathfrak{t}/|U_0|}. \tag{L77}$$

$$\hat{\mathcal{H}} = \mathcal{H}_0 + \sum_m (U_m - \Sigma)|m\rangle\langle m| + \Sigma, \tag{L78}$$

$$\hat{\mathcal{H}}_0^\Sigma = \mathcal{H}_0 + \Sigma, \quad \hat{\mathcal{H}}_1^\Sigma = \sum_m (U_m - \Sigma)|m\rangle\langle m| \tag{L79}$$

$$\hat{G}_0^\Sigma(\mathcal{E}) = \hat{G}_0(\mathcal{E} - \Sigma). \tag{L80}$$

$$\hat{G} = \hat{G}_0^\Sigma + \hat{G}_0^\Sigma \hat{T}^\Sigma \hat{G}_0^\Sigma, \tag{L81}$$

$$\hat{T}^\Sigma \approx \sum_m \hat{T}_m^\Sigma, \tag{L82}$$

$$\hat{T}_m^\Sigma = \frac{|m\rangle(U_m - \Sigma)\langle m|}{1 - (U_m - \Sigma)\langle m|\hat{G}_0^\Sigma|m\rangle} \tag{L83}$$

$$\hat{G} = \hat{G}_0^\Sigma + \hat{G}_0^\Sigma \hat{T}^\Sigma \hat{G}_0^\Sigma. \tag{L84}$$

$$\overline{\hat{G}} = \hat{G}_0^{\Sigma}(\mathcal{E}) = \hat{G}_0(\mathcal{E} - \Sigma), \tag{L85}$$

$$\overline{T_m} = 0 \tag{L86}$$

$$\Rightarrow \int dU \mathcal{P}(U) \frac{(U-\Sigma)}{1-(U-\Sigma)\langle 0|\hat{G}_0^{\Sigma}|0\rangle} = 0. \tag{L87}$$

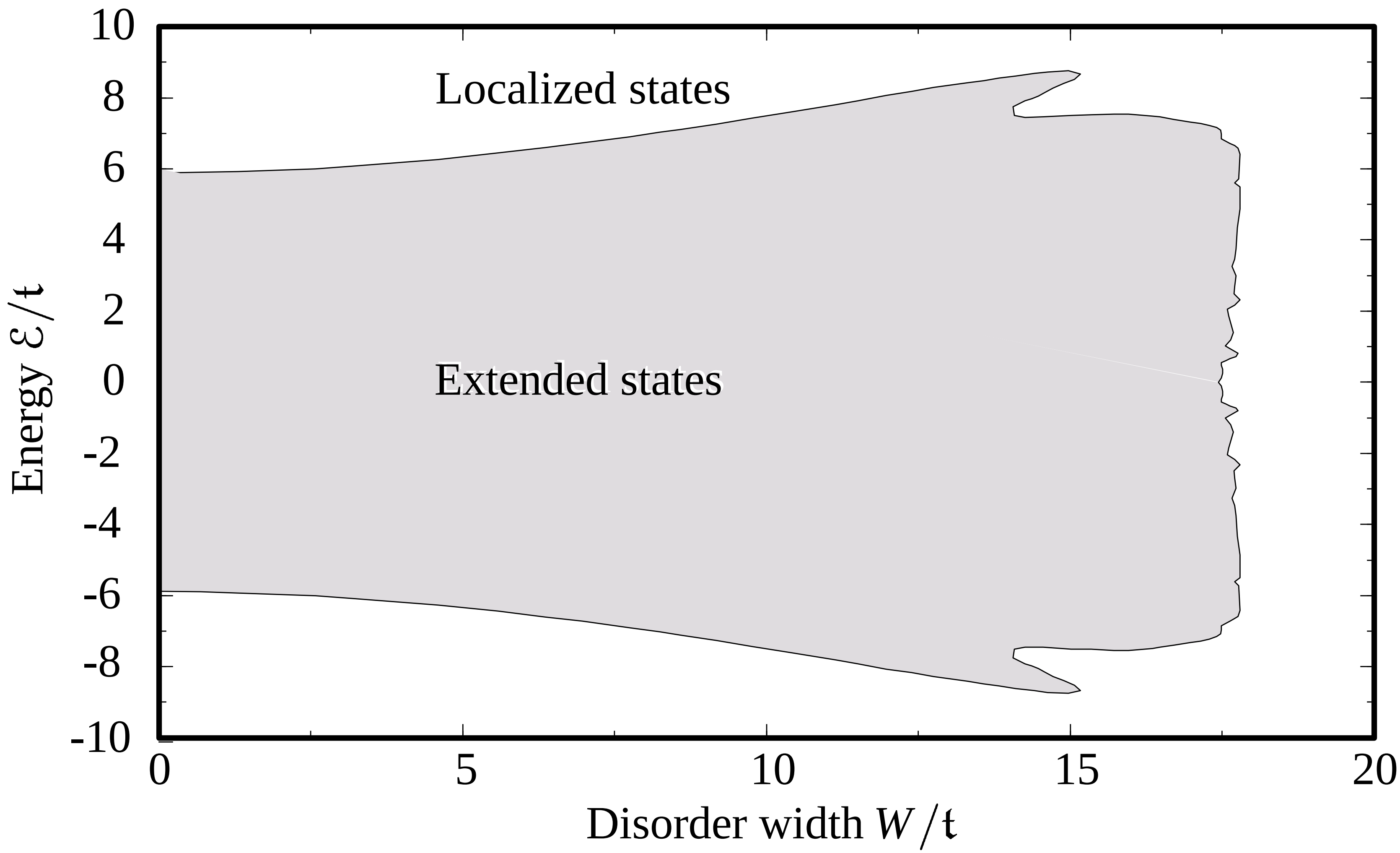


Figure 5: Calculation of the mobility edge.

$$\mathcal{P}(U)=\frac{1}{W}\theta\left(\frac{W}{2}-U\right)\theta\left(\frac{W}{2}+U\right). \tag{L88}$$

$$\langle l|\hat{G}_0|m\rangle=\frac{\delta_{lm}}{\mathcal{E}-U_l}; \tag{L89}$$

$$\lambda^{-1}\equiv\lim_{m\to\infty}-\frac{1}{2m}\overline{\ln|\langle 0|\hat{G}|m\rangle|^2}, \tag{L90}$$

$$\langle m|\hat{G}(\mathcal{E}-i\eta)|0\rangle=\sum_n\frac{\langle m|\mathcal{E}_n\rangle\langle\mathcal{E}_n|0\rangle}{\mathcal{E}-\mathcal{E}_n-i\eta}. \tag{L91}$$

$$\langle m|\hat{G}(\mathcal{E}-i\eta)|0\rangle=\mathcal{V}\int d\mathcal{E}'\,D(\mathcal{E}')\frac{\langle m|\mathcal{E}'\rangle\langle\mathcal{E}'|0\rangle}{\mathcal{E}-\mathcal{E}'-i\eta} \tag{L92}$$

$$\approx\quad\frac{\mathcal{V}\lambda}{N}D(\mathcal{E})i\pi\langle m|\mathcal{E}\rangle \tag{L93}$$

$$\approx\quad\frac{\mathcal{V}\lambda}{N}D(\mathcal{E})i\pi e^{i\phi}e^{-m/\lambda}, \tag{L94}$$

$$\mathfrak{t} \sum_{\langle l'm' \rangle} |l'\rangle\langle m'|, \tag{L95}$$

$$\langle l|\hat{G}|m\rangle = \langle l|\hat{G}_0|m\rangle + \langle l|\hat{G}_0 \sum_{\langle l_1 m_1\rangle} |l_1\rangle \mathfrak{t} \langle m_1|\hat{G}_0|m\rangle + \ldots. \tag{L96}$$

$$l = l_1 \to m_1 = l_2 \to m_2 \ldots \to m \tag{L97}$$

$$\langle l|\hat{G}_0|l\rangle \mathfrak{t} \langle l+1|\hat{G}_0|l+1\rangle \mathfrak{t} \ldots \mathfrak{t} \langle m|\hat{G}_0|m\rangle. \tag{L98}$$

$$\langle l|\hat{G}|m\rangle = \langle l|\hat{G}|l\rangle \mathfrak{t} \langle l+1|\hat{G}^l|m\rangle. \tag{L99}$$

$$\langle l|\hat{G}|m\rangle = \langle l|\hat{G}|l\rangle \mathfrak{t} \langle l+1|\hat{G}^l|l+1\rangle \mathfrak{t} \langle l+2|\hat{G}^{l+1}|l+2\rangle \ldots \mathfrak{t} \langle m|\hat{G}^{m-1}|m\rangle. \tag{L100}$$

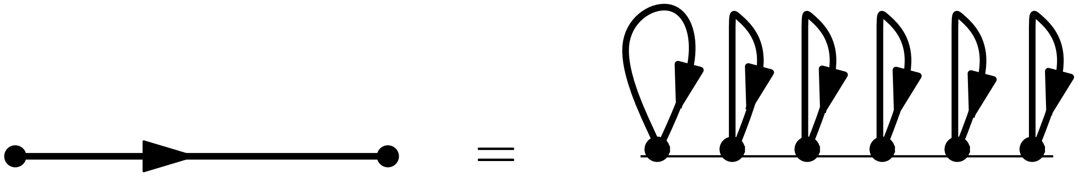


Figure 6: Diagram corresponding to Eq. (L100).

$$\lambda^{-1} = -\overline{\ln[|\langle l+1|\mathfrak{t}\hat{G}^l|l+1\rangle|]}; \tag{L101}$$

$$\langle l+1|\hat{G}^l|l+1\rangle = \langle l+1|\hat{G}_0|l+1\rangle + \left[\begin{array}{ll} & \langle l+1|\hat{G}_0|l+1\rangle \\ \times\mathfrak{t} & \langle l+2|\hat{G}^{l+1}|l+2\rangle \\ \times\mathfrak{t} & \langle l+1|\hat{G}^l|l+1\rangle \end{array}\right] \tag{L102}$$

$$\Rightarrow \quad \langle l+1|\hat{G}^l|l+1\rangle = \frac{1}{\mathcal{E} - U_{l+1} - \mathfrak{t}^2\langle l+2|\hat{G}^{l+1}|l+2\rangle}. \tag{L103}$$

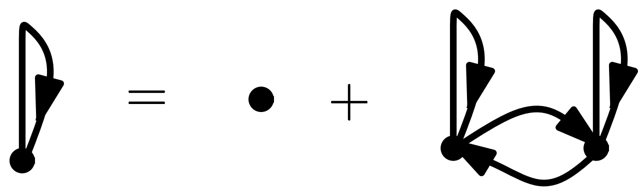


Figure 7: Diagram corresponding to Eq. (L103).

$$\mathcal{F}(g,\mathcal{E}) = \int \prod_m [dU_m \mathcal{P}(U_m)]\delta(g - \langle 1|\mathfrak{t}\hat{G}^0(\mathcal{E})|1\rangle) \tag{L104}$$

$$= \int \prod_m [dU_m \mathcal{P}(U_m)] \delta\left(g - \frac{\mathfrak{t}}{\mathcal{E} - U_1 - \mathfrak{t}^2 \langle 2|\hat{G}^1|2\rangle}\right) \quad \text{(L105)}$$

$$= \int \frac{\mathfrak{t}}{g^2} \prod_{m \neq 1} [dU_m \mathcal{P}(U_m)] \mathcal{P}\left(\mathcal{E} - \frac{\mathfrak{t}}{g} - \mathfrak{t}^2 \langle 2|\hat{G}^1|2\rangle\right) \quad \text{(L106)}$$

$$= \frac{\mathfrak{t}}{g^2} \int \prod_m [dU_m \mathcal{P}(U_m)] \int dg' \, \mathcal{P}\left(\mathcal{E} - \frac{\mathfrak{t}}{g} - \mathfrak{t} g'\right) \delta(g' - \mathfrak{t}\langle 2|\hat{G}^1|2\rangle) \quad \text{(L107)}$$

$$= \frac{\mathfrak{t}}{g^2} \int dg' \, \mathcal{P}\left(\mathcal{E} - \frac{\mathfrak{t}}{g} - \mathfrak{t} g'\right) \mathcal{F}(g', \mathcal{E}). \quad \text{(L108)}$$

$$\lambda^{-1} = 0.1142 \frac{\overline{U^2}}{\mathfrak{t}^2}. \quad \text{(L109)}$$

$$\lambda = \frac{105.045 \mathfrak{t}^2}{W^2}. \quad \text{(L110)}$$

$$R_H \equiv h/e^2 = 25813\,\Omega. \tag{L111}$$

$$R_1(l) = R_1(L/L_0). \tag{L112}$$

$$R_2(l) = R_2(L/L_0), \tag{L113}$$

$$R_d \sim L^{2-d} \tag{L114}$$

$$R \sim e^{A_d L/L_0}. \tag{L115}$$

$$\beta_d(R) = \frac{L}{R}\frac{\partial R}{\partial L} = \frac{\partial \ln R}{\partial \ln L} = L\frac{\partial \ln R_d(L/L_0)}{\partial L} \tag{L116}$$

$$\beta_d(R) \sim 2-d, \tag{L117}$$

$$\beta_d(R) \sim \frac{A_d L}{L_0} \sim \ln R. \tag{L118}$$

$$\ln(L/L_0) = \int \frac{d\ln R}{\beta_d(\ln R)} \tag{L119}$$

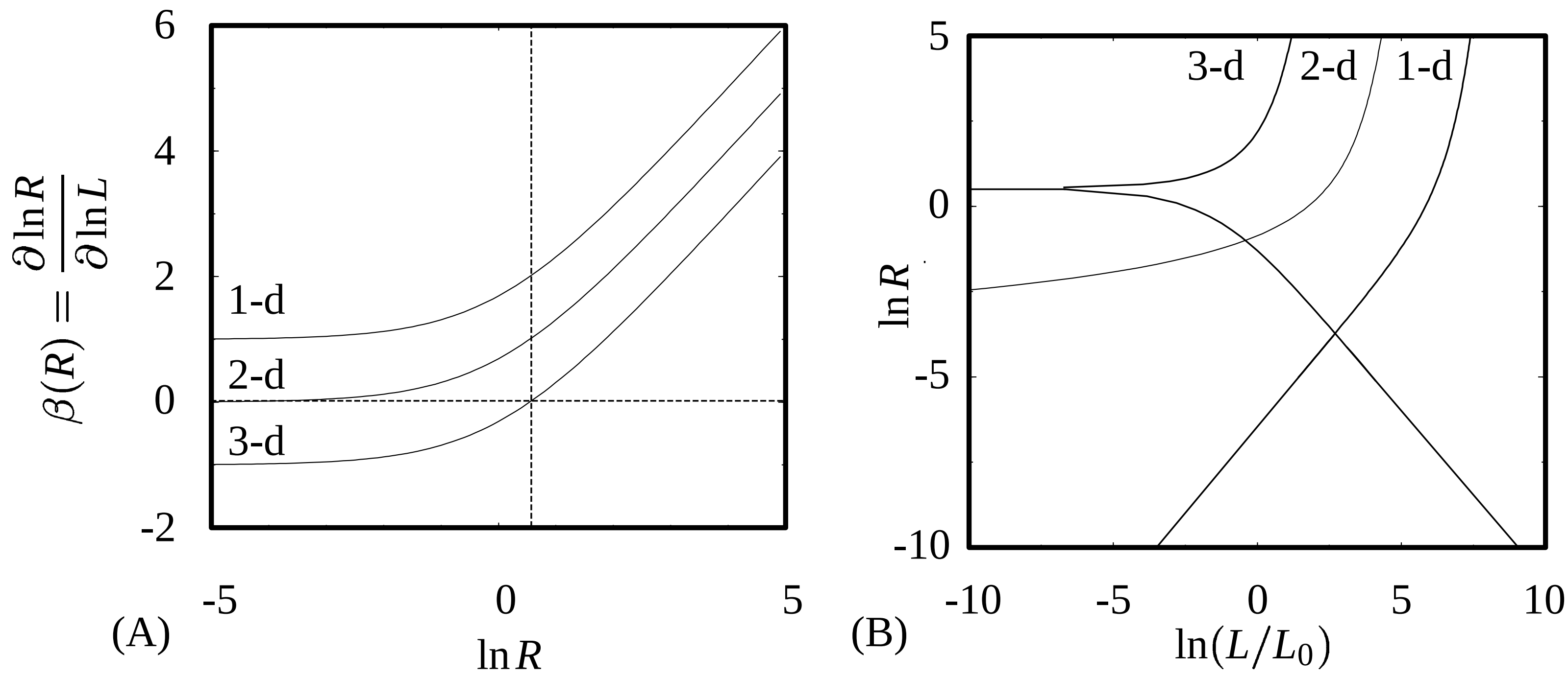


Figure 8: Scaling functions

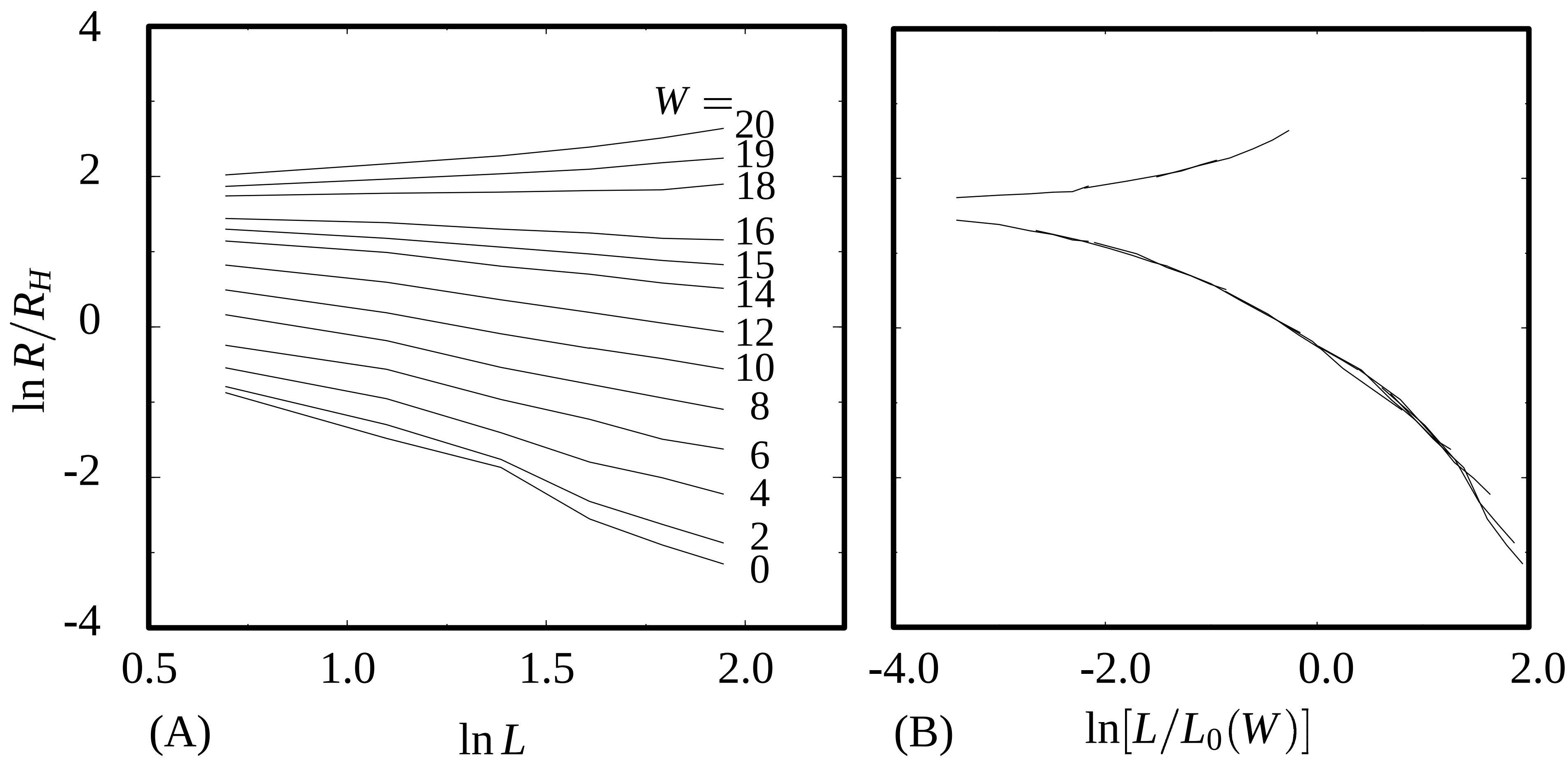


Figure 9: Three-dimensional scaling function for square lattice with diagonal disorder.

Comparison with Experiment

$$R = R_3 \left(\frac{l_T}{L_0} \right). \tag{L120}$$

$$R = R_3 \left(\frac{l_T}{L_0} \right) \frac{l_T}{L}. \tag{L121}$$

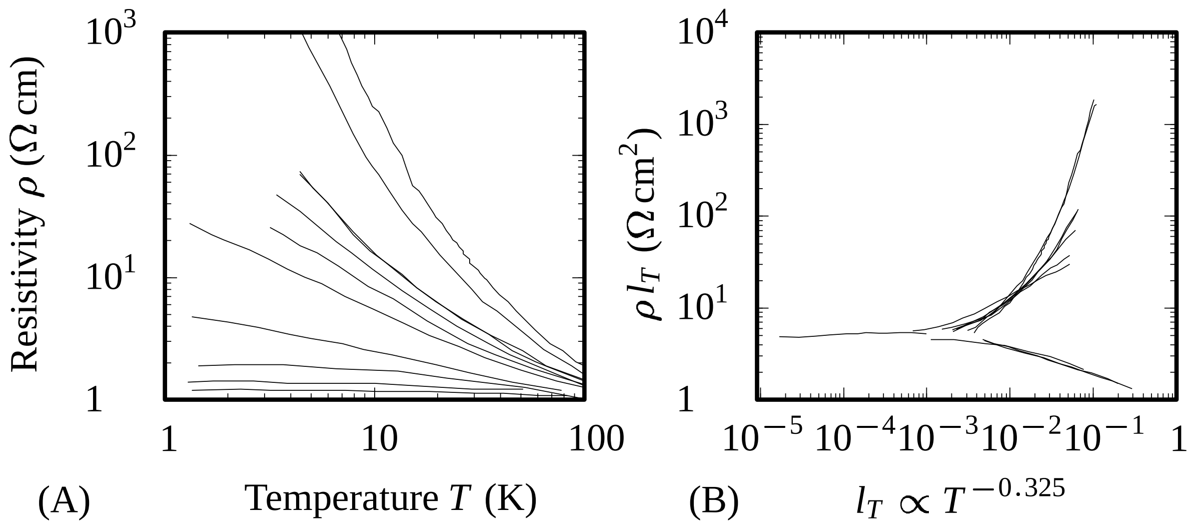
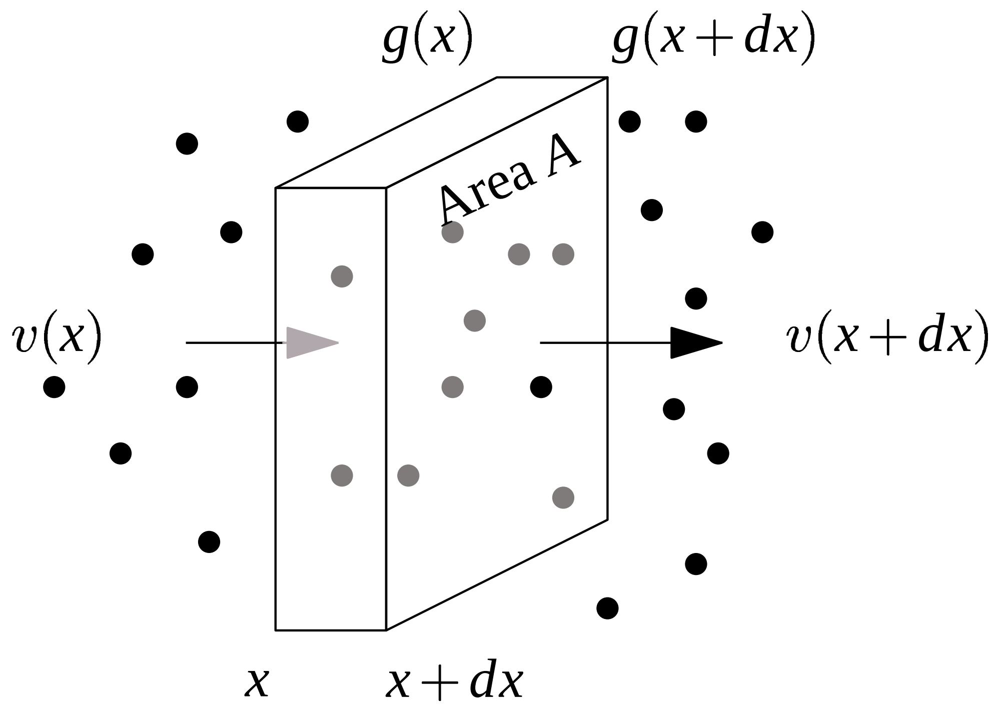


Figure 10: (A) Measurement of resistivity versus temperature in PPV, Ahlskog et al. (1997), p. 6779.

Transport and Fermi Liquids



Definitions

- ☞ Boltzmann Equation
- ☞ Relaxation Time Approximation
- ☞ Onsager Relations
- ☞ Holes
- ☞ Wiedemann–Franz Law
- ☞ Seebeck, Peltier, and Thomson Effects
- ☞ Classical Hall Effect
- ☞ Magnetoresistance
- ☞ Fermi Liquid Theory
- ☞ Quasi–Particles
- ☞ Zero Sound

Suppose have Hamiltonian structure:

$$\dot{\vec{r}} = \frac{\partial \mathcal{H}}{\partial \vec{p}}, \quad \dot{\vec{p}} = -\frac{\partial \mathcal{H}}{\partial \vec{r}}, \tag{L1}$$

In particular case of electrons in semi–classical approximation (discard anomalous velocity)

$$\mathcal{H}(\vec{r},\vec{p}) = \mathcal{E}(\vec{p}+\vec{A}e/c) - eV(\vec{r}), \tag{L2}$$

$$\dot{\vec{r}} \quad = \quad \frac{\partial \mathcal{E}}{\partial \hbar \vec{k}} \equiv \vec{v} \tag{L3a}$$

$$\hbar \dot{\vec{k}} \quad = \quad -e\vec{E} - \frac{e\vec{v}}{c} \times \vec{B}, \tag{L3b}$$

where $\hbar \vec{k}$ is defined by

$$\hbar \vec{k} \quad = \quad \vec{p} + e\vec{A}/c. \tag{L3c}$$

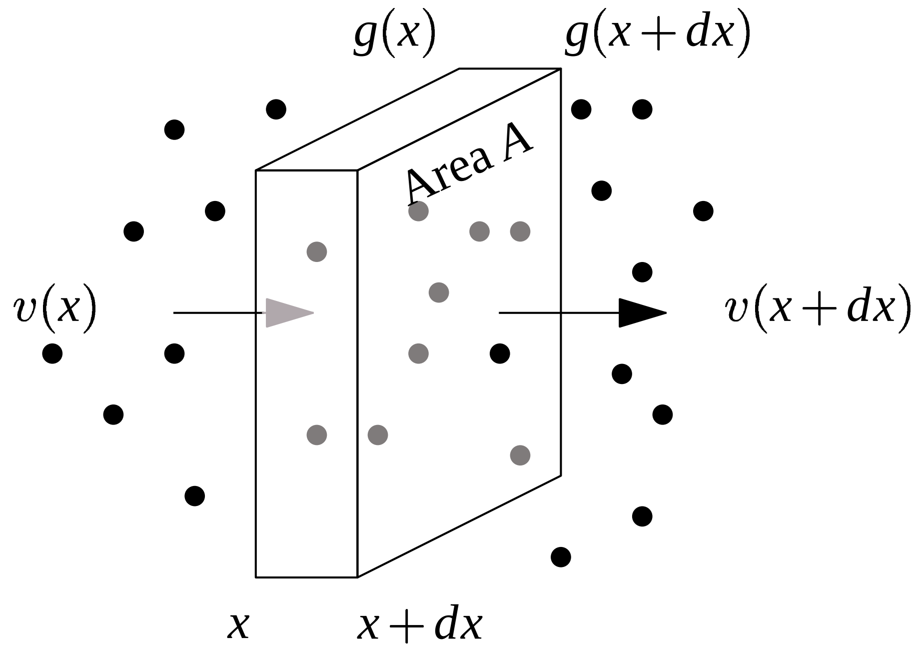


Figure 1:

Let $g(x)$ be the number of particles per volume. Then the number entering volume Adx minus the number leaving it is

$$? \qquad ? \tag{L4}$$

$$\frac{\partial g}{\partial t} = ? \qquad ? \tag{L5}$$

Continuity Equation

For a system with flows in more than one dimension,

$$\frac{\partial g}{\partial t} = -\sum_l \frac{\partial}{\partial x_l} v_l(\vec{x}) g(\vec{x}, t). \tag{L6}$$

Occupation Number g

$$g_{\vec{r}\vec{k}}(t)\,d\vec{r}\,D_{\vec{k}}d\vec{k} = 2\frac{d\vec{k}d\vec{r}}{(2\pi)^3}g_{\vec{r}\vec{k}}(t). \tag{L7}$$

$$G = \int [d\vec{k}]\,d\vec{r}\,g_{\vec{r}\vec{k}}\,G_{\vec{r}\vec{k}}. \tag{L8}$$

$$g_{\vec{r}\vec{k}} = f_{\vec{r}\vec{k}} + \text{corrections}, \tag{L9}$$

$$g_{\vec{r}\vec{k}} \approx f_{\vec{r}\vec{k}} - \tau e\frac{\partial f}{\partial \mu}\vec{v}_{\vec{k}}\cdot\vec{E}. \tag{L10}$$

$$\frac{\partial g}{\partial t} = -\frac{\partial}{\partial \vec{r}} \cdot \dot{\vec{r}} g - \frac{\partial}{\partial \vec{k}} \cdot \dot{\vec{k}} g. \tag{L11}$$

$$\frac{\partial g}{\partial t} = -\dot{\vec{r}} \frac{\partial}{\partial \vec{r}} g - \dot{\vec{k}} \frac{\partial}{\partial \vec{k}} g. \tag{L12}$$

$$\frac{\partial g}{\partial t} = -\dot{\vec{r}} \cdot \frac{\partial}{\partial \vec{r}} g - \dot{\vec{k}} \frac{\partial}{\partial \vec{k}} g + \left.\frac{dg}{dt}\right|_{\text{coll.}}, \tag{L13}$$

$$\left.\frac{dg}{dt}\right|_{\text{coll.}} \tag{L14}$$

Relaxation Time Approximation

$$\left.\frac{dg}{dt}\right|_{\text{coll.}} = -\frac{1}{\tau}\left[g_{\vec{r}\vec{k}} - f_{\vec{r}\vec{k}}\right], \tag{L15}$$

Expand about Fermi function appropriate for local conditions:

$$f_{\vec{r}\vec{k}} = \frac{1}{e^{\beta_{\vec{r}}(\mathcal{E}_{\vec{k}}-\mu_{\vec{r}})}+1} \tag{L16}$$

$$\frac{dg}{dt} = \frac{\partial g}{\partial t} + \dot{\vec{r}}\cdot\frac{\partial g}{\partial \vec{r}} + \dot{\vec{k}}\cdot\frac{\partial g}{\partial \vec{k}}, \tag{L17}$$

$$\frac{dg}{dt} = -\frac{g-f}{\tau_{\mathcal{E}}} \tag{L18}$$

$$\Rightarrow g_{\vec{r}\vec{k}}(t) = \int_{-\infty}^{t} dt'\, f(t')\,\frac{e^{-(t-t')/\tau_{\mathcal{E}}}}{\tau_{\mathcal{E}}}. \tag{L19}$$

Relaxation Time Approximation

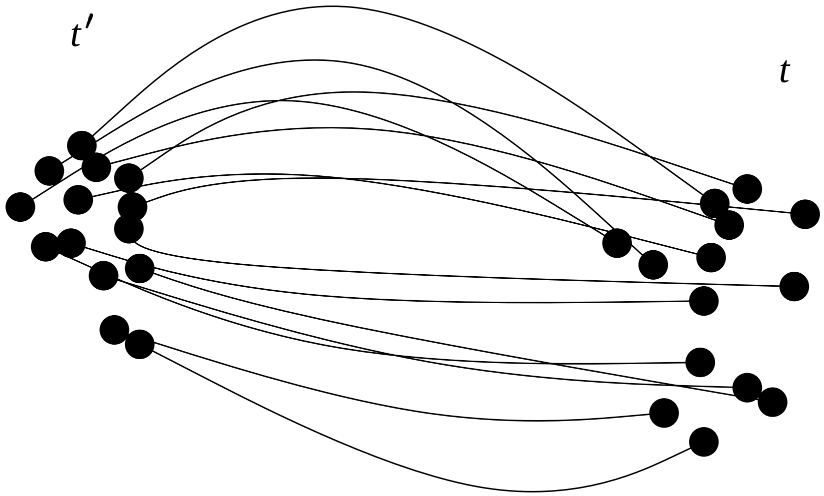


Figure 2: Electrons that at time t end up at $\vec{r}$ and $\vec{k}$.

$$g_{\vec{r}\vec{k}}(t) = f_{\vec{r}\vec{k}} - \int_{-\infty}^{t} dt' e^{-(t-t')/\tau_{\mathcal{E}}} \frac{d}{dt'} f(t'). \tag{L20}$$

$$g_{\vec{r}\vec{k}} = f_{\vec{r}\vec{k}} - \int_{-\infty}^{t} dt' e^{-(t-t')/\tau_{\mathcal{E}}} \left[\dot{\vec{r}}_{t'} \frac{\partial}{\partial \vec{r}} + \dot{\vec{k}}_{t'} \frac{\partial}{\partial \vec{k}}\right] f(t'). \tag{L21}$$

$$\frac{\partial f}{\partial \vec{r}} = \frac{\partial f}{\partial \mathcal{E}} [-\vec{\nabla}\mu - (\mathcal{E} - \mu)\frac{\vec{\nabla} T}{T}], \tag{L22}$$

and

$$\frac{\partial f}{\partial \vec{k}} = \frac{\partial f}{\partial \mathcal{E}} \frac{\partial \mathcal{E}}{\partial \vec{k}} = \frac{\partial f}{\partial \mathcal{E}} \hbar \vec{v}, \tag{L23}$$

$$g = f - \int_{-\infty}^{t} dt' e^{-(t-t')/\tau_{\mathcal{E}}} \vec{v}_{\vec{k}} \cdot \left\{ e\vec{E} + \vec{\nabla}\mu + \frac{\mathcal{E}_{\vec{k}} - \mu}{T} \vec{\nabla} T \right\} \frac{\partial f(t')}{\partial \mu}. \tag{L24}$$

$$g = f - \tau_{\mathcal{E}} \vec{v}_{\vec{k}} \cdot \left\{ e\vec{E} + \vec{\nabla}\mu + \frac{\mathcal{E}_{\vec{k}} - \mu}{T} \vec{\nabla} T \right\} \frac{\partial f}{\partial \mu}. \tag{L25}$$

$$T\frac{\partial S}{\partial t} = \frac{\partial \mathcal{E}}{\partial t} - \mu\frac{\partial N}{\partial t}. \qquad \text{(L26)}$$

$$\vec{J}_N = N\vec{v} \text{ and } \vec{J}_{\mathcal{E}} = \mathcal{E}\frac{\vec{J}_N}{N} \qquad \text{(L27)}$$

$$\frac{\partial N}{\partial t} + \vec{\nabla}\cdot\vec{J}_N = 0 \qquad \text{(L28)}$$

$$\frac{\partial \mathcal{E}}{\partial t} + \vec{\nabla}\cdot\vec{J}_{\mathcal{E}} = \vec{F}\cdot\vec{J}_N, \qquad \text{(L29)}$$

$$T\frac{\partial S}{\partial t} - \mu\vec{\nabla}\cdot\vec{J}_N + \vec{\nabla}\cdot\vec{J}_{\mathcal{E}} = \vec{F}\cdot\vec{J}_N \qquad \text{(L30)}$$

so the rate $\dot{\mathcal{S}}$ at which entropy is generated is

$$\dot{\mathcal{S}} \equiv \frac{\partial S}{\partial t} + \vec{\nabla}\cdot\left[\frac{\vec{J}_{\mathcal{E}} - \mu\vec{J}_N}{T}\right] = \frac{\vec{F}\cdot\vec{J}_N}{T} - \vec{\nabla}\left(\frac{\mu}{T}\right)\cdot\vec{J}_N + \vec{\nabla}\left(\frac{1}{T}\right)\cdot\vec{J}_{\mathcal{E}} \qquad \text{(L31)}$$

Relation to Rate of Production of Entropy

$$\Rightarrow \dot{Q} \quad \equiv \quad T\frac{\dot{\mathcal{S}}}{\mathcal{V}} = \left[-e\vec{E} - \vec{\nabla}\mu - \frac{\vec{\nabla}T}{T}\left(\frac{\mathcal{E}}{N} - \mu\right)\right] \cdot \frac{\vec{J}_N}{\mathcal{V}}. \tag{L32}$$

$$\dot{Q}_{\vec{r}\vec{k}} = \left[-e\vec{E} - \vec{\nabla}\mu - \frac{\vec{\nabla}T}{T}\left(\mathcal{E}_{\vec{k}} - \mu\right)\right] \cdot \vec{v}_{\vec{k}} f_{\vec{k}} \tag{L33}$$

$$g_{\vec{r}\vec{k}} = f_{\vec{r}\vec{k}} + \int_{-\infty}^{t} dt'\, e^{-(t-t')/\tau_{\mathcal{E}}}\, \dot{Q}(t') \frac{\partial}{\partial\mu} \ln f(t'). \tag{L34}$$

Forces and fluxes;

$$X_\alpha = \frac{d\dot{Q}}{dx_\alpha}. \tag{L35}$$

Flux associated with electric field is

$$-e\frac{\vec{J}_N}{\mathcal{V}} = \vec{j}. \tag{L36}$$

Flux associated with temperature gradient is

$$-\frac{1}{T}(\mathcal{E}-\mu)\frac{\vec{J}_N}{\mathcal{V}}. \tag{L37}$$

$$X_\alpha = \sum_\beta L_{\alpha\beta} x_\beta . \tag{L38}$$

$$L_{\alpha\beta}(B) = L_{\beta\alpha}(-B) . \tag{L39}$$

The flux of β in response to force α is the same as the flux of α in response to force β, (provided that one also reverses the sign of the magnetic induction B.)

Heat flux produced by electric field equals electric current produced by temperature gradient.

Derivation:

$$L_{\alpha\beta} = \int [d\vec{k}_t]\, d\vec{r}_t \int_{-\infty}^{t} dt' \frac{d\dot{Q}(t)}{dx_\alpha} e^{-(t-t')/\tau_\mathcal{E}} \left[\frac{\partial}{\partial\mu} \ln f(t')\right] \frac{d\dot{Q}(t')}{dx_\beta} . \tag{L40}$$

$$\mathcal{E}_{\vec{k}} = \mathcal{E}_{\vec{k}_{t'}} \Rightarrow f(t) = f(t'). \tag{L41}$$

Onsager Relations

$$\begin{aligned} t &\rightarrow t'; \; t' \rightarrow t; \\ \vec{B} &\rightarrow -\vec{B} \end{aligned} \tag{L42a}$$

$$\begin{aligned} \vec{k}_{t'} &\rightarrow -\vec{k}_{-t'} \\ \vec{r}_{t'} &\rightarrow \vec{r}_{-t'} \end{aligned} \quad , \tag{L42b}$$

$$\vec{j} = \frac{\vec{J}}{\mathcal{V}} = -e \int [d\vec{k}]\, \vec{v}_{\vec{k}}\, g_{\vec{r}\vec{k}}. \qquad \text{(L43)}$$

$$\frac{\partial j_\alpha}{\partial E_\beta} \equiv \sigma_{\alpha\beta} \qquad \text{(L44)}$$

$$= \; ? \qquad\qquad ? \qquad \text{(L45)}$$

Electrical Current

$$\sigma_{\alpha\beta} = e^2\tau \int [d\vec{k}]\, v_\alpha (-\frac{\partial f_{\vec{k}}}{\partial \hbar k_\beta}) \tag{L46}$$

$$\Rightarrow \sigma_{\alpha\beta} = e^2\tau \int [d\vec{k}]\, f_{\vec{k}} \frac{\partial v_\alpha}{\partial \hbar k_\beta} \tag{L47}$$

$$= e^2\tau \int [d\vec{k}]\, f_{\vec{k}} (\mathbf{M}^{-1})_{\alpha\beta}. \tag{L48}$$

$$\sigma = \frac{ne^2\tau}{m^\star}, \tag{L49}$$

in cubic crystals

$$\frac{1}{m^\star} = \frac{1}{3n} \int [d\vec{k}]\, f_{\vec{k}} \mathrm{Tr}(\mathbf{M}^{-1}). \tag{L50}$$

Conductivity related to effective mass

$$\sigma_{\alpha\beta} = e^2 \int \frac{d\Sigma}{4\pi^3\hbar v} \tau_\varepsilon v_\alpha v_\beta, \tag{L51}$$

Alternative form as Fermi surface average.

Conductivity of filled bands is zero.

Effective Mass and Holes

$$\sigma_{\alpha\beta} = e^2\tau \int_{\substack{\text{occupied}\\ \text{levels}}} [d\vec{k}]\,(\mathbf{M}^{-1})_{\alpha\beta} \tag{L52}$$

$$= -e^2\tau \int_{\substack{\text{unoccupied}\\ \text{levels}}} [d\vec{k}]\,(\mathbf{M}^{-1})_{\alpha\beta}. \tag{L53}$$

$$\mathcal{E}_{\vec{k}} \approx \mathcal{E}_c + \frac{\hbar^2 k^2}{2m_n^\star}. \tag{L54}$$

$$\sigma = \frac{ne^2\tau}{m_n^\star}. \tag{L55}$$

$$\mathcal{E}_{\vec{k}} \approx \mathcal{E}_v - \frac{\hbar^2 k^2}{2m_p^\star}. \tag{L56}$$

$$\sigma = \frac{pe^2\tau}{m_p^\star}. \tag{L57}$$

$$\vec{G} = \vec{E} + \frac{\vec{\nabla}\mu}{e} \tag{L58}$$

Force	*Flux*	
$\vec{G}$	$\vec{j} = -e\vec{J}_N/\mathcal{V}$	$= -e\int \frac{d\vec{r}}{\mathcal{V}} \int [d\vec{k}]\, \vec{v}_{\vec{r}\vec{k}}\, g_{\vec{r}\vec{k}}$ (L59)
$\frac{-\vec{\nabla}T}{T}$	$\vec{j}_Q = (\vec{J}_{\mathcal{E}} - \mu\vec{J}_N)/\mathcal{V}$	$= \int \frac{d\vec{r}}{\mathcal{V}} \int [d\vec{k}]\, (\mathcal{E}_{\vec{k}} - \mu)\vec{v}_{\vec{r}\vec{k}} g_{\vec{r}\vec{k}}.$

$$\vec{j} = \mathbf{L}^{11}\vec{G} + \mathbf{L}^{12}\left(\frac{-\vec{\nabla}T}{T}\right) \tag{L60}$$

$$\vec{j}_Q = \mathbf{L}^{21}\vec{G} + \mathbf{L}^{22}\left(\frac{-\vec{\nabla}T}{T}\right). \tag{L61}$$

$$\mathbf{L}^{11} = \mathfrak{L}^{(0)},\ \mathbf{L}^{12} = \mathbf{L}^{21} = -\frac{1}{e}\mathfrak{L}^{(1)},\ \mathbf{L}^{22} = \frac{1}{e^2}\mathfrak{L}^{(2)}, \tag{L62}$$

$$\mathfrak{L}^{(\nu)}_{\alpha\beta} = e^2 \int [d\vec{k}]\, \tau_{\mathcal{E}} \frac{\partial f}{\partial \mu} v_\alpha v_\beta\, (\mathcal{E}_{\vec{k}} - \mu)^\nu. \tag{L63}$$

$$\sigma_{\alpha\beta}(\mathcal{E}) = \tau_{\mathcal{E}} e^2 \int [d\vec{k}]\, v_\alpha v_\beta\, \delta(\mathcal{E} - \mathcal{E}_{\vec{k}}), \tag{L64}$$

$$\mathcal{L}^{(\nu)}_{\alpha\beta} = \int d\mathcal{E}\, \frac{\partial f}{\partial \mu} (\mathcal{E} - \mu)^\nu \sigma_{\alpha\beta}(\mathcal{E}). \tag{L65}$$

$$\frac{\partial f}{\partial \mu} \approx \delta(\mathcal{E} - \mathcal{E}_F) \tag{L66}$$

$$\mathcal{L}^{(0)}_{\alpha\beta} = \sigma_{\alpha\beta}(\mathcal{E}_F) \tag{L67}$$

$$\mathcal{L}^{(1)}_{\alpha\beta} = \frac{\pi^2}{3}(k_B T)^2 \sigma'_{\alpha\beta}(\mathcal{E}_F) \tag{L68}$$

$$\mathcal{L}^{(2)}_{\alpha\beta} = \frac{\pi^2}{3}(k_B T)^2 \sigma_{\alpha\beta}(\mathcal{E}_F). \tag{L69}$$

$$\vec{j}_Q = \kappa\left(-\vec{\nabla}T\right) \tag{L70}$$

$$0 = \mathbf{L}^{11}\vec{G} + \mathbf{L}^{12}\left(\frac{-\vec{\nabla}T}{T}\right) \tag{L71}$$

$$\Rightarrow \vec{G} = (\mathbf{L}^{11})^{-1}\mathbf{L}^{12}\frac{\vec{\nabla}T}{T}, \tag{L72}$$

$$\vec{j}_Q = \left[\mathbf{L}^{21}(\mathbf{L}^{11})^{-1}\mathbf{L}^{12} - \mathbf{L}^{22}\right]\left(\frac{\vec{\nabla}T}{T}\right) \tag{L73}$$

$$\Rightarrow \kappa = \frac{\mathbf{L}^{22}}{T} + \mathcal{O}\left(\frac{k_B T}{\mathcal{E}_F}\right)^2 \tag{L74}$$

$$\Rightarrow \kappa_{\alpha\beta} = \frac{\pi^2}{3}\frac{k_B^2 T}{e^2}\sigma_{\alpha\beta}. \tag{L75}$$

$$L_0 = \frac{\pi^2}{3}\frac{k_B^2}{e^2} = 2.72 \cdot 10^{-13}\,\mathrm{erg\,cm^{-1}\,K^{-2}} = 2.43 \cdot 10^{-8}\,\mathrm{W \cdot \Omega \cdot K^{-2}} \tag{L76}$$

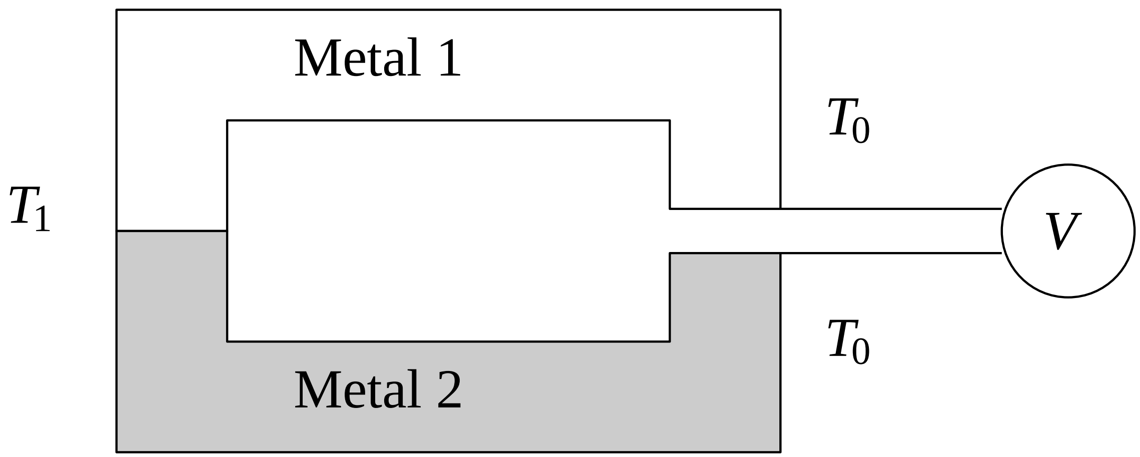


Figure 3: Geometry for Thermopower

$$\vec{G} = \alpha \vec{\nabla} T \quad \text{(L77)}$$

$$\Rightarrow \alpha = (\mathbf{L}^{11})^{-1} \frac{\mathbf{L}^{12}}{T} = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \sigma^{-1} \sigma'. \quad \text{(L78)}$$

Thermopower—Seebeck Effect

Element	Z	L/L_0 300 K	L/L_0 20 K	α (μVK^{-1}) 300 K	α (μVK^{-1}) 100 K	$\mathcal{R}nec$ 300 K	$\mathcal{R}nec$ 100 K
Li	1	0.90	0.22	10.6	4.3	−1.02	−0.16
Na	1	0.91	0.30	−5.8	−2.6	−0.54	−0.50
K	1	0.92		−13.7	−5.2	−0.89	−0.95
Rb	1			−10.2	−3.6	−0.86	−0.91
Cs	1			−0.9		−0.99	
Cu	1	0.91	0.31	1.9	1.2	−0.72	−0.78
Ag	1	0.96	0.70	1.5	0.7	−0.84	−0.84
Au	1	0.96	0.76	1.9	0.8	−0.69	−0.68
Be	2	0.97	0.23	1.7	−2.5	−30.49	−30.49
Mg	2	0.97	0.78	−1.5	−2.1	−1.15	
Ca	2			10.3	1.1		
Sr	2			1.1	−3.0		
Ba	2			12.1	−4.0		
Zn	2	0.92	0.67	2.4	0.7	3.03	3.89
Cd	2	0.97	0.65	2.6	−0.1	2.06	1.48
Hg	2	1.49	0.65			−1.97	
Al	3	0.89	0.72	−1.7	−2.2	−0.96	−0.84
Ga	3			1.8	0.5	−0.96	
In	3			1.7	0.6	−1.00	−0.50
Sn	4			−0.9	−0.0	−0.05	
Pb	4			−1.3	−0.6	0.21	
Sb	5	1.58					
Bi	5	1.07					
Mn	4			−10.0	−2.5	4.41	−23.51
Fe	2	1.36	0.98	16.2	11.6		
Co	2			−30.8	−8.4		
Ni	2	0.83		−19.2	−8.5		

Peltier Effect

$$\vec{j}_Q = \Pi \vec{j}. \tag{L79}$$

$$\Pi = \mathbf{L}^{21}(\mathbf{L}^{11})^{-1} = T\alpha. \tag{L80}$$

$$Z = \frac{\alpha^2}{R\kappa}, \tag{L81}$$

Thomson Effect

$$-T\frac{d\alpha}{dT}\vec{\nabla}T\cdot\vec{j}\equiv-\mu\vec{\nabla}T\cdot\vec{j}, \tag{L82}$$

$$T\frac{d\alpha}{dT}, \tag{L83}$$

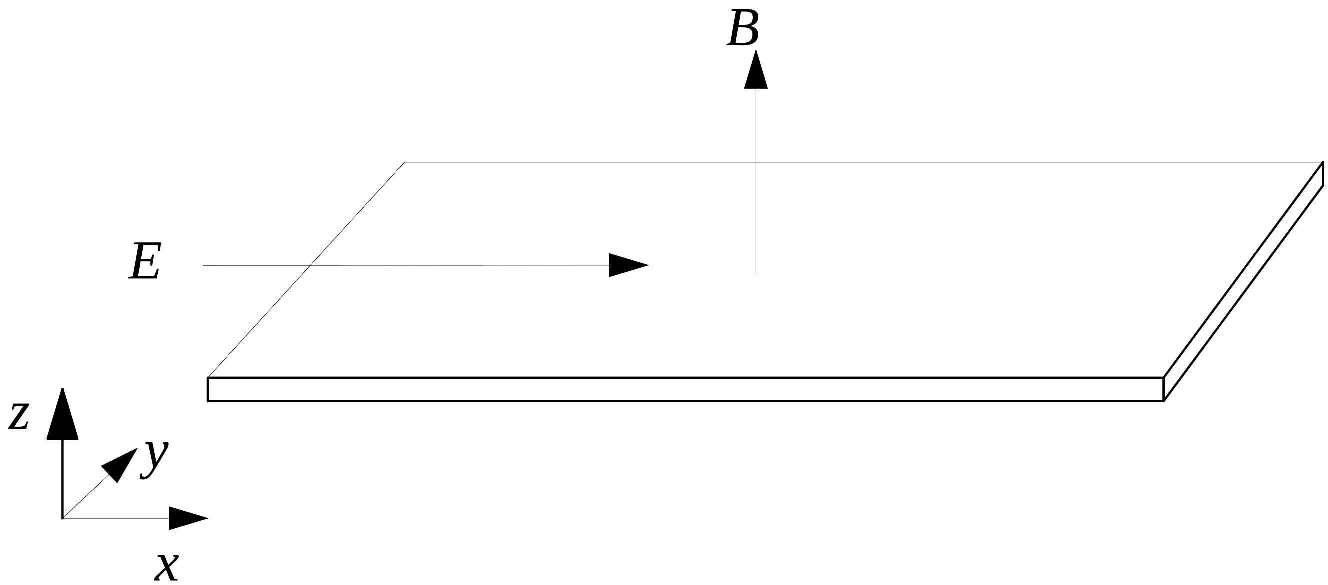


Figure 4: Geometry of the Hall effect.

$$\hbar\dot{\vec{k}} = -e\frac{\vec{v}}{c}\times\vec{B} - e\vec{E} \quad \text{(L84)}$$

$$\Rightarrow \vec{B}\times\hbar\dot{\vec{k}} + e\vec{B}\times\vec{E} = -e\vec{B}\times\left(\frac{\vec{v}}{c}\times\vec{B}\right) = -\frac{e}{c}\vec{v}_\perp B^2 \quad \text{(L85)}$$

$$\Rightarrow \vec{v}_\perp = -\frac{\hbar c}{e}\frac{\vec{B}\times\dot{\vec{k}}}{B^2} - c\frac{\vec{B}\times\vec{E}}{B^2}. \quad \text{(L86)}$$

$$g - f = \int_{-\infty}^{t} dt'\, e^{-(t-t')/\tau_{\mathcal{E}}} \left[\frac{c\hbar}{e} \frac{\vec{B} \times \dot{\vec{k}}}{B^2} \right] \cdot e\vec{E} \frac{\partial f}{\partial \mu} \tag{L87}$$

$$= \int_{-\infty}^{t} dt'\, e^{-(t-t')/\tau_{\mathcal{E}}} \frac{c\hbar}{B^2} \dot{\vec{k}} \cdot \left[\vec{E} \times \vec{B} \right] \frac{\partial f}{\partial \mu} \tag{L88}$$

$$= \frac{c\hbar}{B^2} \left(\vec{k} - \langle \vec{k} \rangle \right) \cdot \left[\vec{E} \times \vec{B} \right] \frac{\partial f}{\partial \mu} \tag{L89}$$

where

$$\langle \vec{k} \rangle = \frac{1}{\tau_{\mathcal{E}}} \int_{-\infty}^{t} dt'\, e^{-(t-t')/\tau_{\mathcal{E}}} \vec{k}_{(t')}. \tag{L90}$$

Hall Effect

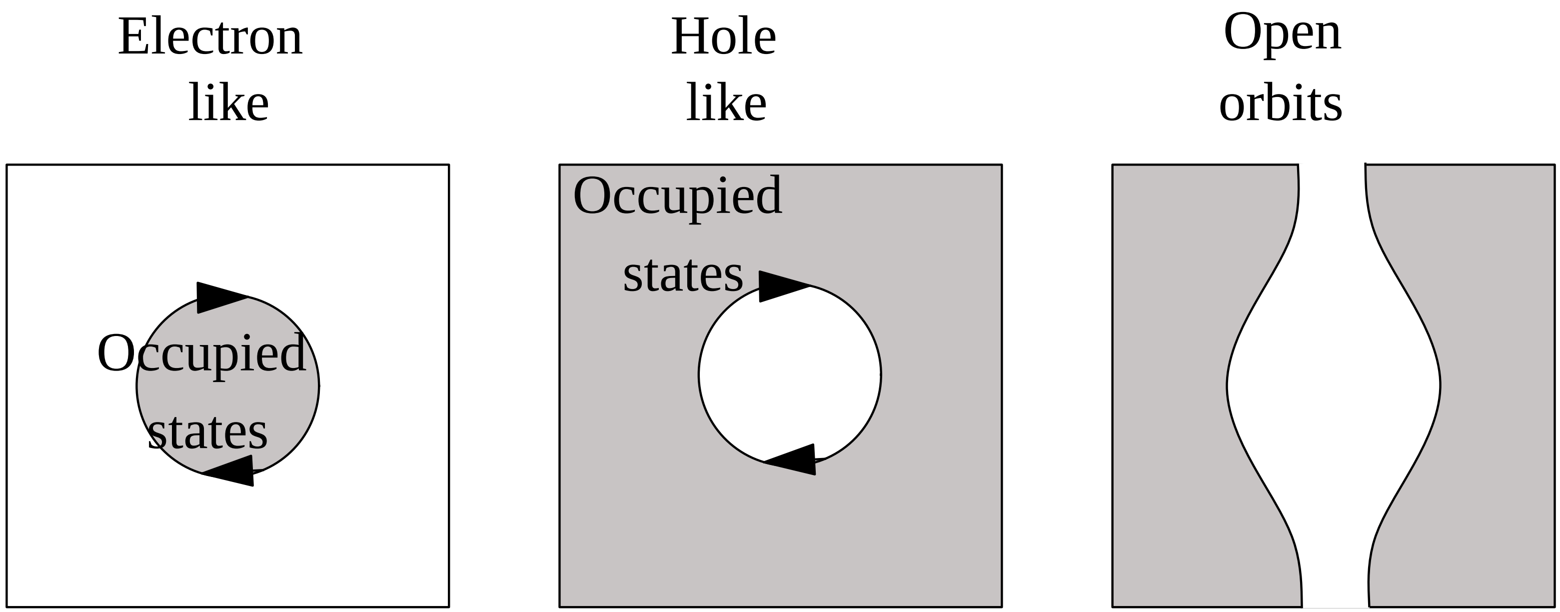


Figure 5: Electron-like, hole-like, and open orbits for the Hall effect.

$$\vec{j} = -e\int [d\vec{k}]\,\vec{v}_{\vec{k}}\frac{\partial f}{\partial \mu}\frac{\hbar c}{B^2}\vec{k}\cdot(\vec{E}\times\vec{B}) \quad \text{(L91)}$$

$$= e\int [d\vec{k}]\,\frac{\partial f}{\partial \hbar\vec{k}}\frac{\hbar c}{B^2}\vec{k}\cdot(\vec{E}\times\vec{B}) \quad \text{(L92)}$$

$$= \left\{\frac{ec}{B^2}\int [d\vec{k}]\,\frac{\partial}{\partial\vec{k}}\left(f\vec{k}\cdot(\vec{E}\times\vec{B})\right)\right\} - \frac{nec}{B^2}(\vec{E}\times\vec{B}) \quad \text{(L93)}$$

Hall Effect

$$\vec{j} = -\frac{nec}{B^2}(\vec{E} \times \vec{B}). \qquad \text{(L94)}$$

$$\vec{j} = \frac{pec}{B^2}(\vec{E} \times \vec{B}), \qquad \text{(L95)}$$

$$p = \int [d\vec{k}]\,(1 - f_{\vec{k}}) \qquad \text{(L96)}$$

$$\mathcal{R} = -\frac{E_x}{B j_y}. \qquad \text{(L97)}$$

Magnetoresistance

$$\vec{E} = \rho \vec{j} \tag{L98}$$

$$\sigma \propto \begin{pmatrix} \mathcal{C}\dfrac{\mathcal{T}}{\tau_{\mathcal{E}}}\dfrac{\mathcal{R}}{B} & \dfrac{\mathcal{R}}{B} \\ -\dfrac{\mathcal{R}}{B} & \mathcal{C}\dfrac{\mathcal{T}}{\tau_{\mathcal{E}}}\dfrac{\mathcal{R}}{B} \end{pmatrix} \tag{L99}$$

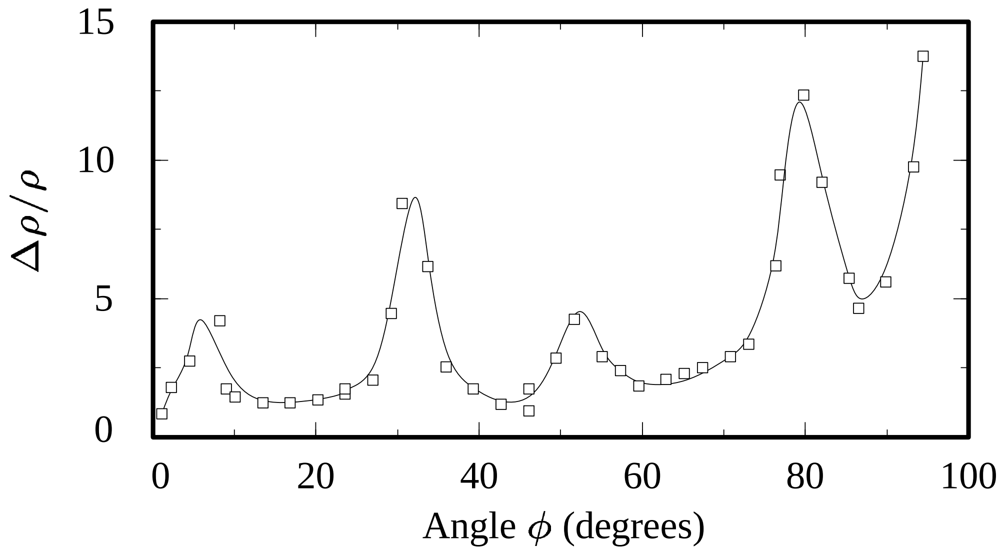


Figure 6: [Source: Alekseevskii and Gaidukhov (1960), p. 673.]

Giant Magnetoresistance (GMR) and Collossal Magnetoresistance (CMR)...new read heads.

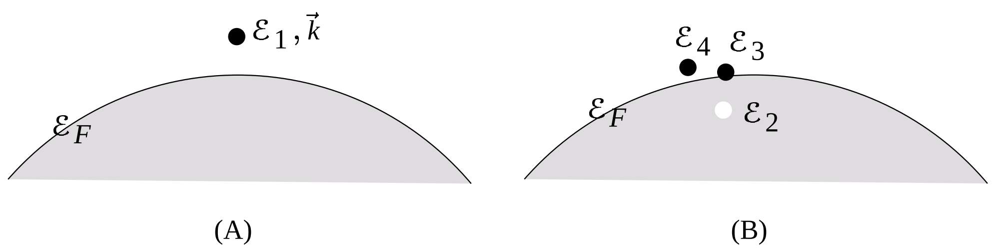


Figure 7: Fermi sea

Lifetime of quasiparticles large near Fermi surface

$$\hat{U}_{\rm int} = \sum_{\substack{\vec{k}'\vec{q}\vec{k} \\ \sigma\sigma'}} U_{\vec{k}'\vec{q}\vec{k}} \hat{c}^{\dagger}_{\vec{k}'-\vec{q},\sigma'} \hat{c}^{\dagger}_{\vec{k}+\vec{q},\sigma} \hat{c}_{\vec{k},\sigma} \hat{c}_{\vec{k}',\sigma'} . \tag{L100}$$

$$\mathcal{P}(\vec{k} \to \vec{k}') = \int \left(\prod_{l=2}^{4} d\mathcal{E}_l D(\mathcal{E}_l) \right) \frac{2\pi}{\hbar} \delta(\mathcal{E}_1 + \mathcal{E}_2 - \mathcal{E}_3 - \mathcal{E}_4) |\langle \Psi^{\rm f} | \hat{U}_{\rm int} | \Psi^{\rm i} \rangle|^2 . \tag{L101}$$

$$\mathcal{P}(\vec{k} \to \vec{k}') \propto \int_{2\mathcal{E}_F - \mathcal{E}_1}^{\mathcal{E}_F} d\mathcal{E}_2 \int_{\mathcal{E}_F}^{\mathcal{E}_1 + \mathcal{E}_2 - \mathcal{E}_F} d\mathcal{E}_3 \propto (\mathcal{E}_1 - \mathcal{E}_F)^2 \propto \tau^{-1} . \tag{L102}$$

Statistical Mechanics of Quasi-Particles

$$\mathcal{E}[\delta f] = \mathcal{E}_0 + \sum_{\vec{k}\sigma} \mathcal{E}^{(0)}_{\vec{k}} \delta f_{\vec{k}} + \frac{1}{2} \sum_{\substack{\vec{k},\vec{k}' \\ \sigma,\sigma'}} \delta f_{\vec{k}} u_{\vec{k}\vec{k}'} \delta f_{\vec{k}'} \ldots . \tag{L103}$$

$$\mathcal{E}_{\vec{k}} \equiv \mathcal{E}^{(0)}_{\vec{k}} + \sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'} \delta f_{\vec{k}'} . \tag{L104}$$

$$f^{(0)}_{\vec{k}} \equiv \theta(\mathcal{E}_F - \mathcal{E}_{\vec{k}}). \tag{L105}$$

$$N = \sum_{\vec{k}\sigma} f_{\vec{k}} \Rightarrow n = \frac{N}{\mathcal{V}} = \frac{1}{3\pi^2} k_F^3 . \tag{L106}$$

$$Z_{\text{gr}} = \sum_{\delta n_{\vec{k}_1} \cdots \delta n_{\vec{k}_N}} \exp\left\{ -\beta\left[\sum_{\vec{k}\sigma} (\mathcal{E}^{(0)}_{\vec{k}} - \mu)\delta n_{\vec{k}} + \frac{1}{2} \sum_{\substack{\vec{k}\vec{k}' \\ \sigma\sigma'}} \delta n_{\vec{k}} u_{\vec{k}\vec{k}'} \delta n_{\vec{k}'} \right] \right\}. \tag{L107}$$

$$\delta n_{\vec{k}} = \delta f_{\vec{k}} + (\delta n_{\vec{k}} - \delta f_{\vec{k}}) \tag{L108}$$

$$Z_{\rm gr} = \sum_{\delta n_{\vec{k}_1}=0,1\ldots} e^{-\beta[\sum_{\vec{k}\sigma} \mathcal{E}^{(0)}_{\vec{k}} - \mu + \sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'}\delta f_{\vec{k}'}]\delta n_{\vec{k}} + \beta\frac{1}{2}\sum_{\substack{\vec{k}\vec{k}'\\ \sigma\sigma'}} \delta f_{\vec{k}} u_{\vec{k}\vec{k}'}\delta f_{\vec{k}'}} \tag{L109}$$

$$= \prod_{\substack{\vec{k}\vec{k}'\\ \sigma\sigma'}} e^{\frac{1}{2}\beta\delta f_{\vec{k}} u_{\vec{k}\vec{k}'}\delta f_{\vec{k}'}} \sum_{\delta n_{\vec{k}_1}\ldots} \prod_{\vec{k}\sigma} e^{-\beta[\mathcal{E}_{\vec{k}}-\mu]\delta n_{\vec{k}}} \tag{L110}$$

$$= \prod_{\substack{\vec{k}\vec{k}'\\ \sigma\sigma'}} e^{\frac{1}{2}\beta\delta f_{\vec{k}} u_{\vec{k}\vec{k}'}\delta f_{\vec{k}'}} \prod_{\vec{k}\sigma}(1+e^{-\beta[\mathcal{E}_{\vec{k}}-\mu]h_{\vec{k}}}), \tag{L111}$$

$$\delta f_{\vec{k}} = \prod_{\substack{\vec{k}\vec{k}'\\ \sigma\sigma'}} e^{\frac{1}{2}\beta\delta f_{\vec{k}} u_{\vec{k}\vec{k}'}\delta f_{\vec{k}'}} \left[\sum_{\delta n_{\vec{k}_1}=0,1\ldots}\right] \delta n_{\vec{k}} \prod_{\vec{k}'\sigma'} e^{-\beta[\mathcal{E}_{\vec{k}'}-\mu]\delta n_{\vec{k}'}} / Z_{\rm gr}, \tag{L112}$$

$$\delta f_{\vec{k}} = \frac{h_{\vec{k}}}{e^{\beta h_{\vec{k}}(\mathcal{E}_{\vec{k}}-\mu)}+1} = \frac{1}{e^{\beta(\mathcal{E}_{\vec{k}}-\mu)}+1} - f^{(0)}_{\vec{k}}. \tag{L113}$$

$$v_F \equiv \left| \frac{\partial \mathcal{E}_{\vec{k}}}{\partial \hbar \vec{k}} |_{k_F} \right| \equiv \frac{\hbar k_F}{m^\star}. \tag{L114}$$

$$\vec{J}_N = \sum_\alpha \langle \Psi | \frac{\hat{P}_\alpha}{m} | \Psi \rangle \tag{L115}$$

$$= \sum_{\vec{k}\sigma} \frac{\vec{k}\hbar}{m} f_{\vec{k}} = \sum_{\vec{k}\sigma} \frac{\vec{k}\hbar}{m} \delta f_{\vec{k}}. \tag{L116}$$

$$1 + \sum_l \vec{p} \cdot \frac{\partial}{\partial \hat{P}_l} = 1 + i \sum_l \vec{p} \cdot \hat{R}_l / \hbar. \tag{L117}$$

$$[1 - i \sum_l \vec{p} \cdot \hat{R}_l / \hbar] \left\{ \sum_l \frac{\hat{P}_l^2}{2m} + \frac{1}{2} \sum_\beta \hat{U}_{\text{int}}(\hat{R}_l, \hat{R}_\beta) \right\} [1 + i \sum_l \vec{p} \cdot \hat{R}_l / \hbar] \tag{L118}$$

$$= \hat{\mathcal{H}} + \sum_l \vec{p} \cdot \frac{\hat{P}_l}{m}. \tag{L119}$$

$$\sum_{\vec{k}\sigma} \mathcal{E}^{(0)}_{\vec{k}} [f_{\vec{k}-d\vec{k}} - f^{(0)}_{\vec{k}}] + \frac{1}{2} \sum_{\substack{\vec{k}\vec{k}' \\ \sigma\sigma'}} [f_{\vec{k}-d\vec{k}} - f^{(0)}_{\vec{k}}] u_{\vec{k}\vec{k}'} [f_{\vec{k}'-d\vec{k}} - f^{(0)}_{\vec{k}'}] \quad \text{(L120)}$$

$$= \quad d\vec{k} \cdot \sum_{\vec{k}\sigma} f_{\vec{k}} \frac{\partial \mathcal{E}_{\vec{k}}}{\partial \vec{k}} + \sum_{\vec{k}\sigma} \mathcal{E}^{(0)}_{\vec{k}} \delta f_{\vec{k}} + \frac{1}{2} \sum_{\substack{\vec{k}\vec{k}' \\ \sigma\sigma'}} \delta f_{\vec{k}} u_{\vec{k}\vec{k}'} \delta f_{\vec{k}'} . \quad \text{(L121)}$$

$$\vec{J}_N = \sum_{\vec{k}\sigma} v_{\vec{k}} f_{\vec{k}} \quad \text{(L122)}$$

with

$$\vec{v}_k = \frac{\partial \mathcal{E}_{\vec{k}}}{\partial \hbar \vec{k}} . \quad \text{(L123)}$$

Effective Mass

$$\vec{J}_N = \sum_{\vec{k}\sigma} \frac{\partial \mathcal{E}^{(0)}_{\vec{k}}}{\partial \hbar \vec{k}} f_{\vec{k}} + \sum_{\substack{\vec{k}\vec{k}' \\ \sigma\sigma'}} f_{\vec{k}} \frac{\partial}{\partial \hbar \vec{k}} u_{\vec{k}\vec{k}'} \delta f_{\vec{k}'} \quad \text{(L124)}$$

$$= \sum_{\vec{k}\sigma} \frac{\partial \mathcal{E}^{(0)}_{\vec{k}}}{\partial \hbar \vec{k}} \delta f_{\vec{k}} + \sum_{\substack{\vec{k}\vec{k}' \\ \sigma\sigma'}} [\delta f_{\vec{k}} + f^{(0)}_{\vec{k}}] \frac{\partial}{\partial \hbar \vec{k}} u_{\vec{k}\vec{k}'} \delta f_{\vec{k}'} \quad \text{(L125)}$$

$$= \sum_{\vec{k}\sigma} \frac{\partial \mathcal{E}_{\vec{k}}}{\partial \hbar \vec{k}} \delta f_{\vec{k}} - \sum_{\substack{\vec{k}\vec{k}' \\ \sigma\sigma'}} \frac{\partial f^{(0)}_{\vec{k}}}{\partial \hbar \vec{k}} u_{\vec{k}\vec{k}'} \delta f_{\vec{k}'} \quad \text{(L126)}$$

$$= \sum_{\vec{k}\sigma} \vec{v}_{\vec{k}} \delta f_{\vec{k}} + \sum_{\substack{\vec{k}\vec{k}' \\ \sigma\sigma'}} u_{\vec{k}\vec{k}'} \vec{v}_{\vec{k}'} \delta(\mathcal{E}^{(0)}_{\vec{k}'} - \mathcal{E}_F) \delta f_{\vec{k}}. \quad \text{(L127)}$$

$$\frac{\hbar \vec{k}}{m} = \vec{v}_{\vec{k}} + \sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'} \vec{v}_{\vec{k}'} \delta(\mathcal{E}^{(0)}_{\vec{k}'} - \mathcal{E}_F). \quad \text{(L128)}$$

$$= \frac{\hbar\vec{k}}{m^\star} + \sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'} \frac{\hbar\vec{k}'}{m^\star} \delta(\mathcal{E}^{(0)}_{\vec{k}'} - \mathcal{E}_F) \quad \text{(L129)}$$

$$\frac{m^\star}{m} = 1 + \sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'} \frac{\vec{k}' \cdot \vec{k}}{k_F^2} \delta(\mathcal{E}^{(0)}_{\vec{k}'} - \mathcal{E}_F) \quad \text{(L130)}$$

$$= 1 + \mathcal{V} \int dk' D_{\vec{k}'}\, d\Sigma\, \delta(\mathcal{E}^{(0)}_{\vec{k}'} - \mathcal{E}_F)\, u_{\vec{k}\vec{k}'} \hat{k} \cdot \hat{k}' \quad \text{(L131)}$$

$$= 1 + \mathcal{V} \int d\Sigma\, \frac{D(\mathcal{E}_F)}{4\pi} u_{\vec{k}\vec{k}'} \cos\theta \quad \text{(L132)}$$

$$= 1 + \mathcal{V} D(\mathcal{E}_F) \frac{1}{2} \int_{-1}^{1} d(\cos\theta)\, u_{\vec{k}\vec{k}'} \cos\theta. \quad \text{(L133)}$$

Specific Heat

$$C_{\mathcal{V}} = \frac{\partial \mathcal{E}}{\partial T}\Big|_{\mathcal{V}} = \frac{\partial}{\partial T}\Big[\sum_{\vec{k}\sigma} \mathcal{E}^{(0)}_{\vec{k}} \delta f_{\vec{k}} + \frac{1}{2}\sum_{\substack{\vec{k}\vec{k}'\\ \sigma\sigma'}} \delta f_{\vec{k}} u_{\vec{k}\vec{k}'} \delta f_{\vec{k}'}\Big] \quad \text{(L134)}$$

$$= \sum_{\vec{k}\sigma} \mathcal{E}_{\vec{k}} \frac{\partial \delta f_{\vec{k}}}{\partial T}. \quad \text{(L135)}$$

$$\frac{\partial \delta f_{\vec{k}}}{\partial T} = \frac{h_{\vec{k}} e^{\beta h_{\vec{k}}(\mathcal{E}_{\vec{k}}-\mu)}}{[e^{h_{\vec{k}}\beta(\mathcal{E}_{\vec{k}}-\mu)}+1]^2}\left\{\frac{h_{\vec{k}}}{k_B T^2}(\mathcal{E}_{\vec{k}}-\mu) - \frac{h_{\vec{k}}}{k_B T}\sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'}\frac{\partial \delta f_{\vec{k}'}}{\partial T} + \frac{h_{\vec{k}}}{k_B T}\frac{\partial \mu}{\partial T}\right\}. \quad \text{(L136)}$$

$$C_{\mathcal{V}} = \mathcal{V}\int [d\vec{k}]\, \frac{1}{k_B T^2}(\mathcal{E}_{\vec{k}}-\mu)^2 \frac{e^{\beta(\mathcal{E}_{\vec{k}}-\mu)}}{[e^{\beta(\mathcal{E}_{\vec{k}}-\mu)}+1]^2} \quad \text{(L137)}$$

$$= \mathcal{V}\int d\mathcal{E}\, D(\mathcal{E}) \frac{1}{k_B T^2}(\mathcal{E}-\mu)^2 \frac{e^{\beta(\mathcal{E}-\mu)}}{[e^{\beta(\mathcal{E}-\mu)}+1]^2} \quad \text{(L138)}$$

$$\Rightarrow c_{\mathcal{V}} = \frac{\pi^2}{3} k_B^2 T D(\mathcal{E}_F). \quad \text{(L139)}$$

Specific Heat

$$D(\mathcal{E}_F) = \int [d\vec{k}]\, \delta(\mathcal{E}_F - \mathcal{E}_{\vec{k}}) = \int d\mathcal{E}\, \frac{k^2 \delta(\mathcal{E}_F - \mathcal{E})}{\pi^2 \hbar |\partial \mathcal{E}_{\vec{k}} / \partial \hbar \vec{k}|} = \frac{k_F^2}{\pi^2 \hbar v_F} = \frac{m^\star k_F}{\pi^2 \hbar^2}, \qquad \text{(L140)}$$

$$u_{\vec{k}\uparrow\vec{k}'\uparrow} = u_{\vec{k}\downarrow\vec{k}'\downarrow} = u^s_{\vec{k}\vec{k}'} + u^a_{\vec{k}\vec{k}'} \tag{L141}$$

$$u_{\vec{k}\uparrow\vec{k}'\downarrow} = u_{\vec{k}\downarrow\vec{k}'\uparrow} = u^s_{\vec{k}\vec{k}'} - u^a_{\vec{k}\vec{k}'}, \tag{L142}$$

$$u^s_{\vec{k}\vec{k}'} = \sum_{l=0}^{\infty} u^s_l P_l(\cos\theta) \tag{L143}$$

$$u^a_{\vec{k}\vec{k}'} = \sum_{l=0}^{\infty} u^a_l P_l(\cos\theta). \tag{L144}$$

$$u^s_l = \frac{2l+1}{2}\int_{-1}^{1} d(\cos\theta) P_l(\cos\theta) \frac{u_{\vec{k}\uparrow\vec{k}'\uparrow} + u_{\vec{k}\uparrow\vec{k}'\downarrow}}{2} \tag{L145}$$

$$u^a_l = \frac{2l+1}{2}\int_{-1}^{1} d(\cos\theta) P_l(\cos\theta) \frac{u_{\vec{k}\uparrow\vec{k}'\uparrow} - u_{\vec{k}\uparrow\vec{k}'\downarrow}}{2}. \tag{L146}$$

$$F^a_l \equiv \mathcal{V} D(\mathcal{E}_F) u^a_l, \quad F^s_l \equiv \mathcal{V} D(\mathcal{E}_F) u^s_l. \tag{L147}$$

Fermi Liquid Parameters

$$\mathcal{V}D(\mathcal{E}_F)\frac{1}{2}\int_{-1}^{1} d(\cos\theta)\,\cos\theta\, u_{\vec{k}\vec{k}'} \tag{L148}$$

$$= \left(\frac{1}{3}\right)\left(\frac{3}{2}\right)\int_{-1}^{1} d(\cos\theta)\,P_1(\cos\theta)\mathcal{V}D(\mathcal{E}_F)\frac{u_{\vec{k}\uparrow\vec{k}'\uparrow}+u_{\vec{k}\uparrow\vec{k}'\downarrow}}{2} \tag{L149}$$

$$= \frac{1}{3}F_1^s. \tag{L150}$$

$$\frac{m^\star}{m} = 1+\frac{1}{3}F_1^s. \tag{L151}$$

$$c^2 = \frac{\partial P}{\partial \rho}\Big|_S. \tag{L152}$$

$$\begin{aligned} c^2 &= \frac{\mathcal{V}}{m}\frac{\partial P}{\partial N}\Big|_{T\mathcal{V}} = -\frac{\mathcal{V}}{m}\frac{\partial}{\partial N}\frac{\partial F}{\partial \mathcal{V}} = \frac{-\mathcal{V}}{m}\frac{\partial \mu}{\partial \mathcal{V}}\Big|_N && \text{(L153)} \\ &= \frac{N}{m}\frac{\partial \mu}{\partial N}\Big|_{\mathcal{V}} = \frac{N}{m}\frac{\partial^2 F}{\partial N^2}. && \text{(L154)} \end{aligned}$$

$$\begin{aligned} \delta f_{\vec{k}} &= \theta(\mu - \mathcal{E}_{\vec{k}}) - \theta(\mathcal{E}_F - \mathcal{E}_{\vec{k}}|_{\mu=\mathcal{E}_F}) && \text{(L155)} \\ \Rightarrow \frac{\partial \delta f_{\vec{k}}}{\partial \mu} &= \delta(\mathcal{E}_{\vec{k}} - \mu)(1 - \frac{\partial \mathcal{E}_{\vec{k}}}{\partial \mu}) && \text{(L156)} \end{aligned}$$

$$= \delta(\mathcal{E}_{\vec{k}} - \mu)\Big[1 - \sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'}\frac{\partial \delta f_{\vec{k}'}}{\partial \mu}\Big]. \tag{L157}$$

$$A = \sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'} \frac{\partial \delta f_{\vec{k}'}}{\partial \mu}. \tag{L158}$$

$$A = \int [d\vec{k}'] \, u_{\vec{k}\vec{k}'} \delta(\mathcal{E}_{\vec{k}'} - \mu)(1 - A) \tag{L159}$$

$$= B(1 - A), \quad \text{where } B = \sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'} \delta(\mathcal{E}_{\vec{k}'} - \mu) = F_0^s \tag{L160}$$

$$\Rightarrow A = \frac{B}{1+B} = \frac{F_0^s}{1+F_0^s}. \tag{L161}$$

$$\frac{\partial N}{\partial \mu} = \sum_{\vec{k}\sigma} \frac{\partial \delta f_{\vec{k}}}{\partial \mu} \tag{L162}$$

$$= \sum_{\vec{k}\sigma} \delta(\mathcal{E}_{\vec{k}} - \mu)(1 - A) \tag{L163}$$

$$= \mathcal{V} D(\mathcal{E}_F) \frac{1}{1+F_0^s} \tag{L164}$$

$$\Rightarrow c = \sqrt{\frac{n}{mD(\mathcal{E}_F)}(1+F_0^s)} \tag{L165}$$

$$= v_F\sqrt{\frac{m^\star}{3m}(1+F_0^s)}. \tag{L166}$$

$$\frac{\partial \delta f_{\vec{r}\vec{k}}}{\partial t} + \vec{v}_{\vec{k}} \cdot \frac{\partial}{\partial \vec{r}}\left\{\delta f_{\vec{r}\vec{k}} - \frac{\partial f^{(0)}_{\vec{k}}}{\partial \mathcal{E}_{\vec{k}}}\mathcal{E}_{\vec{r}\vec{k}}\right\} = \frac{dg}{dt}\Big|_{\text{coll.}}. \tag{L167}$$

$$(\omega - \vec{q}\cdot\vec{v}_{\vec{k}})\delta f_{\vec{k}} - \delta(\mathcal{E}_{\vec{k}} - \mathcal{E}_F)\vec{q}\cdot\vec{v}_{\vec{k}}(\sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'}\delta f_{\vec{k}'}) = 0. \tag{L168}$$

$$\phi_{\vec{k}}\delta(\mathcal{E}_F - \mathcal{E}_{\vec{k}}) = \delta f_{\vec{k}}. \tag{L169}$$

$$[\omega - \vec{q}\cdot\vec{v}_{\vec{k}}]\phi_{\vec{k}} - \vec{q}\cdot\vec{v}_{\vec{k}}\sum_{\vec{k}'\sigma'} u_{\vec{k}\vec{k}'}\phi_{\vec{k}'} = 0. \tag{L170}$$

$$[\omega - \vec{q}\cdot\vec{v}_{\vec{k}}]\phi_{\vec{k}} - \vec{q}\cdot\vec{v}_{\vec{k}} F_0^s \int \frac{d\Sigma}{4\pi}\phi_{\vec{k}'} = 0. \tag{L171}$$

$$\Rightarrow \phi_{\vec{k}} = \frac{\vec{q}\cdot\vec{v}_{\vec{k}}}{\omega - \vec{q}\cdot\vec{v}_{\vec{k}}} F_0^s \int \frac{d\Sigma}{4\pi}\phi_{\vec{k}'}. \tag{L172}$$

$$\phi(\cos\theta) = \sum_{l=0}^{\infty} P_l(\cos\theta)\phi_l \tag{L173}$$

$$\Rightarrow \phi(\cos\theta) = -\left[1 - \frac{\omega}{\omega - qv_F\cos\theta}\right] F_0^s \phi_0 \tag{L174}$$

$$\Rightarrow \phi_0 = -F_0^s\phi_0 \frac{1}{2}\int_{-1}^{1} d(\cos\theta)\left[1 - \frac{\omega}{\omega - qv_F\cos\theta}\right] \tag{L175}$$

$$= -F_0^s\phi_0\left[1 + \frac{1}{2}\frac{\omega}{qv_F}\ln\left(\frac{\omega - qv_F}{\omega + qv_F}\right)\right] \tag{L176}$$

$$\Rightarrow \quad 1 + F_0^s\left[1 + \frac{1}{2}\frac{\omega}{qv_F}\ln\left(\frac{\omega - qv_F}{\omega + qv_F}\right)\right] = 0. \tag{L177}$$

$$\left\{F_0^s(1+\frac{1}{3}F_1^s)+(\frac{\omega}{qv_F})^2F_1^s\right\}\left[1+\frac{1}{2}\frac{\omega}{qv_F}\ln\left(\frac{\omega-qv_F}{\omega+qv_F}\right)\right]+1+\frac{F_1^s}{3}=0. \qquad \text{(L178)}$$

P(bar)	F_0^s	F_1^s	F_0^a	F_1^a	$m^\star/m$	v_F (m s^{-1})
0	9.15	5.27	−0.700	−0.55	2.76	59.7
3	15.83	6.40	−0.725	−0.73	3.13	54.3

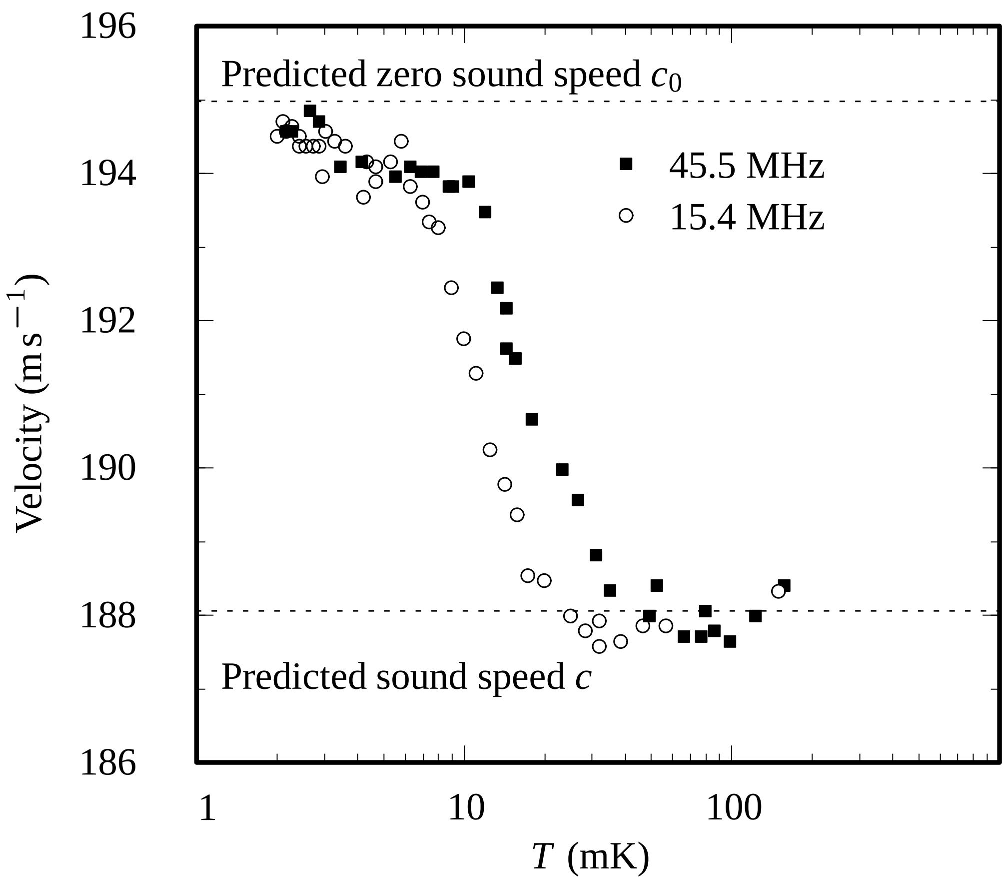
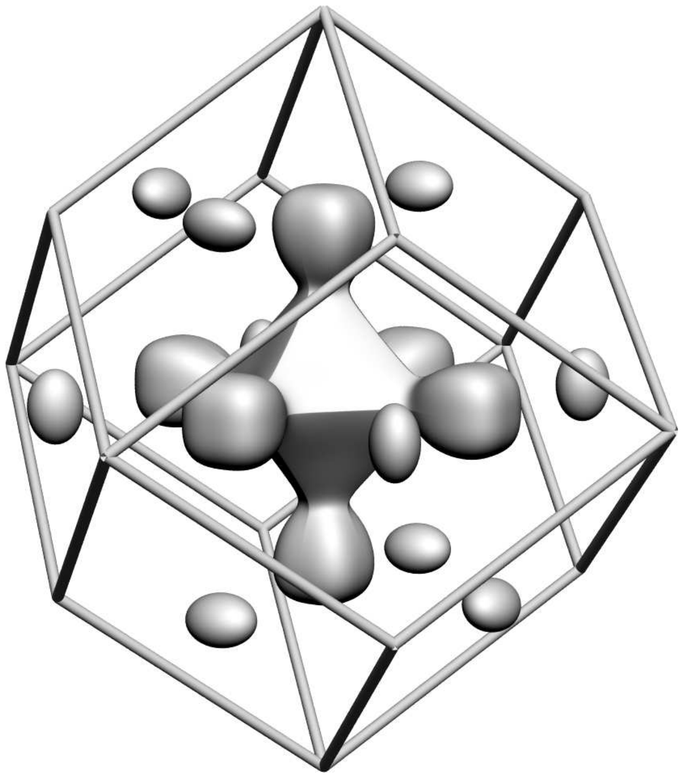


Figure 8: [Source: Abel et al. (1966), p. 76.]

Dynamics of Bloch Electrons



Definitions

- Drude model
- Semiclassical dynamics
- Bloch oscillations
- $\vec{K} \cdot \vec{P}$ method
- Effective mass
- Houston states
- Zener tunneling
- Wave packets
- Anomalous velocity
- Wannier–Stark ladders
- de Haas–van Alphen effect

Drude Model

$$m\dot{\vec{v}} = -e\vec{E} - e\frac{\vec{v}}{c} \times \vec{B} - m\frac{\vec{v}}{\tau}, \tag{L1}$$

In the absence of an electric field,

$$\vec{v}(t) = \vec{v}_0 e^{-t/\tau}. \tag{L2}$$

In the presence of one

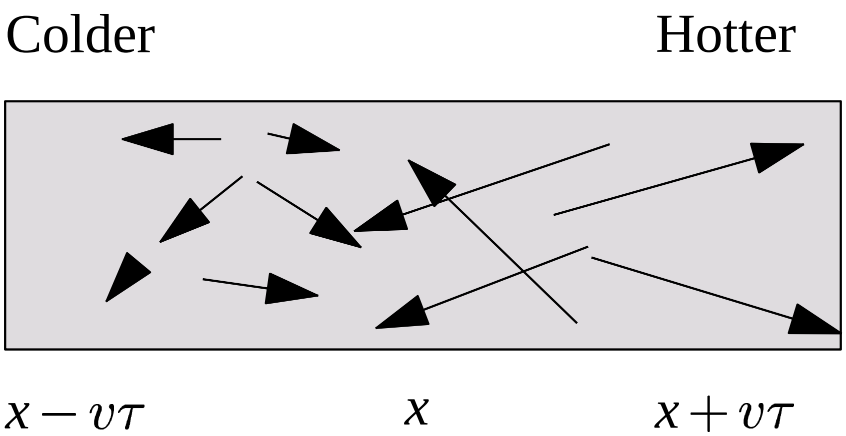
$$\vec{v}(t) = ? \qquad ? + [\vec{v}_0 + \frac{\tau e}{m}\vec{E}]e^{-t/\tau} \tag{L3}$$

$$\vec{v} = ? \qquad ? \tag{L4}$$

$$\vec{j} \quad = \quad -ne\vec{v} = \frac{ne^2\tau}{m}\vec{E} \tag{L5}$$

$$\Rightarrow \sigma \quad = \quad \frac{ne^2\tau}{m}, \tag{L6}$$

$$\tau = \frac{m}{ne^2\rho} = \frac{3.55\cdot 10^{-13}\,\mathrm{s}}{n/[10^{22}\,\mathrm{cm}^{-3}]\;\rho/[\mu\Omega\,\mathrm{cm}]} \tag{L7}$$



$$j_{\mathcal{E}} = \frac{n}{2}v_x\left[\mathcal{E}(x-v_x\tau)-\mathcal{E}(x+v_x\tau)\right] \approx -nv_x^2\tau\frac{\partial\mathcal{E}}{\partial x} = -nv_x^2\tau\frac{\partial\mathcal{E}}{\partial T}\frac{\partial T}{\partial x} \tag{L8}$$

$$= -\frac{2n}{m}\frac{1}{2}mv_x^2 c_V\tau\frac{\partial T}{\partial x} = -\frac{\tau n}{m}\frac{3k_B^2 T}{2}\frac{\partial T}{\partial x} \tag{L9}$$

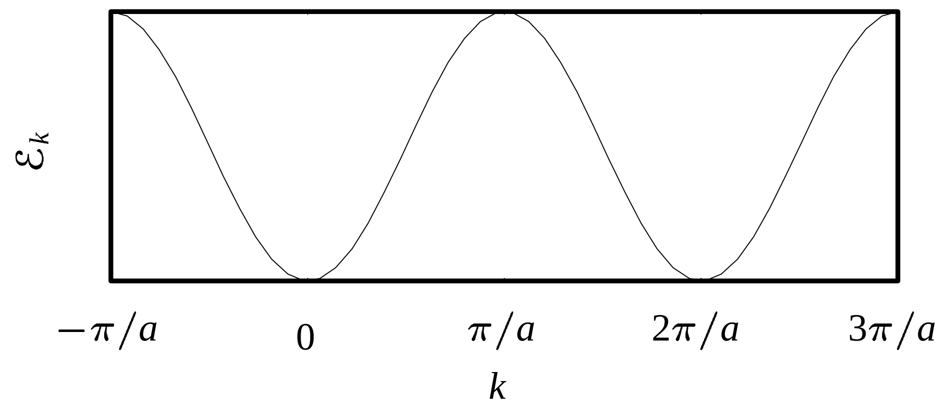
$$\Rightarrow \frac{\kappa}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 = 1.24\cdot 10^{-13}\mathrm{erg\,cm^{-1}\,K^{-2}}. \tag{L10}$$

Semiclassical Electron Dynamics

$$\dot{\vec{r}} = \frac{1}{\hbar}\frac{\partial \mathcal{E}_{\vec{k}}}{\partial \vec{k}}. \tag{L11}$$

$$\hbar\dot{\vec{k}} = -e\vec{E} - \frac{e}{c}\dot{\vec{r}} \times \vec{B} \tag{L12}$$

Bloch Oscillations



$$\mathcal{E}_k = -2\mathfrak{t}\cos ak, \tag{L13}$$

$$\hbar\dot{k} = -eE \tag{L14}$$

$$\Rightarrow k = -eEt/\hbar \tag{L15}$$

$$\Rightarrow \dot{r} = -\frac{2\mathfrak{t}a}{\hbar}\sin\left(\frac{aeEt}{\hbar}\right) \tag{L16}$$

$$\Rightarrow r = \frac{2\mathfrak{t}}{eE}\cos\left(\frac{aeEt}{\hbar}\right). \tag{L17}$$

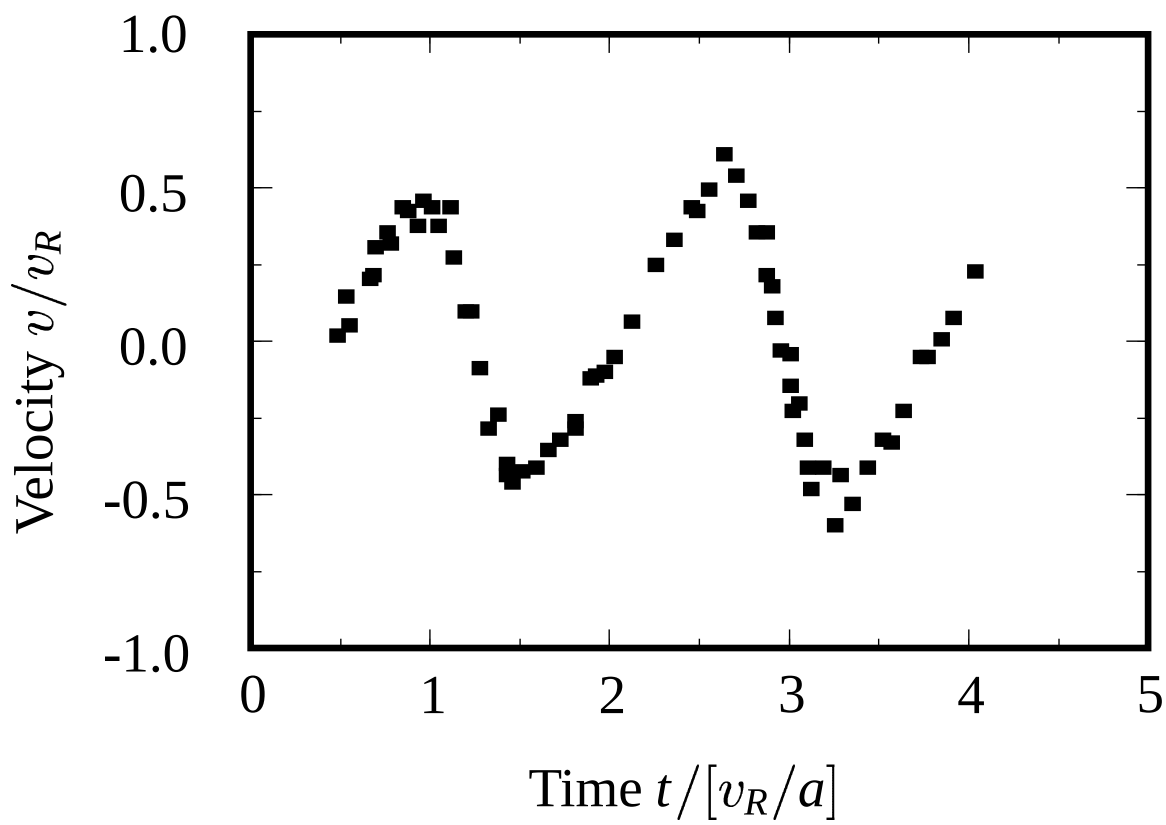


Figure 1: [Source: ben Dahan et al. (1996), p. 4510.]

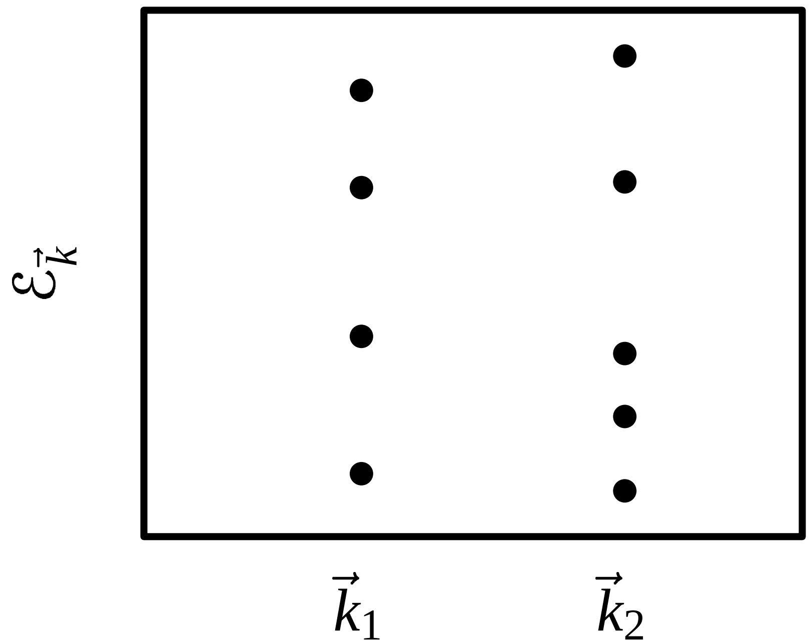


Figure 2: Which eigenvalues belong to the same band?

$$\hat{\mathcal{H}}_{\vec{k}+\vec{\delta k}} = \frac{\hbar^2}{2m}[-\vec{\nabla}^2 - 2i(\vec{k}+\vec{\delta}k)\cdot\vec{\nabla} + |\vec{k}+\vec{\delta}k|^2]u(\vec{r}) + U(\vec{r})u(\vec{r}) = \mathcal{E}u(\vec{r}). \tag{L18}$$

$$\hat{\mathcal{H}}^{(1)}_{\vec{k}} = -\frac{\hbar^2}{2m}\left[-\delta k^2 - 2\vec{\delta}k\cdot\vec{k} + 2i\vec{\delta}k\cdot\vec{\nabla}\right]. \tag{L19}$$

$$\mathcal{E}_{n,\vec{k}+\vec{\delta k}} = \mathcal{E}_{n\vec{k}} + \mathcal{E}^{(1)}_{n\vec{k}} + \mathcal{E}^{(2)}_{n\vec{k}} + \ldots . \tag{L20}$$

$$\mathcal{E}^{(1)}_{n\vec{k}} = \langle u_{n\vec{k}} | (\frac{\hbar^2}{m}) \vec{\delta k} \cdot (\vec{k} - i\vec{\nabla}) | u_{n\vec{k}} \rangle . \tag{L21}$$

$$(\vec{k} - i\vec{\nabla}) e^{-i\vec{k}\cdot\vec{r}} = -ie^{-i\vec{k}\cdot\vec{r}} \vec{\nabla} . \tag{L22}$$

$$\mathcal{E}^{(1)}_{n\vec{k}} \quad = \quad \frac{\hbar}{m} \langle \psi_{n\vec{k}} | \vec{\delta k} \cdot \hat{P} | \psi_{n\vec{k}} \rangle \tag{L23}$$

$$\Rightarrow \frac{\partial \mathcal{E}_{n\vec{k}}}{\partial \vec{k}} \quad = \quad \frac{\hbar}{m} \langle \psi_{n\vec{k}} | \hat{P} | \psi_{n\vec{k}} \rangle \tag{L24}$$

$$\Rightarrow \frac{\partial \mathcal{E}_{n\vec{k}}}{\partial \hbar \vec{k}} \quad = \quad \langle \hat{v} \rangle \equiv \vec{v}_{n\vec{k}} . \tag{L25}$$

$$\frac{d}{dt}\langle\hat{v}_\alpha\rangle = \sum_\beta \frac{\partial\langle\hat{v}_\alpha\rangle}{\partial k_\beta}\frac{\partial k_\beta}{\partial t} \tag{L26}$$

$$\Rightarrow \frac{d}{dt}\langle\hat{v}\rangle = \hbar\mathbf{M}^{-1}\dot{\vec{k}}, \tag{L27}$$

where

$$(\mathbf{M}^{-1})_{\alpha\beta} \equiv \frac{1}{\hbar^2}\frac{\partial^2\mathcal{E}_{n\vec{k}}}{\partial k_\alpha\partial k_\beta}. \tag{L28}$$

Proceeding to second order....

$$(\mathbf{M}^{-1})_{\alpha\beta} = \frac{1}{m}\delta_{\alpha\beta} + \frac{1}{m^2}\sum_{n'\neq n}\frac{\langle\psi_{n\vec{k}}|\hat{P}_\alpha|\psi_{n'\vec{k}}\rangle\langle\psi_{n'\vec{k}}|\hat{P}_\beta|\psi_{n\vec{k}}\rangle + \text{c.c.}}{\mathcal{E}_{n\vec{k}} - \mathcal{E}_{n'\vec{k}}} \tag{L29}$$

Potential of form $-\vec{E}\cdot\vec{r}$ conflicts with periodic boundary conditions.

$$\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} - \vec{\nabla} V. \tag{L30}$$

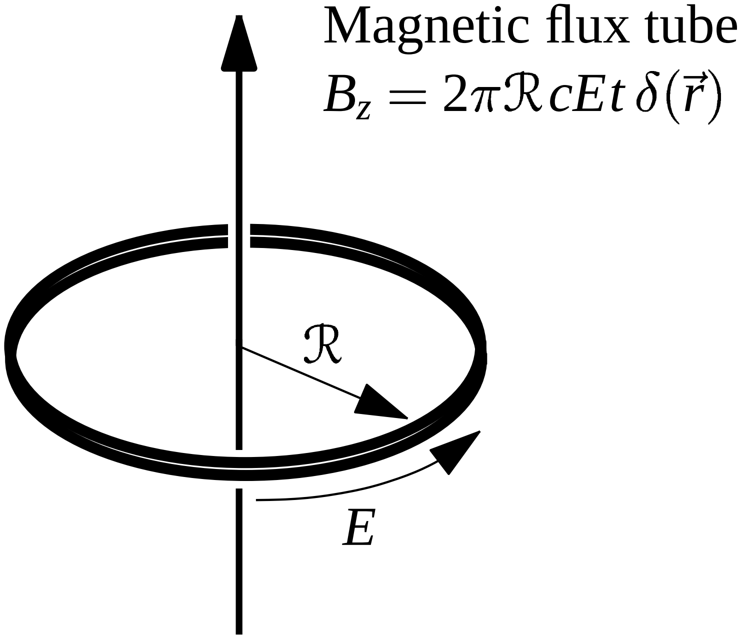


Figure 3: A thin tube of increasing magnetic flux through a loop of wire.

$$\hat{\mathcal{H}} = \frac{1}{2m}\left(\hat{P} + \frac{e}{c}A\right)^2 + \hat{U}(\hat{R}), \tag{L31}$$

Electrons in Electric Field

$$A = -cEt. \tag{L32}$$

$$\left[\frac{1}{2m}\left(\hat{P} + \frac{e}{c}A\right)^2 + \hat{U}\right]\tilde{\phi}(x,t) = \mathcal{E}_t\tilde{\phi}(x,t). \tag{L33}$$

$$\tilde{\phi}(x+L) = \tilde{\phi}(x). \tag{L34}$$

$$\tilde{\phi}(x,t) = e^{-ieAx/\hbar c}\phi(x,t). \tag{L35}$$

$$[\frac{\hat{P}^2}{2m} + \hat{U}]\phi(x,t) = \mathcal{E}_t\phi(x,t). \tag{L36}$$

$$\phi_{nk(t)}(x) = e^{ik(t)x}u_{nk(t)}(x). \tag{L37}$$

$$e^{-ieA(x+L)/\hbar c}e^{ik(t)(x+L)}u_{nk(t)}(x+L) \quad = \quad ? \qquad\qquad ? \tag{L38}$$

$$\Rightarrow \frac{-eA}{\hbar c} + k(t) = \frac{2\pi l}{L}. \quad \text{(L39)}$$

$$\Rightarrow \frac{eEt}{\hbar} + k(t) = \frac{2\pi l}{L}. \quad \text{(L40)}$$

(L41)

$$\hbar \dot{k} = -eE. \quad \text{(L42)}$$

$$\exp\left[\frac{i}{\hbar}\int_0^x dx' \sqrt{2m(-\mathcal{E}_g)}\right] \tag{L43}$$

$$\sim \exp\left[-x\sqrt{\frac{2m\mathcal{E}_g}{\hbar^2}}\right] \tag{L44}$$

$$\sim \exp\left[-\frac{\mathcal{E}_g}{eE}\sqrt{\frac{2m\mathcal{E}_g}{\hbar^2}}\right]. \tag{L45}$$

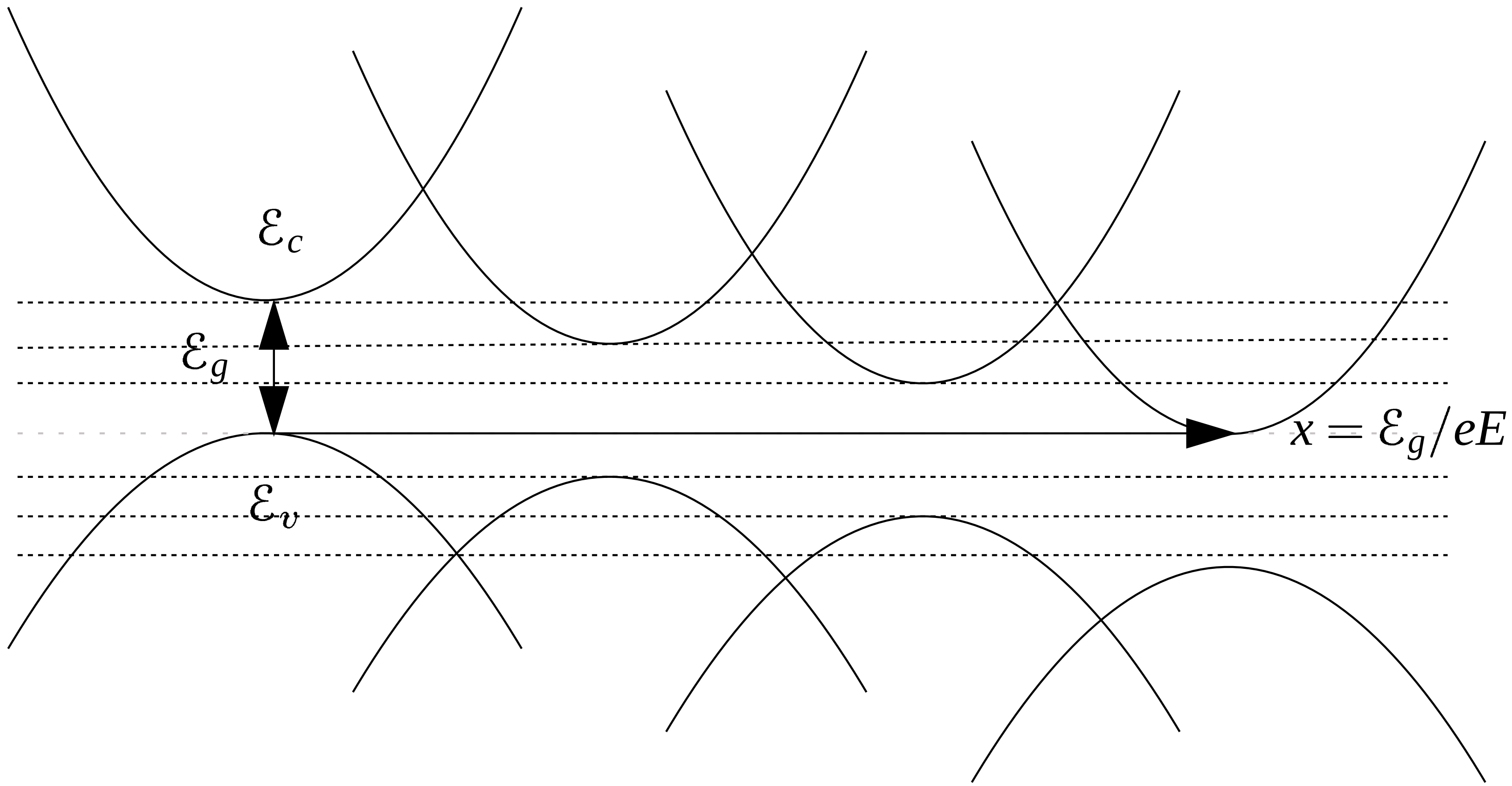


Figure 4: Energy diagram of Zener tunneling.

$$|\psi(t)\rangle = \sum_{n'} C_{n'}(t)|\tilde{\phi}_{n'k(t)}\rangle. \tag{L46}$$

Zener Tunneling

$$i\hbar\frac{\partial|\psi\rangle}{\partial t} = \hat{\mathcal{H}}|\psi\rangle \tag{L47}$$

$$\begin{aligned}
\hat{\mathcal{H}}|\psi\rangle &= \sum_{n'} C_{n'}(t)\mathcal{E}_{n'k(t)}|\tilde{\phi}_{n'k(t))}\rangle && \text{(L48)}\\
&= i\hbar\sum_{n'}\frac{\partial C_{n'}}{\partial t}|\tilde{\phi}_{n'k(t)}\rangle + C_{n'}(t)\frac{\partial}{\partial k}|\tilde{\phi}_{n'k(t)}\rangle\dot{k} && \text{(L49)}\\
\Rightarrow \langle\tilde{\phi}_{nk(t)}|\hat{\mathcal{H}}|\psi\rangle &= C_n(t)\mathcal{E}_{nk(t)} && \text{(L50)}\\
&= i\hbar\frac{\partial C_n}{\partial t} - \sum_{n'} iC_{n'}\langle\tilde{\phi}_{nk(t)}|\frac{\partial\tilde{\phi}_{n'k(t)}}{\partial k}\rangle eE. && \text{(L51)}
\end{aligned}$$

$$\begin{aligned}
C_1\mathcal{E}_{1k(t)} &= i\hbar\frac{\partial C_1}{\partial t} && \text{(L52)}\\
\Rightarrow C_1 &= \exp\left[-\frac{i}{\hbar}\int_0^t dt'\,\mathcal{E}_{1k(t')}\right]. && \text{(L53)}
\end{aligned}$$

$$\alpha_2(t) = C_2(t) \exp\left[\frac{i}{\hbar}\int_0^t dt' \mathcal{E}_{2k(t')}\right], \tag{L54}$$

$$\dot{\alpha}_2 = \langle \tilde{\phi}_{2k(t)} | \frac{\partial \tilde{\phi}_{1k(t)}}{\partial k} \rangle \frac{eE}{\hbar} \exp\left[\frac{i}{\hbar}\int_0^t dt' (\mathcal{E}_{2k(t')} - \mathcal{E}_{1k(t')})\right]. \tag{L55}$$

$$\alpha_2(\mathfrak{T}) \approx \frac{L}{N}\int_0^{\mathfrak{T}} dt\, \frac{eE}{\hbar} \exp\left[\frac{i}{\hbar}\int_0^t dt' (\mathcal{E}_{2k(t')} - \mathcal{E}_{1k(t')})\right]. \tag{L56}$$

$$\alpha_2(\mathfrak{T}) \approx \frac{L}{N}\int_0^{2\pi N/L} dk \exp\left[\frac{-i}{eE}\int_0^k dk' (\mathcal{E}_{2k'} - \mathcal{E}_{1k'})\right]. \tag{L57}$$

$$\frac{1}{m^\star} = \left[\frac{1}{m_v^\star} + \frac{1}{m_c^\star}\right] \tag{L58}$$

gives

$$\mathcal{E}_{2k'} - \mathcal{E}_{1k'} = \mathcal{E}_g + \frac{\hbar^2 k'^2}{2m^\star}. \tag{L59}$$

$$\mathcal{E}_g + \frac{\hbar^2 q^2}{2m^\star} = 0. \tag{L60}$$

$$\alpha_2(\mathcal{T}) \sim \exp\left[\frac{-i}{eE}\int_0^q dk'\,\mathcal{E}_g + \frac{\hbar^2 k'^2}{2m^\star}\right]. \tag{L61}$$

$$\sim \exp\left[\frac{-2i}{3eE} q\mathcal{E}_g\right] \tag{L62}$$

$$\sim \exp\left[\frac{-2\mathcal{E}_g^{3/2}}{3eE}\sqrt{\frac{2m^\star}{\hbar^2}}\right] \tag{L63}$$

$$\sim \exp\left[-3.41\cdot 10^7\,[\mathcal{E}_g/\mathrm{eV}]^{3/2}[m^\star/m]^{1/2}/[E\cdot\mathrm{cm\,V}^{-1}]\right]. \tag{L64}$$

$$W_{\vec{r}_c\vec{k}_c}(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{k}} w_{\vec{k}\vec{k}_c} e^{-ie\vec{A}(\vec{r}_c)\cdot\vec{r}/\hbar c - i\vec{k}\cdot\vec{r}_c}\psi_{\vec{k}}(\vec{r}). \tag{L65}$$

Calculations from here on out too complex to present at board...

$$1 = \langle W_{\vec{r}_c\vec{k}_c}|W_{\vec{r}_c\vec{k}_c}\rangle = \frac{1}{N}\sum_{\vec{k}\vec{k}'}\int d\vec{r}\, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}_c} w_{\vec{k}\vec{k}_c} w^*_{\vec{k}'\vec{k}_c}\psi^*_{\vec{k}'}(\vec{r})\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{k}\vec{k}'} w_{\vec{k}\vec{k}_c} w^*_{\vec{k}'\vec{k}_c}\delta_{\vec{k}\vec{k}'} \tag{L66}$$

$$\Rightarrow 1 \quad = \quad \sum_{\vec{k}} |w_{\vec{k}\vec{k}_c}|^2. \tag{L67}$$

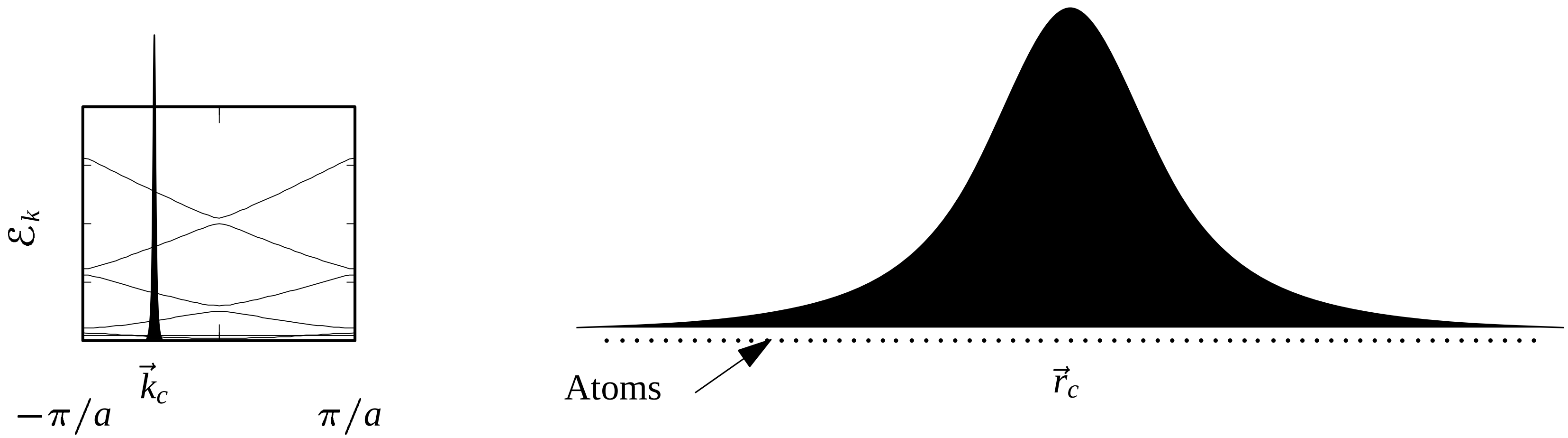


Figure 5: A wave packet viewed in real and reciprocal space

$$w_{\vec{k}\vec{k}_c} = |w|_{\vec{k}-\vec{k}_c} e^{i(\vec{k}-\vec{k}_c)\cdot\vec{\mathcal{R}}_{\vec{k}_c}}, \tag{L68}$$

where

$$\vec{\mathcal{R}}_{\vec{k}_c} = i\int_\Omega d\vec{r}\, u^*_{\vec{k}_c}(\vec{r})\frac{\partial}{\partial\vec{k}_c}u_{\vec{k}_c}(\vec{r}). \tag{L69}$$

$$\langle W_{\vec{r}_c\vec{k}_c}|\vec{r}-\vec{r}_c|W_{\vec{r}_c\vec{k}_c}\rangle = \langle W_{\vec{r}_c\vec{k}_c}|\vec{r}|W_{\vec{r}_c\vec{k}_c}\rangle - r_c \tag{L70}$$

$$= \int \frac{d\vec{r}}{N} \sum_{\vec{k}\vec{k}'} w^*_{\vec{k}\vec{k}_c} w_{\vec{k}'\vec{k}_c} e^{i(\vec{k}'-\vec{k})\cdot(\vec{r}-\vec{r}_c)} u^*_{\vec{k}}(\vec{r}) u_{\vec{k}'}(\vec{r}) [\vec{r}-\vec{r}_c] \quad \text{(L71)}$$

$$\text{(L72)}$$

$$= \int \frac{d\vec{r}}{N} \sum_{\vec{k}'\vec{k}} w^*_{\vec{k}\vec{k}_c} w_{\vec{k}'\vec{k}_c} u^*_{\vec{k}}(\vec{r}) u_{\vec{k}'}(\vec{r}) \frac{\partial}{\partial i\vec{k}'} e^{i(\vec{k}'-\vec{k})\cdot(\vec{r}-\vec{r}_c)} \quad \text{(L73)}$$

$$= -\int \frac{d\vec{r}}{N} \sum_{\vec{k}'\vec{k}} w^*_{\vec{k}\vec{k}_c} u^*_{\vec{k}}(\vec{r}) e^{i(\vec{k}'-\vec{k})\cdot(\vec{r}-\vec{r}_c)} \frac{\partial}{\partial i\vec{k}'} [w_{\vec{k}'\vec{k}_c} u_{\vec{k}'}(\vec{r})] \quad \text{(L74)}$$

$$= -\int_\Omega d\vec{r} \sum_{\vec{k}'\vec{k}} \delta_{\vec{k}\vec{k}'} w^*_{\vec{k}\vec{k}_c} u^*_{\vec{k}}(\vec{r}) \frac{\partial}{\partial i\vec{k}'} [w_{\vec{k}'\vec{k}_c} u_{\vec{k}'}(\vec{r})] \quad \text{(L75)}$$

$$= -\int_\Omega d\vec{r} \sum_{\vec{k}} |w|^2_{\vec{k}-\vec{k}_c} u^*_{\vec{k}}(\vec{r}) \frac{1}{w_{\vec{k}\vec{k}_c}} \frac{\partial}{\partial i\vec{k}} [w_{\vec{k}\vec{k}_c} u_{\vec{k}}(\vec{r})] \quad \text{(L76)}$$

$$= \int_\Omega d\vec{r}\, i u^*_{\vec{k}_c}(\vec{r}) \frac{\partial}{\partial \vec{k}_c} u_{\vec{k}_c}(\vec{r}) - \frac{\partial}{\partial i\vec{k}} \ln w_{\vec{k}\vec{k}_c} \Big|_{\vec{k}=\vec{k}_c} = 0 \quad \text{(L77)}$$

$$\Rightarrow \quad \langle W_{\vec{r}_c\vec{k}_c}|\vec{r}|W_{\vec{r}_c\vec{k}_c}\rangle = \vec{r}_c \tag{L78}$$

$$\mathcal{L} = \langle W_{\vec{r}_c\vec{k}_c}|i\hbar\frac{\partial}{\partial t}|W_{\vec{r}_c\vec{k}_c}\rangle - \langle W_{\vec{r}_c\vec{k}_c}|\hat{\mathcal{H}} - eV(\vec{r})|W_{\vec{r}_c\vec{k}_c}\rangle \tag{L79}$$

$$\hat{\mathcal{H}} = \frac{1}{2m}[\hat{P} + \frac{e\vec{A}(\vec{r})}{c}]^2 + U(\vec{r}) \tag{L80}$$

$$[\frac{\hat{P}^2}{2m} + U(\vec{r})]\psi_{\vec{k}} = \mathcal{E}_{\vec{k}}\psi_{\vec{k}}. \tag{L81}$$

$$\langle W_{\vec{r}_c\vec{k}_c}|i\hbar\frac{\partial}{\partial t}|W_{\vec{r}_c\vec{k}_c}\rangle = \frac{e\vec{r}_c}{c}\cdot\frac{d\vec{A}(\vec{r}_c)}{dt} + \hbar\vec{k}_c\cdot\dot{\vec{r}}_c + \hbar\dot{\vec{k}}_c\cdot\vec{\mathcal{R}}_{\vec{k}_c} \tag{L82a}$$

$$\langle W_{\vec{r}_c\vec{k}_c}|\hat{\mathcal{H}} - eV(\vec{r})|W_{\vec{r}_c\vec{k}_c}\rangle = \mathcal{E}_{\vec{k}_c} + \frac{e}{2mc}\vec{B}\cdot\vec{L}_{\vec{k}_c} - eV(\vec{r}_c) \tag{L82b}$$

with

$$\vec{L}_{\vec{k}_c} = \frac{\hbar}{2}\int_\Omega d\vec{r}\,[\frac{\partial u_{\vec{k}_c}}{\partial i\vec{k}_c}^* - \vec{\mathcal{R}}_{\vec{k}_c}u^*_{\vec{k}_c}]\times[\frac{\partial}{\partial i\vec{r}} + \vec{k}_c]u_{\vec{k}_c} + \text{c.c.}. \tag{L82c}$$

$$\frac{\partial \mathcal{L}}{\partial \vec{r}_c} = \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_c} \quad \text{and} \quad \frac{\partial \mathcal{L}}{\partial \vec{k}_c} = \frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot{\vec{k}}_c}. \tag{L83}$$

$$\hbar\dot{\vec{k}}_c = -e\vec{E} - \frac{e}{c}\dot{\vec{r}}_c \times \vec{B} \tag{L84a}$$

$$\dot{\vec{r}}_c = \frac{1}{\hbar}\left[\frac{\partial \mathcal{E}_{\vec{k}_c}}{\partial \vec{k}_c} + \frac{e}{2mc}\vec{B}\cdot\frac{\partial \vec{L}_{\vec{k}_c}}{\partial \vec{k}_c}\right] - \dot{\vec{k}}_c \times \vec{\Omega}, \tag{L84b}$$

Recover expected semiclassical dynamics, but with corrections due to anomalous velocity $\vec{\Omega}$.

$$\vec{B}(\vec{r}) = \frac{\partial}{\partial \vec{r}} \times \vec{A}(\vec{r}) \tag{L85a}$$

$$\vec{\Omega}(\vec{k}) = \frac{\partial}{\partial \vec{k}} \times \vec{\mathcal{R}}(\vec{k}). \tag{L85b}$$

Conditions for validity of Semiclassical Dynamics

$$\frac{eE}{k_F} \ll \mathcal{E}_g \sqrt{\frac{\mathcal{E}_g}{\mathcal{E}_F}}. \tag{L86}$$

$$2\pi\hbar/\mathfrak{T} \ll \mathcal{E}_g \sqrt{\frac{\mathcal{E}_g}{\mathcal{E}_F}}. \tag{L87}$$

$$\mathcal{H} = \sum_l \dot{Q}_l P_l - \mathcal{L}; \quad P_l = \frac{\partial \mathcal{L}}{\partial \dot{Q}_l}. \tag{L88}$$

$$\vec{p} = \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}} = \hbar \vec{k} - \frac{e\vec{A}}{c} \Rightarrow \hbar \vec{k} = \vec{p} + e\vec{A}/c \tag{L89a}$$

$$\vec{\pi} = \frac{\partial \mathcal{L}}{\partial \dot{\vec{k}}} = \hbar \vec{\mathcal{R}}_{\vec{k}}, \tag{L89b}$$

$$\mathcal{H} = \mathcal{E}_{\vec{k}} - eV(\vec{r}) + (e/2mc)\vec{B}\cdot\vec{L}_{\vec{k}} \equiv \mathcal{E}(\vec{p} + e\vec{A}/c) - eV(\vec{r}) + (e/2mc)\vec{B}\cdot\vec{L}_{\vec{k}}. \tag{L90}$$

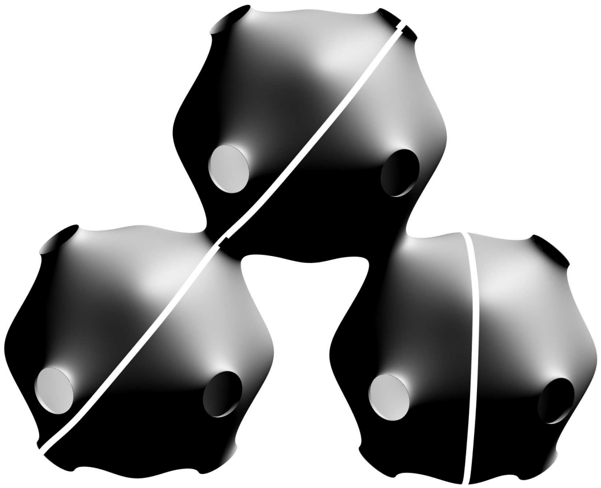


Figure 6: Energy contours on the Fermi surface of copper, showing open and closed orbits.

$$i\hbar\frac{\partial}{\partial t}|W\rangle = \hat{\mathcal{H}}|W\rangle. \tag{L91}$$

$$i\hbar\frac{\partial}{\partial t}|W\rangle = \mathcal{H}|W\rangle, \tag{L92}$$

$$e^{-i\mathcal{H}t/\hbar}. \tag{L93}$$

$$\mathcal{H}\mathcal{T} = 2\pi\hbar j, \tag{L94}$$

$$2\pi\hbar j = \int dt \sum_l P_l \frac{\partial\mathcal{H}}{\partial P_l} = \oint \sum_l dQ_l P_l, \tag{L95}$$

$$\oint \quad d\vec{k} \quad \cdot\vec{\mathcal{R}}_{\vec{k}} + d\vec{r}\cdot[\vec{k} - \frac{e\vec{A}}{\hbar c}] = 2\pi j \tag{L96}$$

$$\Rightarrow \oint \quad d\vec{k} \quad \cdot(\vec{\mathcal{R}}_{\vec{k}} - \vec{r}) - d\vec{r}\cdot\frac{e\vec{A}}{\hbar c} = 2\pi j. \tag{L97}$$

$$\Gamma = \oint d\vec{k} \cdot \vec{\mathcal{R}}_{\vec{k}}, \tag{L98}$$

$$2\pi j = \oint d\vec{k} \cdot (\vec{\mathcal{R}}_{\vec{k}} - \vec{r}) = \Gamma - \int_0^K d\vec{k} \cdot \vec{r} = \Gamma - K \langle \vec{r} \rangle \tag{L99}$$

$$\Rightarrow \langle \vec{r} \rangle = \frac{\Gamma - 2\pi j}{K}. \tag{L100}$$

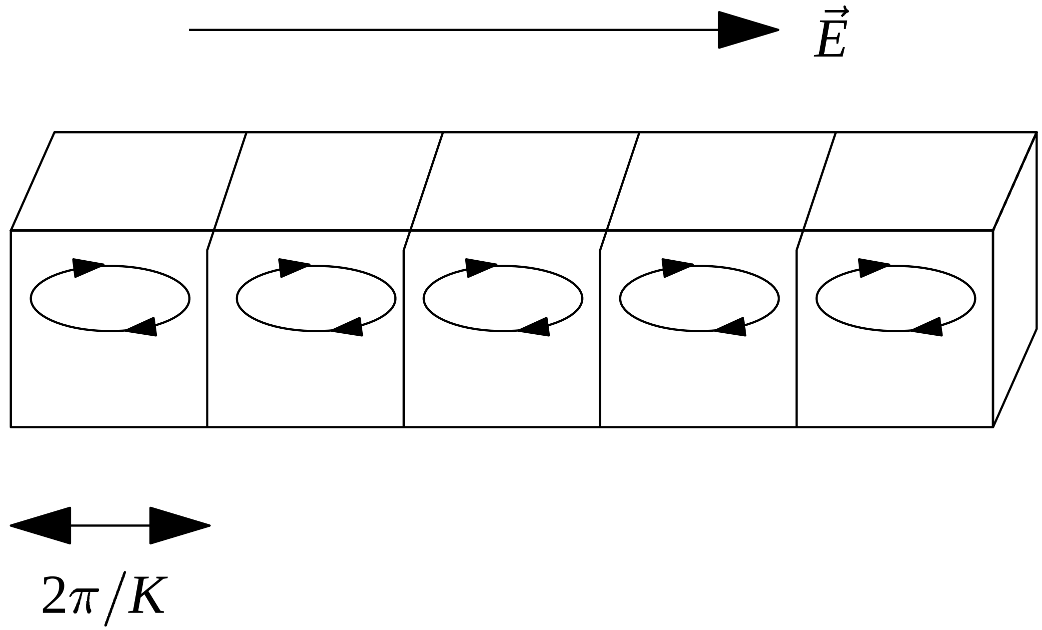
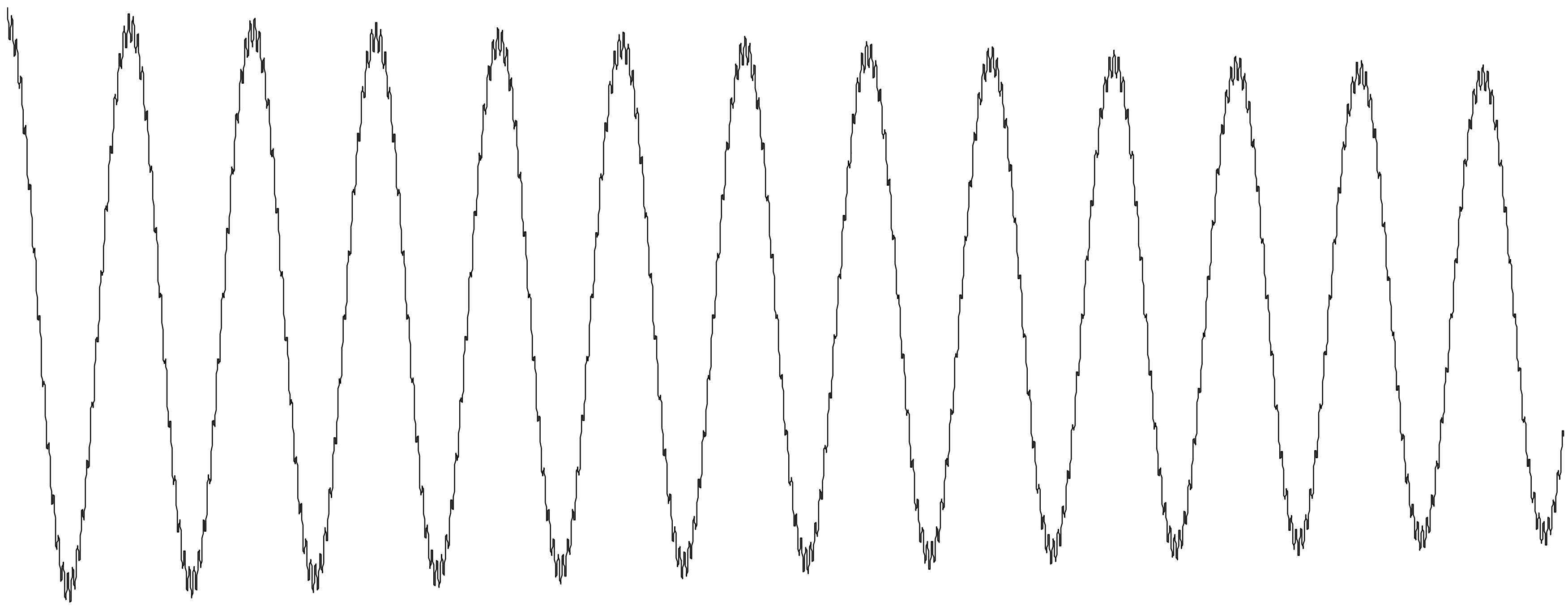


Figure 7: The Wannier–Stark ladder is a collection of electrons trapped in Bloch oscillations by an intense electric field, and spaced at intervals of $2\pi/K$, where $\vec{K}$ is a reciprocal lattice vector.

$$\vec{A} = \frac{1}{2}\vec{B} \times \vec{r}, \tag{L101}$$

$$\dot{\vec{k}} = \frac{-e\dot{\vec{r}}}{\hbar c} \times \vec{B} \qquad \Rightarrow \quad \vec{k}(t) - \vec{k}(0) = \frac{-e}{\hbar c}[\vec{r}(t) - \vec{r}(0)] \times \vec{B} \tag{L102}$$

$$\Rightarrow \vec{B} \times (\vec{k}(t) - \vec{k}(0)) \quad = \quad \frac{-e}{\hbar c}[\vec{r}(t) - \vec{r}(0)]B^2 + \frac{e}{\hbar c}\vec{B} \cdot [\vec{r}(t) - \vec{r}(0)]\vec{B}. \tag{L103}$$



74 kG 69 kG

Figure 8: Sketch of de Haas–van Alphen oscillations of magnetization M in gold similar to those measured by Shoenberg and Vanderkooy (1970).

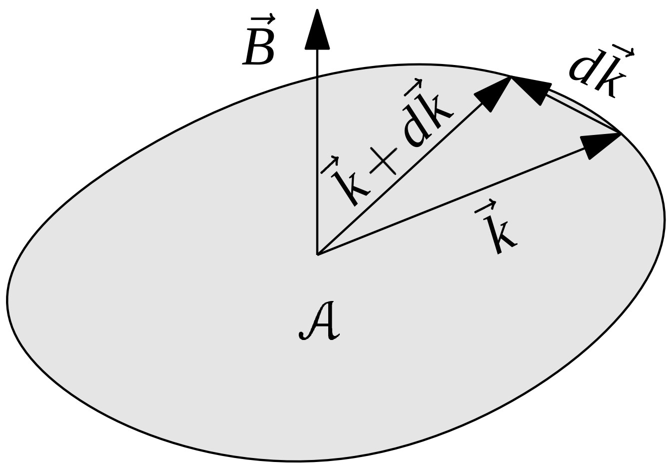
$$2\pi j = \Gamma - \int_0^{\mathcal{T}} dt \left[\frac{e\vec{A}}{c\hbar} \cdot \dot{\vec{r}} - \frac{e}{\hbar c} (\dot{\vec{r}} \times \vec{B}) \cdot \vec{r} \right] \quad \text{(L104)}$$

$$= \quad \Gamma + \int_0^{\mathcal{T}} dt\, \frac{e}{2\hbar c} \vec{r} \cdot (\dot{\vec{r}} \times \vec{B}) \tag{L105}$$

$$= \quad \Gamma + \int_0^{\mathcal{T}} dt\, \frac{\hbar c}{2eB} \left(\frac{\vec{B}}{B} \times \vec{k} \right) \cdot \dot{\vec{k}} \tag{L106}$$

$$= \quad \Gamma + \oint d\vec{k} \cdot \frac{\hbar c}{2eB} \left(\frac{\vec{B}}{B} \times \vec{k} \right) \tag{L107}$$

$$\Rightarrow 2\pi j \quad = \quad \Gamma + \mathcal{A} \frac{\hbar c}{eB}, \tag{L108}$$



$$\frac{\mathcal{A}}{B} \frac{\hbar c}{2\pi e} \quad = \quad 1.05 \cdot 10^4 \frac{\mathcal{A} \cdot \text{Å}^2}{[B/\text{T}]} = j - \Gamma/2\pi \tag{L109a}$$

$$\Rightarrow \mathcal{A} \quad = \quad 9.52 \cdot 10^{-5} \frac{1}{\Delta(1/B)} [\text{Å}^{-2}/\text{T}]. \tag{L109b}$$

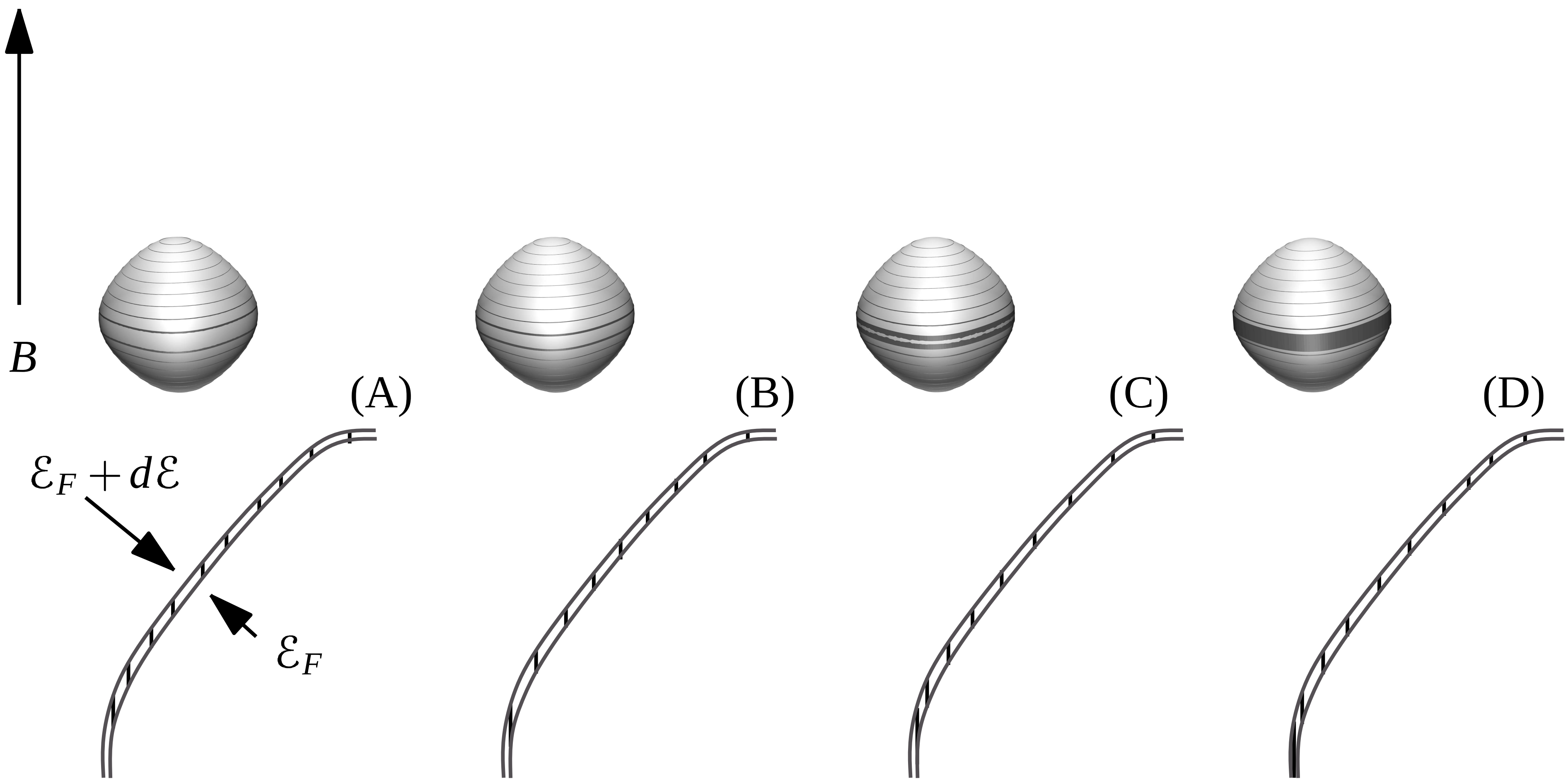


Figure 9:

Experimental Measurements of Fermi Surfaces

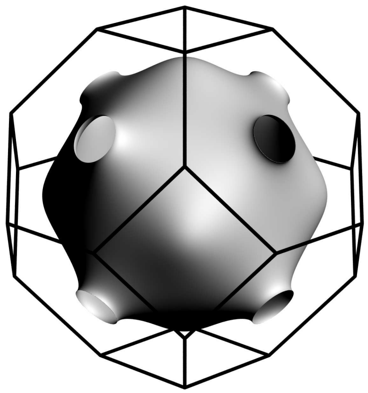


Figure 10: Fermi surface of copper, Shoenberg (1984).

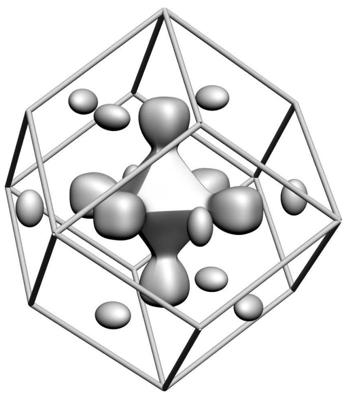
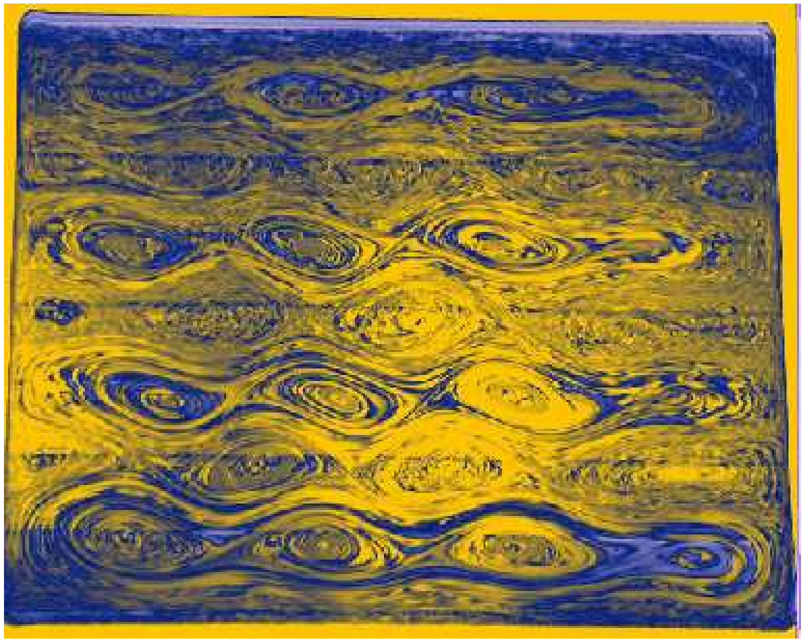


Figure 11: The Fermi surface of tungsten, Girvan et al. (1968).

Fluid Mechanics



Euler's Equation

$$\vec{v}(\vec{r}+\vec{v}dt,t+dt) = \vec{v}(\vec{r},t)+\vec{f}(\vec{r},t)dt/\rho \tag{L1}$$

$$\Rightarrow \quad \frac{\partial\vec{v}}{\partial t}+(\vec{v}\cdot\vec{\nabla})\vec{v}=\frac{\vec{f}}{\rho}. \tag{L2}$$

$$\frac{\partial\vec{v}}{\partial t}+(\vec{v}\cdot\vec{\nabla})\vec{v}+\frac{\vec{\nabla}P}{\rho}=0. \tag{L3}$$

$$\frac{\partial\rho}{\partial t}=-\vec{\nabla}\cdot\rho\vec{v}. \tag{L4}$$

$$\begin{aligned}
0 &= \frac{\partial\rho v_\alpha}{\partial t}-v_\alpha\frac{\partial\rho}{\partial t}+\rho\sum_\beta v_\beta\frac{\partial}{\partial r_\beta}v_\alpha+\frac{\partial}{\partial r_\alpha}P & \text{(L5)}\\
&= \frac{\partial\rho v_\alpha}{\partial t}+v_\alpha\sum_\beta\frac{\partial}{\partial r_\beta}\rho v_\beta+\rho\sum_\beta v_\beta\frac{\partial}{\partial r_\beta}v_\alpha+\frac{\partial}{\partial r_\alpha}P & \text{(L6)}\\
&= \frac{\partial\rho v_\alpha}{\partial t}+\sum_\beta\frac{\partial}{\partial r_\beta}\{\rho v_\alpha v_\beta+\delta_{\alpha\beta}P\}. & \text{(L7)}
\end{aligned}$$

Euler's Equation

$$\sigma_{\alpha\beta} = -\rho v_\alpha v_\beta - \delta_{\alpha\beta} P, \tag{L8}$$

$$\frac{\partial \rho v_\alpha}{\partial t} = \sum_\beta \frac{\partial}{\partial r_\beta} \sigma_{\alpha\beta}. \tag{L9}$$

$$\vec{\nabla} \cdot \vec{v} = 0, \tag{L10}$$

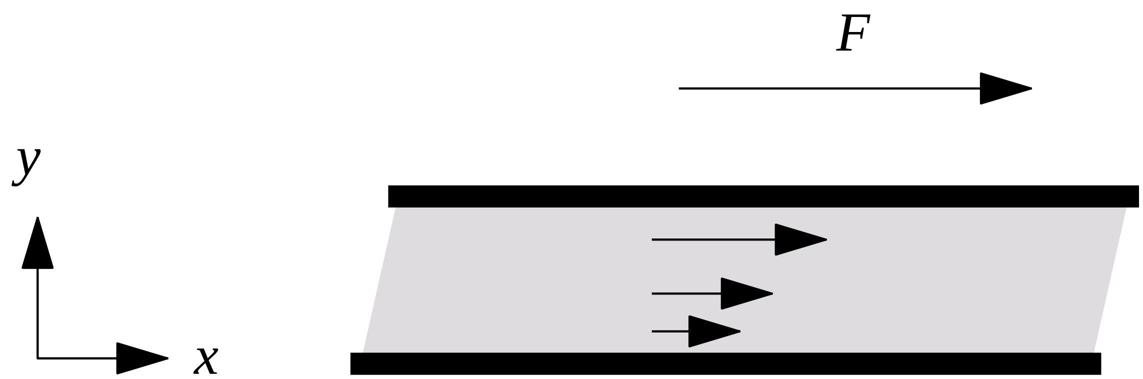


Figure 1: When liquid is sheared between two plates, the force is proportional to the shearing speed and is inversely proportional to the separation d.

$$\frac{F}{A} = \eta \frac{\partial v_x}{\partial y}, \tag{L11}$$

Gas	η (g/[cm·sec])	Liquid	η (g/[cm·sec])
He	$1.99 \cdot 10^{-4}$	NH_3	$14 \cdot 10^{-4}$
Ne	$3.17 \cdot 10^{-4}$	H_2O	$82 \cdot 10^{-4}$
Ar	$2.27 \cdot 10^{-4}$	CO_2	$6.0 \cdot 10^{-4}$
Kr	$2.55 \cdot 10^{-4}$	Hg	$160 \cdot 10^{-4}$
Xe	$2.33 \cdot 10^{-4}$	Glycerine	$85\,000 \cdot 10^{-4}$
H_2	$0.89 \cdot 10^{-4}$		
N_2	$1.79 \cdot 10^{-4}$		
O_2	$2.07 \cdot 10^{-4}$		
F_2	$2.36 \cdot 10^{-4}$		
Cl_2	$1.37 \cdot 10^{-4}$		
CO	$1.78 \cdot 10^{-4}$		
CO_2	$1.50 \cdot 10^{-4}$		
Air	$1.85 \cdot 10^{-4}$		

Navier–Stokes Equation

$$\sigma'_{\alpha\beta} = \eta\left[\frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha}\right] + \left[\zeta - \frac{2}{3}\eta\right]\delta_{\alpha\beta}\sum_\gamma \frac{\partial v_\gamma}{\partial r_\gamma}; \tag{L12}$$

$$\sigma_{\alpha\beta} = -\rho v_\alpha v_\beta - \delta_{\alpha\beta}P + \eta\left[\frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha}\right]. \tag{L13}$$

$$\rho\frac{\partial\vec{v}}{\partial t} + \rho(\vec{v}\cdot\vec{\nabla})\vec{v} = -\vec{\nabla}P + \eta\nabla^2\vec{v}. \tag{L14}$$

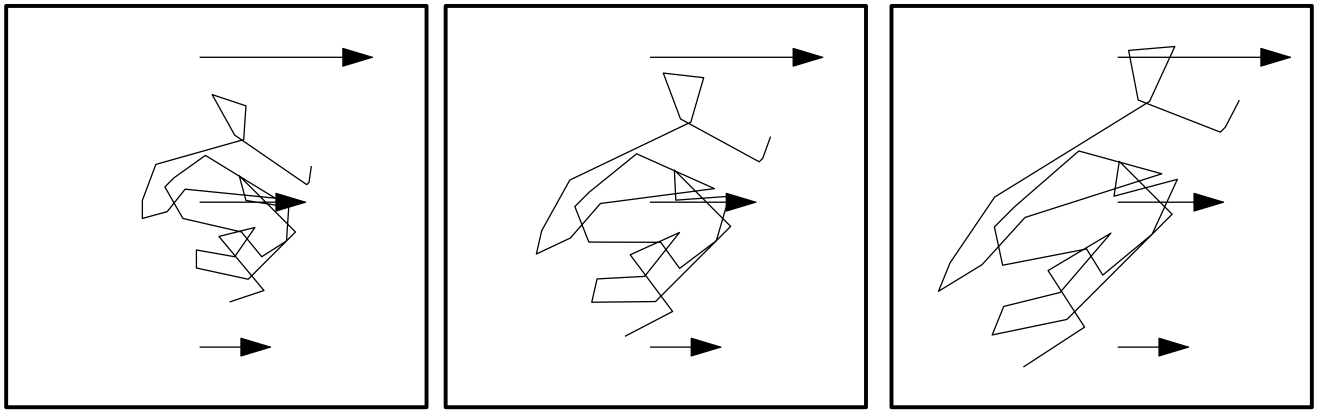


Figure 2:

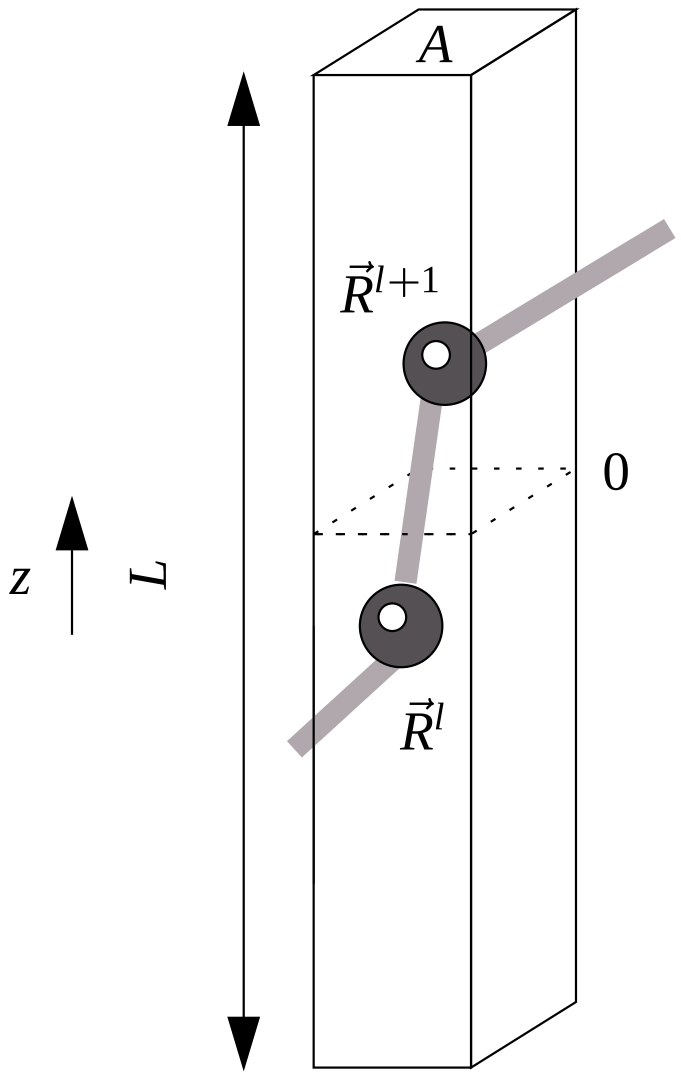


Figure 3:

$$g(\vec{R}^l, \vec{R}^{l+1}) = \frac{1}{\mathcal{V}} g(\vec{R}^{l+1} - \vec{R}^l). \tag{L15}$$

$$\sigma_{z\beta} = \frac{1}{A} \int d\vec{R}^l \, d\vec{R}^{l+1} \, \frac{1}{\mathcal{V}} g(\vec{R}^{l+1} - \vec{R}^l) \, \theta(R_z^{l+1}) \theta(-R_z^l) F_\beta^{l+1,l} \tag{L16}$$

$$= \frac{1}{A\mathcal{V}} \int d\vec{s} \, d\vec{t} \, g(\vec{s}) \, \theta(s_z/2 + t_z) \theta(s_z/2 - t_z) F_\beta^{l+1,l} \tag{L17}$$

$$= \frac{1}{\mathcal{V}} \int d\vec{s} \, g(\vec{s}) \, s_z \theta(s_z) F_\beta^{l+1,l} \tag{L18}$$

$$= \frac{1}{\mathcal{V}} \left\langle [R_z^{l+1} - R_z^l] \theta(R_z^{l+1} - R_z^l) F_\beta^{l+1,l} \right\rangle \tag{L19}$$

$$\frac{1}{\mathcal{V}} \left\langle [R_z^{l+1} - R_z^l] \theta(R_z^l - R_z^{l+1}) F_\beta^{l+1,l} \right\rangle . \tag{L20}$$

$$\sigma_{z\beta}^{l,l+1} = \frac{1}{\mathcal{V}} \left\langle [R_z^{l+1} - R_z^l] F_\beta^{l+1,l} \right\rangle \tag{L21}$$

$$= \frac{1}{\mathcal{V}}\left\langle [R_z^{l+1}F_\beta^{l+1,l}\right\rangle + \frac{1}{\mathcal{V}}\left\langle R_z^l F_\beta^{l,l+1}\right\rangle \tag{L22}$$

$$= \frac{1}{\mathcal{V}}\left\langle [R_z^{l+1}F_\beta^{l+1,l}\right\rangle + \frac{1}{\mathcal{V}}\left\langle R_z^{l-1} F_\beta^{l-1,l}\right\rangle . \tag{L23}$$

$$\sigma_{\alpha\beta} = \frac{1}{\mathcal{V}}\sum_{ll'}\left\langle R_\alpha^{l'} F_\beta^{l',l}\right\rangle . \tag{L24}$$

$$\ddot{\vec{R}}^l = \frac{1}{m}\sum_{l'}\vec{F}^{l',l} - b(\dot{\vec{R}}^l - \vec{v}) + \vec{\xi}^l . \tag{L25}$$

$$\langle \xi_\alpha(0)\xi_\beta(t)\rangle = \frac{2b\delta_{\alpha\beta}k_BT\delta(t)}{m} . \tag{L26}$$

$$\dot{\vec{R}}^l = \vec{v} + \frac{\mathcal{K}}{bm}[\vec{R}^{l+1} - 2\vec{R}^l + \vec{R}^{l-1}] + \frac{\vec{\xi}^l}{b} . \tag{L27}$$

$$v_\alpha = \vec{v}_\alpha^0 + \sum_\beta W_{\alpha\beta}R_\beta^l . \tag{L28}$$

$$\dot{\vec{R}}^l = \vec{v}^0 + W\vec{R}^l + \frac{\mathcal{K}}{bm}[\vec{R}^{l+1} - 2\vec{R}^l + \vec{R}^{l-1}] + \frac{\vec{\xi}^l}{b}. \tag{L29}$$

$$\vec{\psi}^k = \frac{1}{\sqrt{N}}\sum_{l=1}^{N} e^{2\pi ilk/N}[\vec{R}^l - \vec{v}^0 t]. \tag{L30}$$

$$\dot{\vec{\psi}}^k = \{W - \omega_k\}\vec{\psi}^k + \frac{\vec{\xi}^k}{b} \tag{L31}$$

with

$$\omega_k = \frac{2\mathcal{K}}{mb}(1 - \cos[2\pi k/N]). \tag{L32}$$

If W is independent of time, one can write

$$\vec{\psi}^k = \int_{-\infty}^{t} dt'\, e^{-(t'-t)[W-\omega_k]}\frac{\xi^k(t')}{b}. \tag{L33}$$

$$\psi_\alpha^{(0)k} = \int_{-\infty}^{t} dt'\, e^{(t'-t)\omega_k}\frac{\xi^k(t')}{b} \tag{L34}$$

Polymeric Solutions

$$\Rightarrow \quad \left\langle \psi_{\alpha}^{(0)k}(t)\psi^{(0)k^*}{}_{\beta}(t')\right\rangle = e^{-|t-t'|\omega_k}\frac{k_BT}{mb\omega_k}\delta_{\alpha\beta}. \tag{L35}$$

$$\psi_\alpha^k \quad \approx \quad \psi_\alpha^{(0)k} + \int_{-\infty}^{t} dt' \sum_\beta W_\beta(t')\psi_\beta^{(0)k}(t') \tag{L36}$$

$$\begin{aligned} \Rightarrow \quad & \langle \psi_\alpha^k(t)\psi_\beta^{*k}(t)\rangle \approx \frac{k_BT}{mb\omega_k}\delta_{\alpha\beta} \\ & + \int_{-\infty}^{t} dt' \sum_{\alpha'} \left\langle \psi_\alpha^{(0)k}(t) W_{\beta\alpha'}(t')\psi_{\alpha'}^{(0)k*}(t')\right\rangle \\ & + \int_{-\infty}^{t} dt' \sum_{\alpha'} \left\langle \psi_\beta^{(0)k*}(t) W_{\alpha\alpha'}(t')\psi_{\alpha'}^{(0)k}(t')\right\rangle. \end{aligned} \tag{L37}$$

$$= \quad \frac{k_BT}{mb\omega_k}\left\{\delta_{\alpha\beta} + \int_{-\infty}^{t} dt'\, e^{-(t-t')\omega_k}[W_{\beta\alpha}(t') + W_{\alpha\beta}(t')]\right\}. \tag{L38}$$

$$\sigma_{\alpha\beta} \quad = \quad \frac{1}{\mathcal{V}}\sum_{ll'}\left\langle F_\beta^{l,l'} R_\alpha^l\right\rangle = -\frac{\mathcal{K}}{\mathcal{V}}\sum_l \left\langle R_\alpha^l (R_\beta^{l+1} - 2R_\beta^l + R_\beta^{l-1})\right\rangle \tag{L39}$$

$$= \frac{\mathcal{K}}{\mathcal{V}} \sum_{k=1}^{N-1} (2 - 2\cos 2\pi k/N) \left\langle \psi_\alpha^k \psi_\beta^{k*} \right\rangle \tag{L40}$$

$$= \frac{mb}{\mathcal{V}} \sum_{k=1}^{N-1} \omega_k \left\langle \psi_\alpha^k \psi_\beta^{k*} \right\rangle \tag{L41}$$

$$= \frac{k_B T}{\mathcal{V}} \sum_{k=1}^{N-1} \left[\delta_{\alpha\beta} + \frac{W_{\alpha\beta} + W_{\beta\alpha}}{\omega_k} \right] \tag{L42}$$

$$= \frac{k_B T}{\mathcal{V}} \left[N\delta_{\alpha\beta} + 2 \sum_{k=1}^{N/2} \frac{W_{\alpha\beta} + W_{\beta\alpha}}{\omega_k} \right] \tag{L43}$$

$$\approx \frac{k_B T}{\mathcal{V}} \left[N\delta_{\alpha\beta} + 2 \sum_{k=1}^{\infty} \frac{W_{\alpha\beta} + W_{\beta\alpha}}{\frac{2\mathcal{K}}{mb} \frac{1}{2} \left(\frac{2\pi k}{N} \right)^2} \right] \tag{L44}$$

$$= \frac{k_B T}{\mathcal{V}} \left[N\delta_{\alpha\beta} + (W_{\alpha\beta} + W_{\beta\alpha}) \frac{mbN^2}{12\mathcal{K}} \right] \tag{L45}$$

$$\sigma_{xy} = \frac{k_B T}{\mathcal{V}} mb \frac{N^2}{12\mathcal{K}} \frac{\partial v_x}{\partial y}. \tag{L46}$$

$$\delta\eta = \frac{c}{N} k_B T mb \frac{N^2}{12\mathcal{K}} \tag{L47}$$

$$= \frac{c}{N} mb \frac{N^2 a^2}{12} \tag{L48}$$

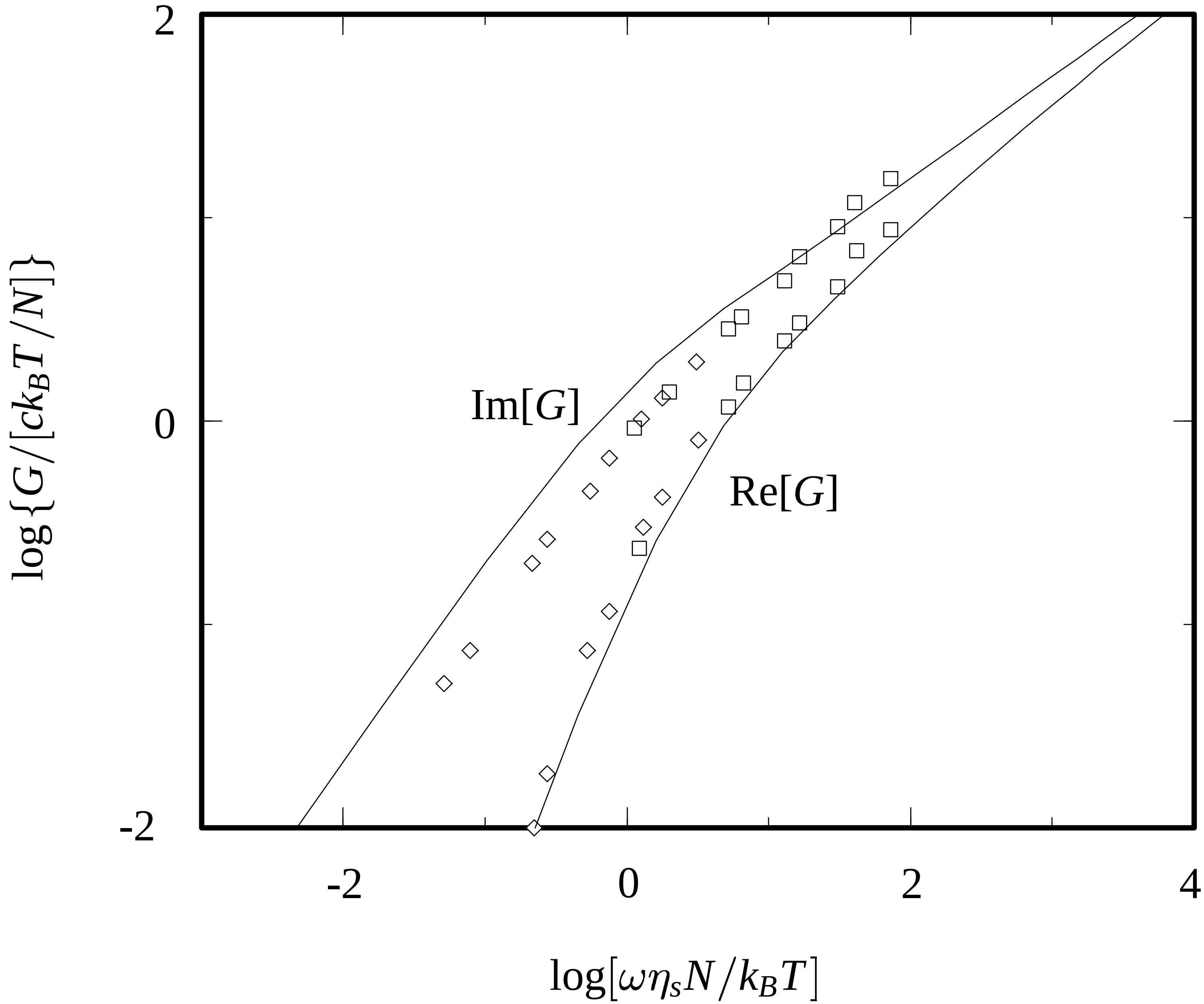


Figure 4: [Source: Ferry (1980), p. 197.]

Polymeric Solutions

$$\sigma_{xy} = \sum_{k=1}^{N-1} \frac{W_0 k_B T}{\mathcal{V}(\omega_k^2 + \omega^2)} [\omega_k \cos \omega t + \omega \sin \omega t]. \tag{L49}$$

$$G(\omega) = \frac{k_B T}{\mathcal{V}} \sum_{k=1}^{N-1} \frac{\omega(\omega + i\omega_k)}{\omega_k^2 + \omega^2}. \tag{L50}$$

$$\det|\sigma - \lambda I| = -\lambda^3 + \lambda^2 I_1 + \lambda I_2 + I_3 = 0 \quad \text{(L51a)}$$

with

$$I_1 = \sum_{\alpha} \sigma_{\alpha\alpha} \quad \text{(L51b)}$$

$$I_2 = \frac{1}{2} \sum_{\alpha\beta} \{\sigma_{\alpha\beta}\sigma_{\alpha\beta} - \sigma_{\alpha\alpha}\sigma_{\beta\beta}\} \quad \text{(L51c)}$$

$$I_3 = \det|\sigma|. \quad \text{(L51d)}$$

$$\sigma = \frac{1}{3} \sum_{\alpha} \sigma_{\alpha\alpha} \quad \text{(L52)}$$

$$s_{\alpha\beta} = \sigma_{\alpha\beta} - \sigma\delta_{\alpha\beta}. \quad \text{(L53)}$$

$$J_2 = \frac{1}{2} \sum_{\alpha\beta} s_{\alpha\beta} s_{\alpha\beta} \quad \text{(L54a)}$$

$$J_3 = \det|s|. \tag{L54b}$$

$$\sqrt{J_2} = \kappa. \tag{L55}$$

$$\dot{e}^{\mathrm{p}}_{\alpha\beta} = \begin{cases} w[\sqrt{J_2} - \kappa] s_{\alpha\beta} & \text{if } \sqrt{J_2} - \kappa > 0 \\ 0 & \text{otherwise.} \end{cases} \tag{L56}$$

$$W = \int dt' \sum_{\alpha\beta} \dot{e}^{\mathrm{p}}_{\alpha\beta} \sigma_{\alpha\beta}. \tag{L57}$$

$$de^{\mathrm{p}}_{\alpha\beta} = C ds_{\alpha\beta}. \tag{L58}$$

$$dW = C \sum_{\alpha\beta} \sigma_{\alpha\beta} ds_{\alpha\beta} \tag{L59}$$

$$= C \sum_{\alpha\beta} s_{\alpha\beta} ds_{\alpha\beta} \tag{L60}$$

$$= \quad C dJ_2, \tag{L61}$$

$$d\kappa = \kappa' C\, dJ_2. \tag{L62}$$

$$C = \frac{1}{2\kappa'\sqrt{J_2}} \tag{L63}$$

$$\Rightarrow de^{\mathrm{p}}_{\alpha\beta} = \frac{ds_{\alpha\beta}}{2\kappa'\sqrt{J_2}}. \tag{L64}$$

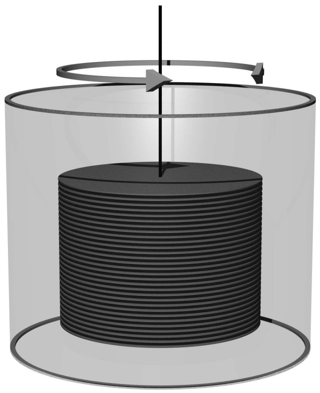


Figure 5:

$$\omega = \sqrt{\frac{\mathcal{K}}{I_0 + I_F}}. \tag{L65}$$

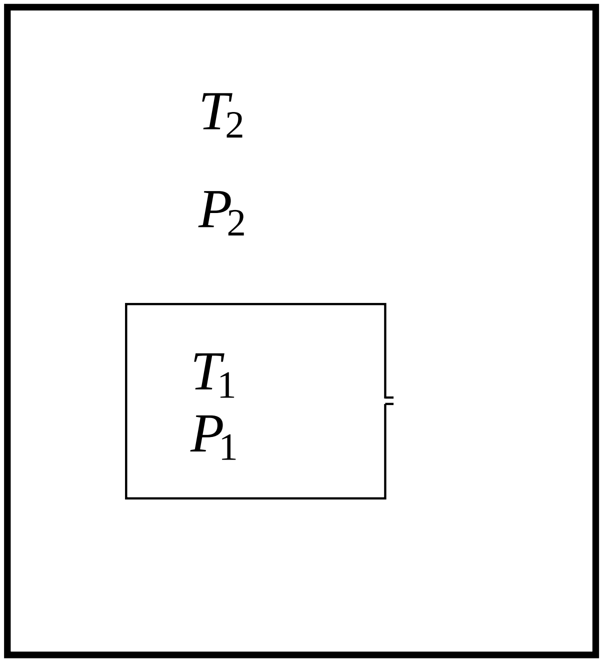


Figure 6:

$$0 = \frac{\partial G}{\partial N_1} = \frac{\partial G_1(N_1) + G_2(N - N_1)}{\partial N_1}\Big|_{TP} \quad \text{(L66)}$$

$$\Rightarrow \frac{\partial G_1}{\partial N_1} = \frac{\partial G_2}{\partial N_2} \Rightarrow \mu_1(T_1, P_1) = \mu_2(T_2, P_2). \quad \text{(L67)}$$

$$\frac{\partial \mathcal{E}_1(S_1, \mathcal{V}_1)}{\partial S_1} = \frac{\partial \mathcal{E}_2(S_2, \mathcal{V}_2)}{\partial S_2} \Rightarrow T_1 = T_2; \quad \text{(L68)}$$

$$\frac{\partial \mu_2}{\partial T_2}\Delta T + \frac{\partial \mu_2}{\partial P_2}\Delta P = 0 \tag{L69}$$

$$\Rightarrow \quad s\Delta T = \frac{1}{\rho}\Delta P \Rightarrow \frac{\Delta P}{\Delta T} = \rho s. \tag{L70}$$

$$\frac{\partial \vec{v}_s}{\partial t} + (\vec{v}_s \cdot \vec{\nabla})\vec{v}_s = -\frac{\vec{\nabla}\mu}{m}. \tag{L71}$$

$$d\mu = \frac{\mathcal{V}}{N} dP - \frac{S}{N} dT, \tag{L72}$$

$$\frac{\partial \vec{v}_s}{\partial t} + (\vec{v}_s \cdot \vec{\nabla})\vec{v}_s = -\frac{\vec{\nabla}P}{\rho} + s\vec{\nabla}T. \tag{L73}$$

$$\rho_s \left\{ \frac{\partial \vec{v}_s}{\partial t} + (\vec{v}_s \cdot \vec{\nabla})\vec{v}_s \right\} + \rho_n \left\{ \frac{\partial \vec{v}_n}{\partial t} + (\vec{v}_n \cdot \vec{\nabla})\vec{v}_n \right\} = -\vec{\nabla}P + \eta \nabla^2 \vec{v}_n. \tag{L74}$$

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho_n \vec{v}_n + \rho_s \vec{v}_s) = 0 \tag{L75}$$

$$\frac{\partial \rho s}{\partial t} = -\vec{\nabla} \cdot \rho s \vec{v}_n \tag{L76}$$

$$\frac{\partial \vec{v}_s}{\partial t} = -\frac{\vec{\nabla} P}{\rho} + s \vec{\nabla} T \tag{L77}$$

$$\rho_s \frac{\partial \vec{v}_s}{\partial t} + \rho_n \frac{\partial \vec{v}_n}{\partial t} = -\vec{\nabla} P. \tag{L78}$$

$$\frac{\partial^2 \rho}{\partial t^2} = \nabla^2 P. \tag{L79}$$

$$\frac{\partial s}{\partial t} = \frac{1}{\rho} \frac{\partial s \rho}{\partial t} - \frac{s}{\rho} \frac{\partial \rho}{\partial t} \tag{L80}$$

$$= \frac{-1}{\rho} \vec{\nabla} \cdot \rho s \vec{v}_n + \frac{s}{\rho} \vec{\nabla} \cdot (\rho_n \vec{v}_n + \rho_s \vec{v}_s) \tag{L81}$$

$$= \frac{s\rho_s}{\rho}\vec{\nabla}\cdot(\vec{v}_s-\vec{v}_n). \quad \text{(L82)}$$

Solving Eqs. (L77) and (78) for $\partial(\vec{v}_s-\vec{v}_n)/\partial t$ gives

$$\frac{\partial}{\partial t}(\vec{v}_s-\vec{v}_n) = s\frac{\rho}{\rho_n}\vec{\nabla}T \quad \text{(L83)}$$

$$\Rightarrow \frac{\partial^2 s}{\partial t^2} = s^2\frac{\rho_s}{\rho_n}\nabla^2 T. \quad \text{(L84)}$$

$$\frac{\partial\rho}{\partial P}\Big|_T \frac{\partial^2 P^{(1)}}{\partial t^2} + \frac{\partial\rho}{\partial T}\Big|_P \frac{\partial^2 T^{(1)}}{\partial t^2} = \nabla^2 P^{(1)} \quad \text{(L85)}$$

$$\frac{\partial s}{\partial P}\Big|_T \frac{\partial^2 P^{(1)}}{\partial t^2} + \frac{\partial s}{\partial T}\Big|_P \frac{\partial^2 T^{(1)}}{\partial t^2} = s^2\frac{\rho_s}{\rho_n}\nabla^2 T^{(1)}. \quad \text{(L86)}$$

$$\frac{\partial\rho}{\partial P}\Big|_T P^{(1)} + \frac{\partial\rho}{\partial T}\Big|_P T^{(1)} = c^{-2}P^{(1)} \quad \text{(L87a)}$$

$$\frac{\partial s}{\partial P}\Big|_T P^{(1)} + \frac{\partial s}{\partial T}\Big|_P T^{(1)} = c^{-2}s^2\frac{\rho_s}{\rho_n}T^{(1)}. \quad \text{(L87b)}$$

$$\left(1 - \frac{c^{-2}s^2\rho_s/\rho_n}{\frac{\partial s}{\partial T}\big|_P}\right)\left(1 - \frac{c^{-2}}{\frac{\partial \rho}{\partial P}\big|_T}\right) = \frac{\frac{\partial s}{\partial P}\big|_T \frac{\partial \rho}{\partial T}\big|_P}{\frac{\partial \rho}{\partial P}\big|_T \frac{\partial s}{\partial T}\big|_P} \tag{L88}$$

$$= \frac{C_P - C_V}{C_P} \tag{L89}$$

$$\approx 0. \tag{L90}$$

$$c_1 = \sqrt{\frac{\partial P}{\partial \rho}\Big|_T} \tag{L91}$$

and

$$c_2 = \sqrt{\frac{Ts^2}{C_P}\frac{\rho_s}{\rho_n}} \tag{L92}$$

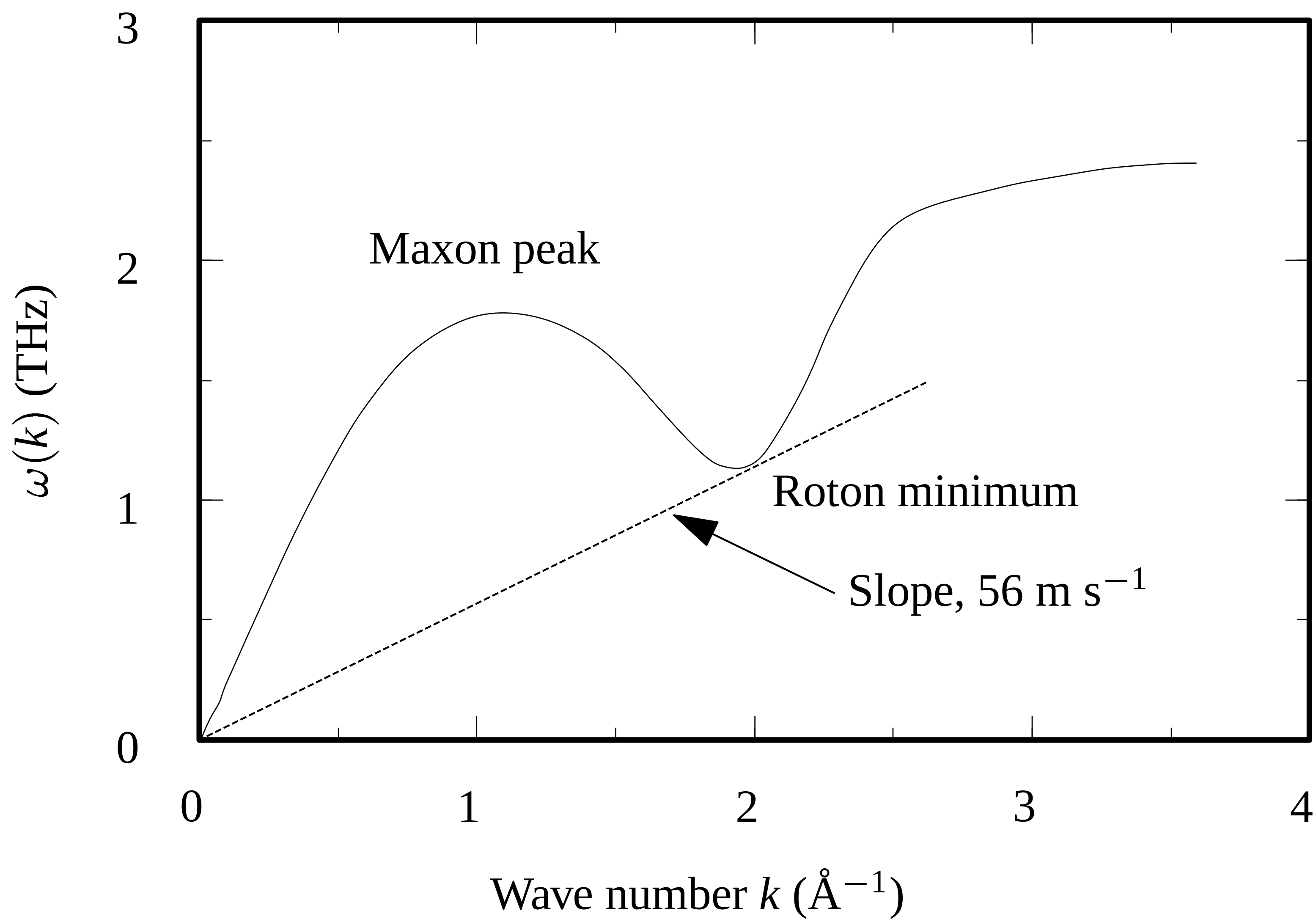


Figure 7: [Source: Donnelly (1991), p. 46.]

Origin of Superfluidity

$$\Psi(\vec{r}) = \int d^N\vec{r}\,\psi_N^*(\vec{r}_1\ldots\vec{r}_N)\psi_{N+1}(\vec{r}_1\ldots\vec{r}_N,\vec{r}) \tag{L93}$$

$$\hat{\mathcal{H}}_N = \sum_{l=1}^{N}\frac{\hat{P}_l^2}{2m} + U(\vec{r}_1\ldots\vec{r}_N) \tag{L94}$$

$$\frac{\partial\Psi}{\partial t} = \int d^N\vec{r}\,\frac{-i}{\hbar}\left\{\psi_{N+1}\hat{\mathcal{H}}_N\psi_N^* - \psi_N^*\mathcal{H}_{N+1}\psi_{N+1}\right\} \tag{L95}$$

$$= \int d^N\vec{r}\,\frac{-i}{\hbar}\psi_N^*\left\{\frac{-\hbar^2\nabla_{\vec{r}}^2}{2m} + U_{N+1}(\vec{r}_1\ldots\vec{r}_N,\vec{r}) - U_N(\vec{r}_1\ldots\vec{r}_N)\right\}\psi_{N+1}. \tag{L96}$$

$$\frac{-\hbar}{i}\frac{\partial\Psi}{\partial t} = \frac{-\hbar^2\nabla^2}{2m}\Psi + \mu\Psi. \tag{L97}$$

$$\Psi(\vec{r}) = \sqrt{n}e^{i\phi}. \tag{L98}$$

$$\frac{\partial n}{\partial t} = -\vec{\nabla} \cdot \frac{\hbar}{m} \vec{\nabla} \phi n, \quad \text{(L99)}$$

$$\vec{v}_s = \frac{\hbar}{m} \vec{\nabla} \phi \quad \text{(L100)}$$

$$\hbar \frac{\partial \phi}{\partial t} = -(\mu + m v_s^2/2) + \frac{\hbar^2}{2m} \frac{\nabla^2 \sqrt{n}}{\sqrt{n}}. \quad \text{(L101)}$$

$$m \frac{\partial \vec{v}_s}{\partial t} + m \vec{\nabla} \frac{v_s^2}{2} = -\vec{\nabla} \mu \quad \text{(L102)}$$

$$\Rightarrow \frac{\partial \vec{v}_s}{\partial t} + (\vec{v}_s \cdot \vec{\nabla}) \vec{v}_s = -\frac{\vec{\nabla} \mu}{m} \quad \text{(L103)}$$

$$\int_{\mathcal{C}} d\vec{s} \cdot \vec{v}_s = 2\pi l \hbar / m \quad \text{(L104)}$$

$$\Rightarrow \int_{\mathcal{A}} d^2 r \, \hat{z} \cdot \vec{\nabla} \times \vec{v}_s = \kappa = l \frac{h}{m}. \quad \text{(L105)}$$

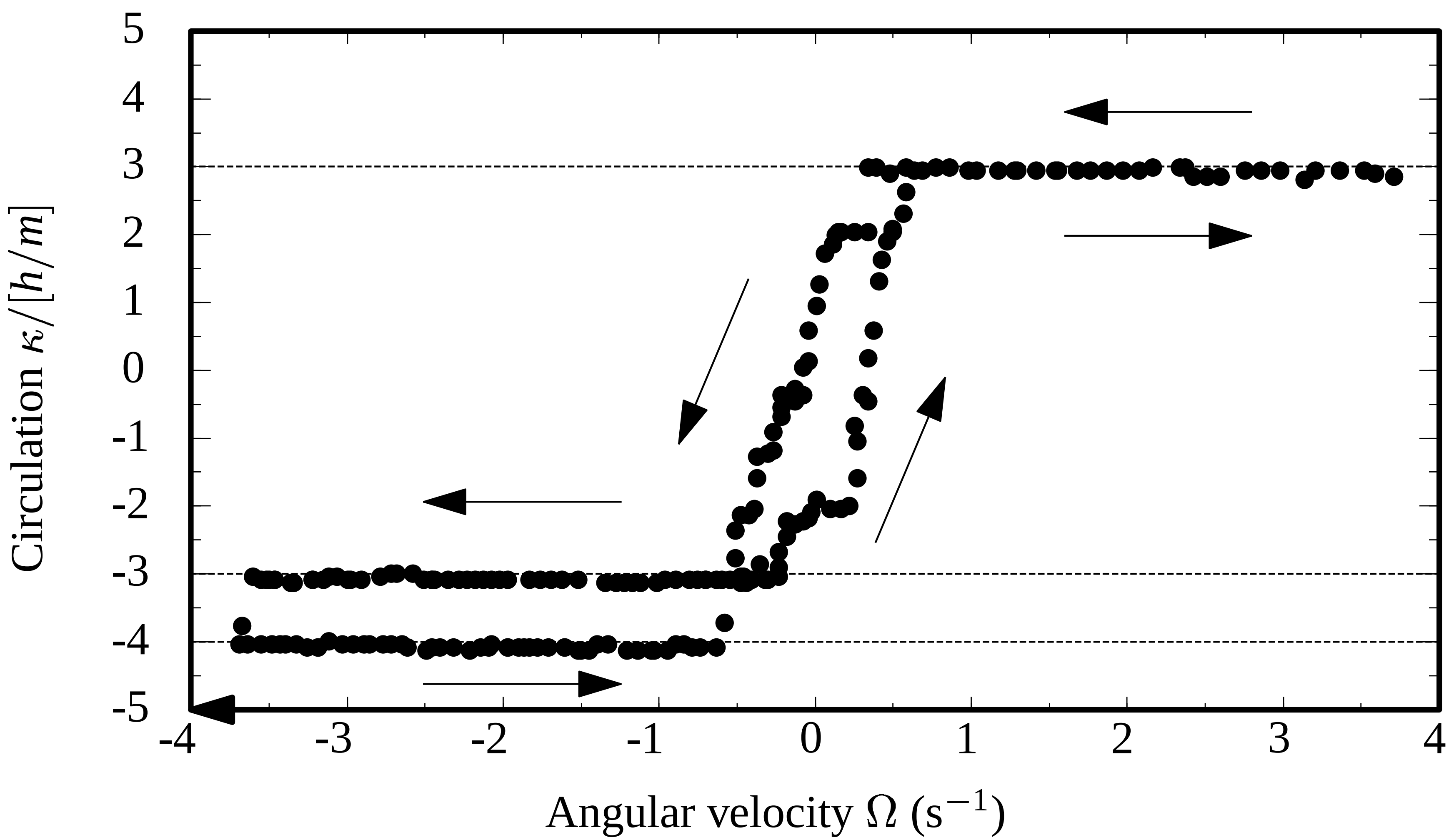


Figure 8: [Source, Karn et al. (1980), p. 1799.]

$$\mathcal{E}_v = \int d\vec{r}\, \tfrac{1}{2}\, \rho v^2(\vec{r}) = \tfrac{1}{2}\rho\kappa^2 R(\eta - \tfrac{3}{2}), \quad \eta = \ln(8R/a) \qquad \text{(L106)}$$

$$P_{\rm v} = \left| \int d\vec{r}\, \rho \vec{v}(\vec{r}) \right| = \rho\kappa\pi R^2 \tag{L107}$$

$$v_{\rm v} = \frac{\partial \mathcal{E}_{\rm v}}{\partial P_{\rm v}} = \frac{\kappa(\eta - \frac{1}{2})}{4\pi R}. \tag{L108}$$

$$\mathcal{E}_{\rm tot} = \mathcal{E}_{\rm v} - P_{\rm v} v_{\rm s} \tag{L109}$$

$$\frac{d\mathcal{E}_{\rm tot}}{dR} = 0 \Rightarrow \frac{\partial \mathcal{E}_{\rm v}}{\partial P_{\rm v}} \frac{\partial P_{\rm v}}{\partial R} - \frac{\partial P_{\rm v}}{\partial R} v_{\rm s} = 0 \quad \Rightarrow v_{\rm s} = v_{\rm v}. \tag{L110}$$

$$i\hbar\frac{\partial}{\partial t}\phi = \left[\sum_l -\frac{\hbar^2\nabla_l^2}{2m} + \hat{U}\right]\phi. \tag{L111}$$

$$\phi\nabla_l\phi^* - \phi^*\nabla_l\phi = 0. \tag{L112}$$

$$\psi(\vec{r}_1\ldots\vec{r}_N) = \exp[\sum_l \Psi(\vec{r}_l,t)]\,\phi(\vec{r}_1\ldots\vec{r}_N) = e^{\sum\Psi_l}\phi. \tag{L113}$$

$$N = 1/\sqrt{\int d^N\vec{r}|\psi|^2} \tag{L114}$$

$$\mathfrak{L} = \int d^N\vec{r}\,\phi^* e^{\sum_{l'}\Psi^*(\vec{r}_{l'})}\left[i\hbar\frac{\partial}{\partial t} + \sum_l \frac{\hbar^2\nabla_l^2}{2m} - \hat{U}\right] e^{\sum_{l''}\Psi(\vec{r}_{l''})}\phi. \tag{L115}$$

$$\int e^{\sum\Psi_{l'}^*}\phi^*\,\nabla_l^2\, e^{\sum\Psi_{l''}}\phi \tag{L116}$$

$$= \int e^{\sum \Psi^*_{l'}} \phi^* \left[\phi \nabla_l^2 e^{\sum \Psi_{l''}} + 2 \vec{(} \nabla_l e^{\sum \Psi_{l''}}) \cdot (\vec{\nabla}_l \phi) + e^{\sum \Psi_{l''}} \nabla_l^2 \phi \right] \quad \text{(L117)}$$

$$= \int e^{\sum \Psi^*_{l'}} \left[|\phi|^2 \nabla_l^2 e^{\sum \Psi_{l''}} + (\vec{\nabla}_l e^{\sum \Psi_{l''}}) \cdot (\vec{\nabla}_l |\phi|^2) + e^{\sum \Psi_{l''}} \phi^* \nabla_l^2 \phi \right] \quad \text{(L118)}$$

$$= \int e^{\sum \Psi^*_{l'}} |\phi|^2 \nabla_l^2 e^{\sum \Psi_{l'}} - |\phi|^2 \vec{\nabla}_l \cdot e^{\sum \Psi^*_{l'}} (\vec{\nabla}_l e^{\sum \Psi_{l''}}) + e^{\sum \Psi^*_{l'} + \Psi_{l'}} \phi^* \nabla_l^2 \phi \quad \text{(L119)}$$

$$= \int e^{\sum \Psi^*_{l'} + \Psi_{l'}} \left[\phi^* \nabla_l^2 \phi - |\phi|^2 |\nabla_l \Psi_l|^2 \right]. \quad \text{(L120)}$$

$$\mathfrak{L} = \int d^N \vec{r} \, |\phi|^2 e^{\sum_{l'} \Psi^*_{l'} + \Psi_{l'}} \sum_l \left[i\hbar \frac{\partial \Psi_l}{\partial t} - \frac{\hbar^2}{2m} |\vec{\nabla}_l \Psi_l|^2 \right]. \quad \text{(L121)}$$

$$\frac{\delta}{\delta \Psi^*} \left[\mathfrak{L} - \mu \int d^N \vec{r} \, |\phi^2| e^{\sum_{l'} \Psi^*_{l'} + \Psi_{l'}} \right] = 0. \quad \text{(L122)}$$

Lagrangian Theory of Wave Function

$$n_1(\vec{r}) = \int d^N\vec{r}\,|\phi|^2 e^{\sum_{l'}\Psi^*_{l'}+\Psi_{l'}} \sum_l \delta(\vec{r}-\vec{r}_l) \quad \text{(L123)}$$

$$S(\vec{r},\vec{r}') = \frac{\mathcal{V}}{N}\int d^N\vec{r}\,|\phi|^2 e^{\sum_{l'}\Psi^*_{l'}+\Psi_{l'}} \sum_{ll'} \delta(\vec{r}-\vec{r}_l)\delta(\vec{r}'-\vec{r}_{l'}). \quad \text{(L124)}$$

$$-\frac{\hbar^2}{2m}\vec{\nabla}\cdot n_1\vec{\nabla}\Psi(\vec{r}) = \sum_{ll'}\int d^N\vec{r}|\psi|^2\delta(\vec{r}_{l'}-\vec{r})\left[i\hbar\frac{\partial\Psi_l}{\partial t} - \frac{\hbar^2}{2m}|\nabla\Psi_l|^2 - \mu\right] \quad \text{(L125)}$$

$$= \frac{N}{\mathcal{V}}\int d\vec{r}'\left[i\hbar\frac{\partial\Psi(\vec{r}')}{\partial t} - \frac{\hbar^2}{2m}|\nabla\Psi(\vec{r}')|^2 - \mu\right]S(\vec{r},\vec{r}'). \quad \text{(L126)}$$

$$\frac{\hbar^2k^2}{2m}\Psi(\vec{q},\omega) = [\hbar\omega\Psi(\vec{q},\omega) - \mu\delta(\vec{q})\delta(\omega)]S(\vec{q}) \quad \text{(L127)}$$

$$\Rightarrow \hbar\omega(\vec{q}) = \frac{\hbar^2q^2}{2mS(\vec{q})} = \frac{6.02k_B[q\cdot\text{Å}]^2}{S(q)}\text{K}, \quad \text{(L128)}$$

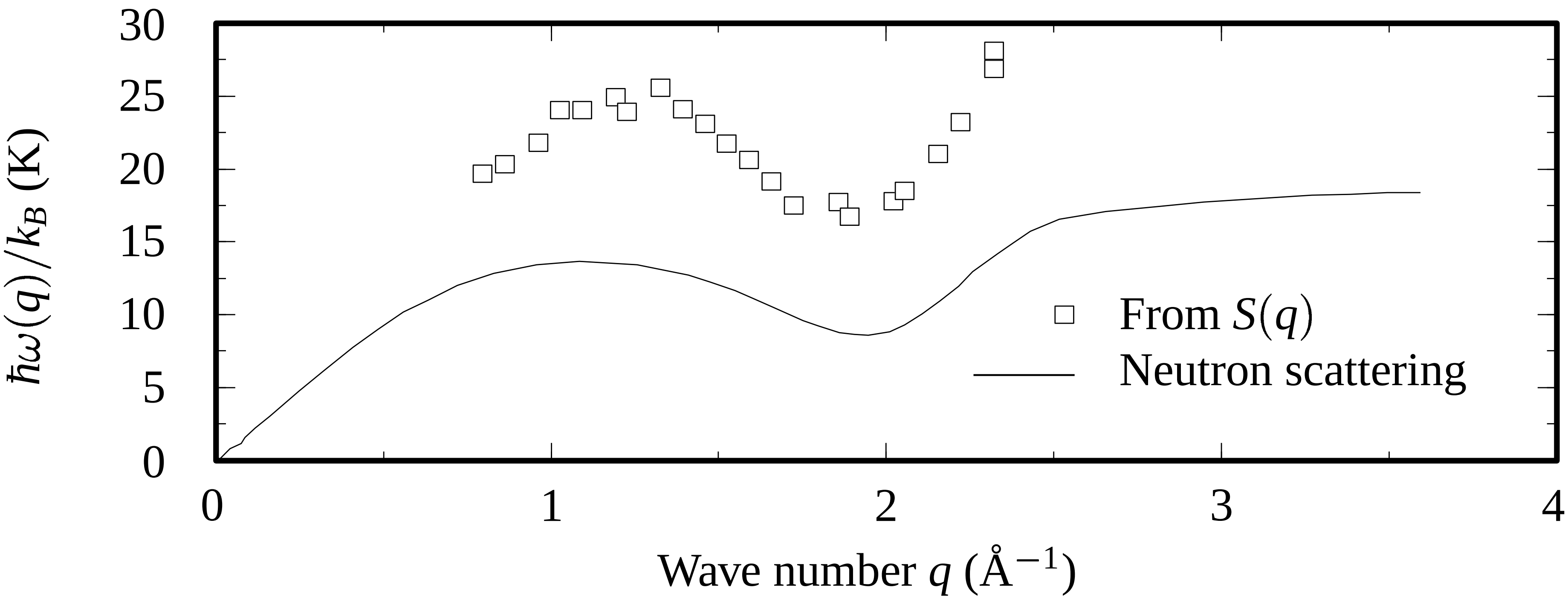
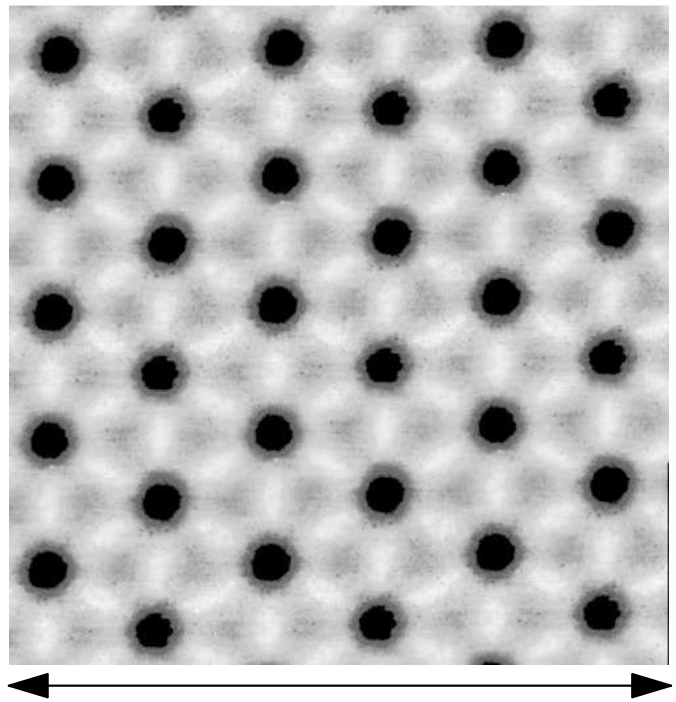


Figure 9: The neutron scattering data are from Donnelly (1991) p. 46, and data for $S(q)$ are from Svensson et al. (1980).

Need something....



(B)

Definitions

- Perfect Diamagnetism
- Landau–Ginzburg Equations
- Type I and Type II Superconductors
- Flux Quantization
- Josephson Effect
- Superconducting Quantum Interference Devices (SQUIDS)
- Isotope Effect and Fröhlich Hamiltonian
- Cooper Problem
- Bardeen Cooper Schrieffer (BCS) Theory
- Bogoliubov Theory
- High-Temperature Superconductors

Idea of Superconductivity

Expulsion of magnetic fields, not infinite conductivity, is the key.

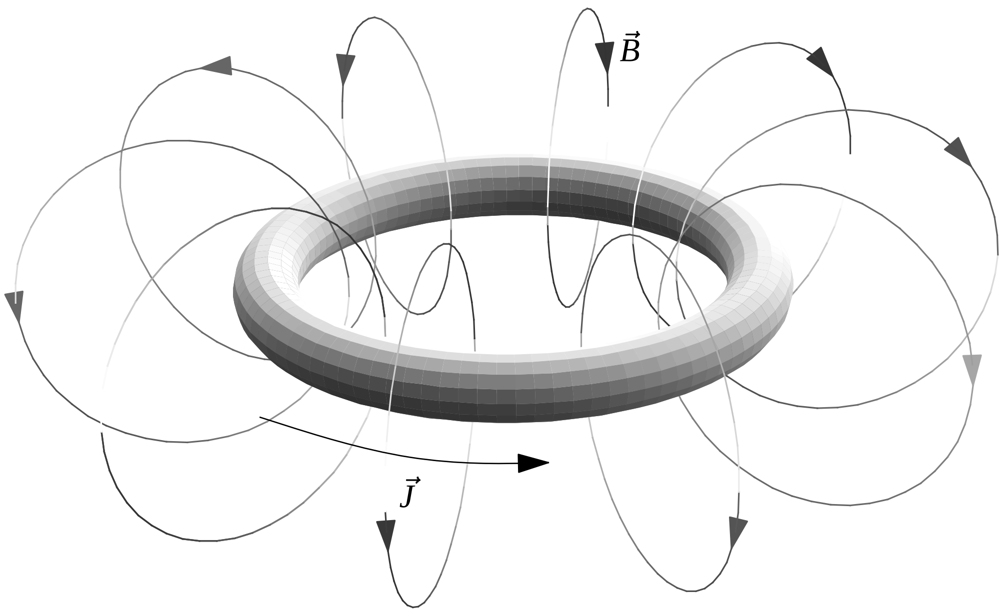


Figure 1: Flux threading a current loop

Wave function is rigid

$$m\dot{\vec{v}} = -e\vec{E} \tag{L1}$$

$$\Rightarrow \frac{\partial \vec{j}}{\partial t} = \frac{ne^2}{m}\vec{E} \tag{L2}$$

$$\Rightarrow \frac{\partial}{\partial t}\vec{\nabla}\times\vec{\nabla}\times\frac{\vec{B}}{\mu} = \frac{4\pi ne^2}{mc}\vec{\nabla}\times\vec{E} \tag{L3}$$

$$\Rightarrow \vec{\nabla}\times\vec{\nabla}\times\frac{\vec{B}}{\mu} = -\frac{4\pi ne^2}{mc^2}(\vec{B}-\vec{B}_0). \tag{L4}$$

$$\vec{B}+\lambda_L^2\vec{\nabla}\times\vec{\nabla}\times\vec{B}=0 \tag{L5}$$

$$\lambda_L=\sqrt{\frac{mc^2}{4\pi\mu ne^2}}. \tag{L6}$$

$$\vec{B}+\lambda_L^2\left(\vec{\nabla}(\vec{\nabla}\cdot\vec{B})-\nabla^2\vec{B}\right)=0. \tag{L7}$$

$$B_z=0. \tag{L8}$$

$$B_x=\lambda_L^2\frac{\partial^2 B_x}{\partial z^2}\ \Rightarrow\ B_x\propto e^{-z/\lambda_L}. \tag{L9}$$

Phenomenological Free Energy

$$\mathfrak{F} = \int d\vec{r}d\vec{r}' \sum_{\alpha\beta} \tfrac{1}{2}A_\alpha(\vec{r})G_{\alpha\beta}(\vec{r}-\vec{r}')A_\beta(\vec{r}') + \delta(\vec{r}-\vec{r}')\frac{1}{8\pi}\vec{B}(\vec{r})\cdot\vec{B}(\vec{r}'). \qquad \text{(L10)}$$

$$[\vec{\nabla}\times\vec{\nabla}\times\frac{\vec{A}(\vec{r})}{4\pi}]_\alpha = -\int d\vec{r}' \sum_\beta G_{\alpha\beta}(\vec{r}-\vec{r}')A_\beta(\vec{r}') \qquad \text{(L11)}$$

$$\Rightarrow j_\alpha(\vec{r}) = \frac{c}{4\pi}[\vec{\nabla}\times\vec{B}]_\alpha = -c\int d\vec{r}' \sum_\beta G_{\alpha\beta}(\vec{r}-\vec{r}')A_\beta(\vec{r}'). \qquad \text{(L12)}$$

$$\sum_\beta \left\{ G_{\alpha\beta}(\vec{k}) + \frac{1}{4\pi}(k^2\delta_{\alpha\beta} - k_\alpha k_\beta) \right\} A_\beta = 0. \qquad \text{(L13)}$$

$$G_{\alpha\beta} \rightarrow \left(\frac{1}{\mu} - 1\right)\frac{1}{4\pi}\left[k^2\delta_{\alpha\beta} - k_\alpha k_\beta\right]. \qquad \text{(L14)}$$

$$\frac{1/\mu - 1}{8\pi} \int d\vec{r} d\vec{r}' \, \delta(\vec{r} - \vec{r}')\vec{A} \cdot \vec{\nabla} \times \vec{\nabla} \times \vec{A} \tag{L15}$$

$$= \quad \frac{1/\mu - 1}{8\pi} \int d\vec{r} \, B(\vec{r})^2. \tag{L16}$$

$$\mathfrak{F} = \frac{1}{8\pi\mu} \int d\vec{r} \, B^2(\vec{r}), \tag{L17}$$

$$\lim_{k\to 0} G_{\alpha\beta} = \frac{1}{4\pi\lambda_L^2} \delta_{\alpha\beta}. \tag{L18}$$

$$\frac{1}{8\pi} \int d\vec{r} \, \frac{1}{\lambda_L^2} A^2(\vec{r}) + |\vec{\nabla} \times \vec{A}|^2, \tag{L19}$$

$$\frac{1}{\lambda_L^2} \vec{A} + \vec{\nabla} \times \vec{\nabla} \times \vec{A} = 0. \tag{L20}$$

$$\vec{B} + \lambda_L^2 \, \vec{\nabla} \times \vec{\nabla} \times \vec{B} = 0, \tag{L21}$$

$$\mathfrak{F} = \mathfrak{F}_{\text{normal}} + \frac{1}{8\pi\mu} B_c^2. \tag{L22}$$

$$\tilde{\mathfrak{G}} \quad = \quad \mathfrak{F} - \vec{B} \cdot \frac{\delta \mathfrak{F}}{\delta \vec{B}} = \mathfrak{F}_{\text{normal}} - \frac{1}{8\pi\mu} B_c^2. \tag{L23}$$

$$\Delta \mathfrak{F} \equiv \mathfrak{F}_{\text{normal}} - \mathfrak{F}_{\text{superconducting}} = \frac{B_c^2}{8\pi\mu}. \tag{L24}$$

$$\Delta \mathfrak{F} = \frac{H_c^2}{8\pi}. \tag{L25}$$

$$\Delta S = \frac{\partial}{\partial T} \Delta \mathfrak{F} = \frac{H_c}{4\pi} \frac{\partial H_c}{\partial T}. \tag{L26}$$

Landau–Ginzburg Free Energy

$$\mathcal{F} = \int \frac{d\vec{r}}{\mathcal{V}} \alpha|\Psi|^2 + \frac{\beta}{2}|\Psi^4| + \frac{1}{8\pi}B^2 + \frac{1}{2m^\star}\left|\left[\frac{\hbar}{i}\vec{\nabla} + \frac{2e}{c}\vec{A}(\vec{r})\right]\Psi(\vec{r})\right|^2. \tag{L27}$$

$$\vec{\nabla} \times \vec{B} = \frac{4\pi}{c}\vec{j}, \tag{L28}$$

$$\vec{j}(\vec{r}) = -\frac{2e\hbar}{2im^\star}[\Psi^*\vec{\nabla}\Psi - \Psi\vec{\nabla}\Psi^*] - \frac{4e^2}{m^\star c}\vec{A}\Psi^*\Psi. \tag{L29a}$$

Minimizing with respect to Ψ^* leads to

$$0 = \left[\alpha + \beta|\Psi|^2 + \frac{1}{2m^\star}\left(\frac{\hbar}{i}\vec{\nabla} + \frac{2e}{c}\vec{A}\right)^2\right]\Psi. \tag{L29b}$$

$$\hat{n}\cdot\left(\frac{\hbar}{i}\vec{\nabla} + \frac{2e}{c}\vec{A}\right)\Psi = 0. \tag{L30}$$

Compare the following lengths:

$$\xi^2 = \frac{\hbar^2}{2m^\star|\alpha|}. \tag{L31}$$

$$\lambda_L^2 = \frac{m^\star c^2 \beta}{4\pi|\alpha|(2e)^2}. \tag{L32}$$

Compound	T_c (K)	H_c (G)	ξ (Å)	λ_L (Å)
Al	1.18	105	13 000–16 000	160–500
Ba (P =20 GPa)	5.3			
Bi (P =8 GPa)	8.55			
Ce (P =5 GPa)	1.7			
Ga	1.09	58.9		
Hg	3.95	340		380–450
Ir	0.10	20.1		
Lu	0.1			
Mo	0.92	98		
P (P =17 GPa)	5.8			
Pb	7.20	803	510–960	390–630
Si (P =12 GPa)	7.1			
Sn	3.7	308	1 000–3 000	340–750
Te (P = 8 GPa)	4.3			
Th	1.37	162		
Ti	0.42	56		
Tl	2.4	180	4200	
U	1.8			
W	0.02	1.07		
Zn	0.85	52		
Zr	0.53	47		
Nb_3Sn	18.5	28	34	1 600
$YBa_2Cu_3O_{7-x}$	92	500	4–8	900–8 000
$HgBa_2Ca_2Cu_3O_y$	135			

$$|\Psi|^2 = \begin{cases} \Psi_0^2 \equiv -\dfrac{\alpha}{\beta} & \text{or} \\ 0. & \end{cases} \tag{L33}$$

$$\frac{\mathcal{F}}{\mathcal{V}} = -\frac{\alpha^2}{2\beta} \tag{L34}$$

$$H_c^2 = \frac{4\pi\alpha^2}{\beta}. \tag{L35}$$

$$\psi = \frac{\Psi}{\Psi_0}, \tag{L36}$$

$$-\xi^2\nabla^2\psi - \psi + \psi|\psi|^2 = 0, \tag{L37}$$

$$-\xi^2\psi'' - \psi + \psi^3 = 0. \tag{L38}$$

$$-\xi^2(\psi')^2 - \psi^2 + \frac{1}{2}\psi^4 = \text{ Const.} \tag{L39}$$

$$\psi' = \frac{1}{\sqrt{2}\xi}(1-\psi^2) \tag{L40}$$

$$\psi = \tanh\frac{x}{\sqrt{2}\xi}. \tag{L41}$$

$$\vec{j} = \frac{c}{4\pi}\vec{\nabla}\times\vec{B} = -\frac{4e^2}{m^\star c}\Psi_0^2\vec{A}. \tag{L42}$$

$$\vec{\nabla}\times\vec{\nabla}\times\vec{B} = -\frac{4\pi}{c}\frac{4e^2}{m^\star c}\Psi_0^2\vec{B} = -\lambda_L^{-2}\vec{B}. \tag{L43}$$

$$\kappa = \lambda_L/\xi = \frac{m^\star c}{e\hbar}\sqrt{\frac{\beta}{8\pi}} \tag{L44}$$

$$\vec{a} = \frac{4e\vec{A}}{c\sqrt{2m^\star|\alpha|}} \tag{L45}$$

$$\psi - \psi|\psi|^2 - (-i\vec{\nabla} + \vec{a}/2)^2\psi = 0 \tag{L46}$$

$$\frac{\lambda_L^2}{\xi^2}\vec{\nabla}\times\vec{\nabla}\times\vec{a} = -\frac{1}{i}(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*) - |\psi|^2\vec{a}. \tag{L47}$$

$$\frac{1}{2m^\star}(-i\hbar\vec{\nabla} + \frac{2e\vec{A}}{c})^2\Psi = -\alpha\Psi. \tag{L48}$$

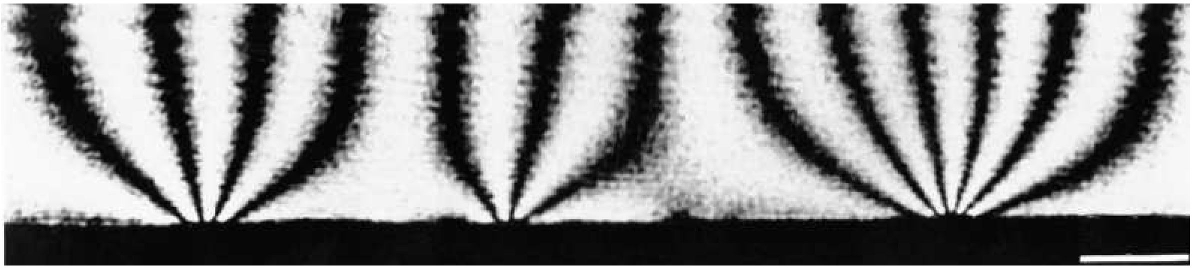
$$\omega_c = \frac{2eH_{c_2}}{m^\star c}, \tag{L49}$$

$$-\alpha = |\alpha| = \frac{e\hbar H_{c_2}}{m^\star c}. \tag{L50}$$

$$\frac{H_{c_2}}{H_c} = \sqrt{2}\kappa. \tag{L51}$$

$$\frac{\tilde{\mathcal{G}}}{A} = \frac{H_c^2}{4\pi}\sqrt{2}\xi\frac{2}{3}, \tag{L52}$$

$$\frac{\tilde{\mathcal{G}}}{A} = -\frac{H_c^2}{8\pi}\lambda_L; \tag{L53}$$



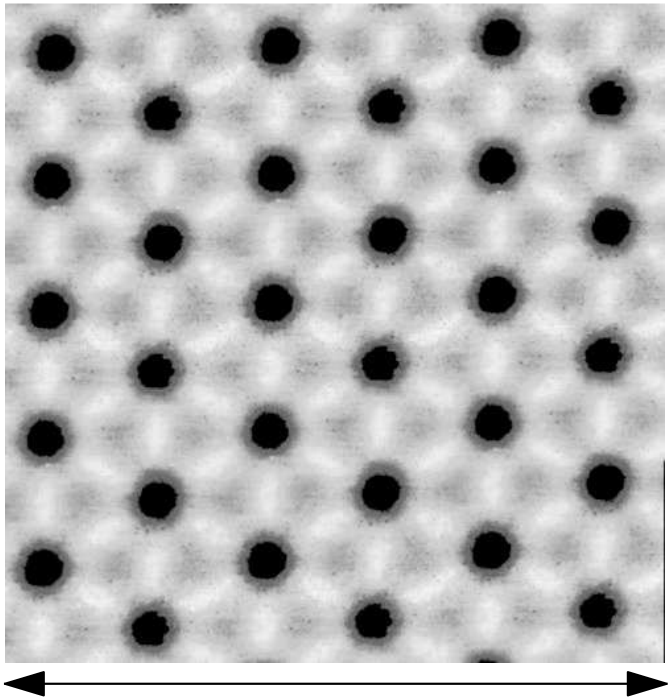


Figure 2: A Type II superconductor is unstable to the formation of flux tubes (A) Magnetic flux entering a lead film [Tonomura et al. (1986)] (B) Top view of an Abrikosov lattice of flux tubes in $NbSe_2$ [S. Pan and A. de Lozanne]

Flux Quantization

$$\vec{j} = -\frac{e^\star \hbar}{2im^\star}[\Psi^*\vec{\nabla}\Psi - \Psi\vec{\nabla}\Psi^*] - \frac{e^{\star 2}}{m^\star c}\vec{A}\Psi^*\Psi. \tag{L54}$$

$$\Psi(\vec{r}) = \Psi_0 e^{i\phi(\vec{r})} \tag{L55}$$

$$\vec{j} = -\frac{\Psi_0^2}{m^\star}\left(\frac{e^{\star 2}}{c}\vec{A} + e^\star\hbar\vec{\nabla}\phi\right) \tag{L56}$$

$$\Rightarrow -\vec{\nabla}\phi = \frac{1}{\hbar}\left(\frac{m^\star}{e^\star\Psi_0^2}\vec{j} + \frac{e^\star}{c}\vec{A}\right). \tag{L57}$$

$$-\int d\vec{s}\cdot\vec{\nabla}\phi = 2\pi l. \tag{L58}$$

$$\int d\vec{s}\cdot\frac{1}{\hbar}\left[\frac{m^\star}{e^\star\Psi_0^2}\vec{j} + \frac{e^\star}{c}\vec{A}\right] = 2\pi l. \tag{L59}$$

$$\frac{e^\star}{c\hbar}\int d\vec{s}\cdot\vec{A} = 2\pi l \quad \text{(L60)}$$

$$\Rightarrow \int d^2r\,B_z = \Phi = \frac{2\pi l\hbar c}{e^\star} = l\frac{e}{e^\star}\Phi_0. \quad \text{(L61)}$$

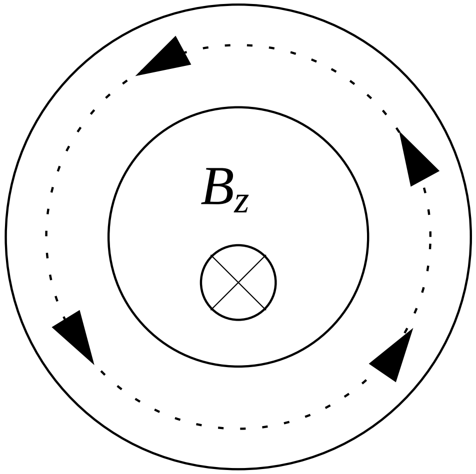


Figure 3: Magnetic flux that pierces a superconducting ring is quantized in units of $\Phi_0/2$.

Flux Quantization

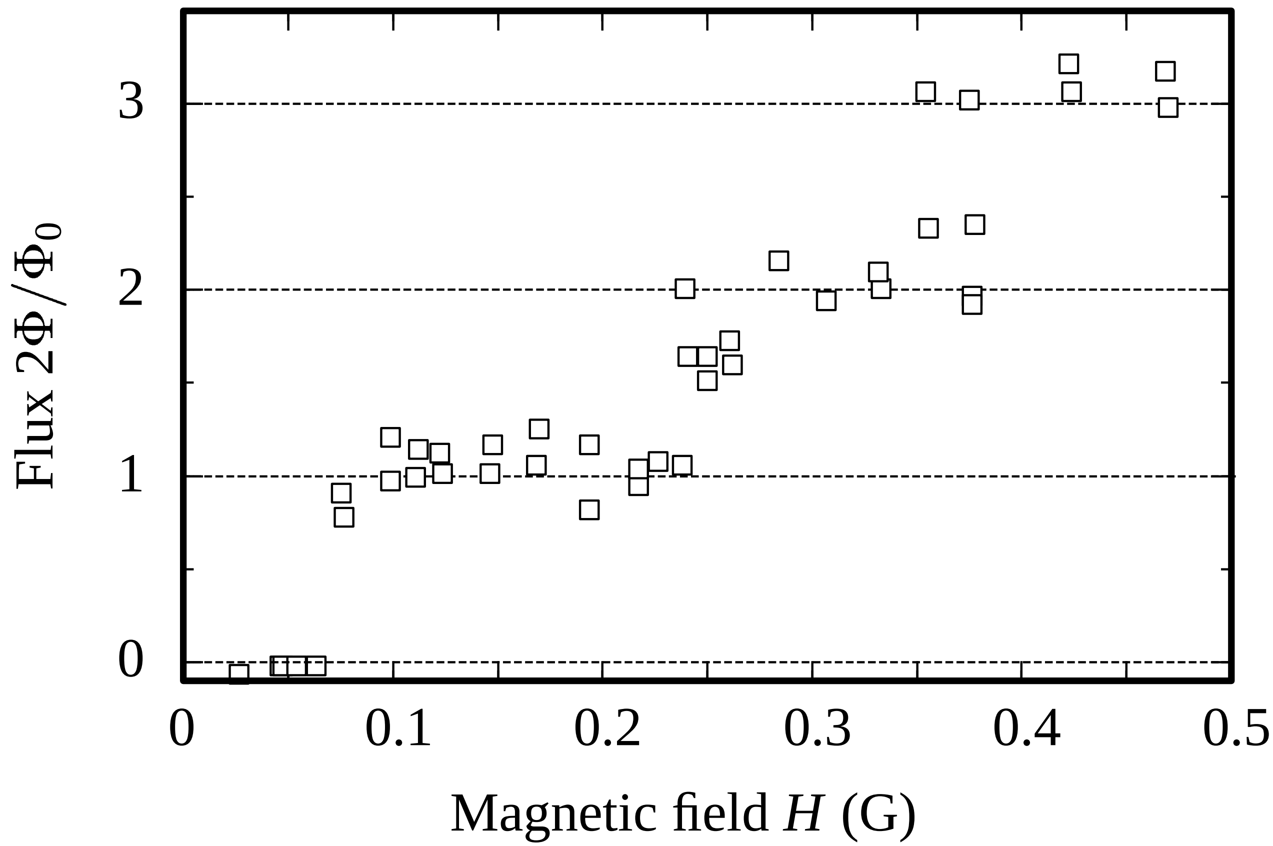


Figure 4: Trapped magnetic flux in a superconducting cylinder as a function of applied field. [Deaver and Fairbank (1961)]

$$\int d\vec{r}\, U(\vec{r}) \left(\Psi_1^*(\vec{r}) \Psi_2(\vec{r}) + \Psi_1(\vec{r}) \Psi_2^*(\vec{r}) \right) \tag{L62}$$

$$= \quad \epsilon \left(\Psi_1^* \Psi_2 + \Psi_1 \Psi_2^* \right), \tag{L63}$$

$$\frac{\partial \Psi_1}{\partial t} = \frac{-i}{\hbar} \left[\mathcal{E}_1 \Psi_1 + \epsilon \Psi_2 \right] \tag{L64a}$$

$$\frac{\partial \Psi_2}{\partial t} = \frac{-i}{\hbar} \left[\mathcal{E}_2 \Psi_2 + \epsilon \Psi_1 \right]. \tag{L64b}$$

$$\Psi_l = \sqrt{n_l} e^{i\phi_l} \tag{L65}$$

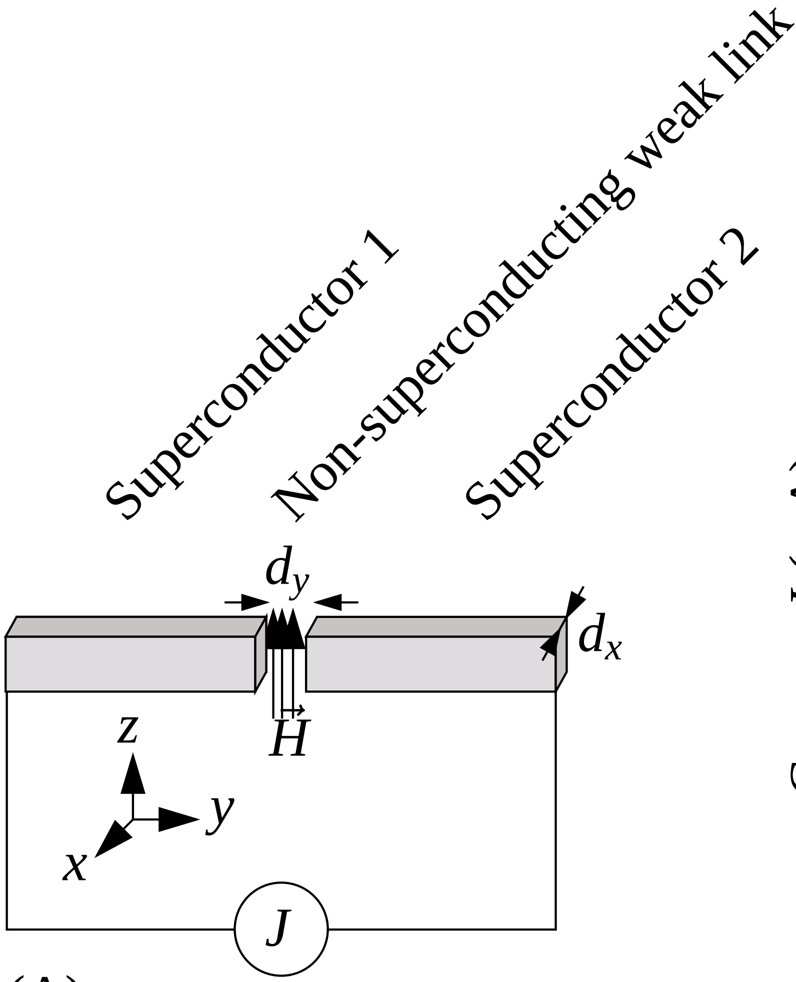
$$\left(\tfrac{1}{2} \frac{\dot{n}_1}{\sqrt{n_1}} + i \sqrt{n_1} \dot{\phi}_1 \right) e^{i\phi_1} = \frac{-i}{\hbar} \left[\mathcal{E}_1 \sqrt{n_1} e^{i\phi_1} + \epsilon \sqrt{n_2} e^{i\phi_2} \right]. \tag{L66}$$

$$\dot{n}_1 = 2 \frac{\epsilon n}{\hbar} \sin\left(\phi_2 - \phi_1 \right) = -\dot{n}_2 = \frac{j}{2e} \tag{L67a}$$

$$\dot{\phi}_2 - \dot{\phi}_1 = \frac{1}{\hbar}(\mathcal{E}_1 - \mathcal{E}_2) = 2e(V_2 - V_1)/\hbar. \qquad \text{(L67b)}$$

$$\vec{j} = \vec{j}_0 \sin(\phi_2 - \phi_1 + \frac{2e}{\hbar c}\int_1^2 d\vec{s}\cdot\vec{A}) \qquad \text{(L68a)}$$

$$\frac{-1}{\hbar}(\mathcal{E}_2 - \mathcal{E}_1) = 2eV/\hbar = \frac{\partial}{\partial t}\left(\phi_2 - \phi_1 + \frac{2e}{\hbar c}\int_1^2 d\vec{s}\cdot\vec{A}\right). \qquad \text{(L68b)}$$



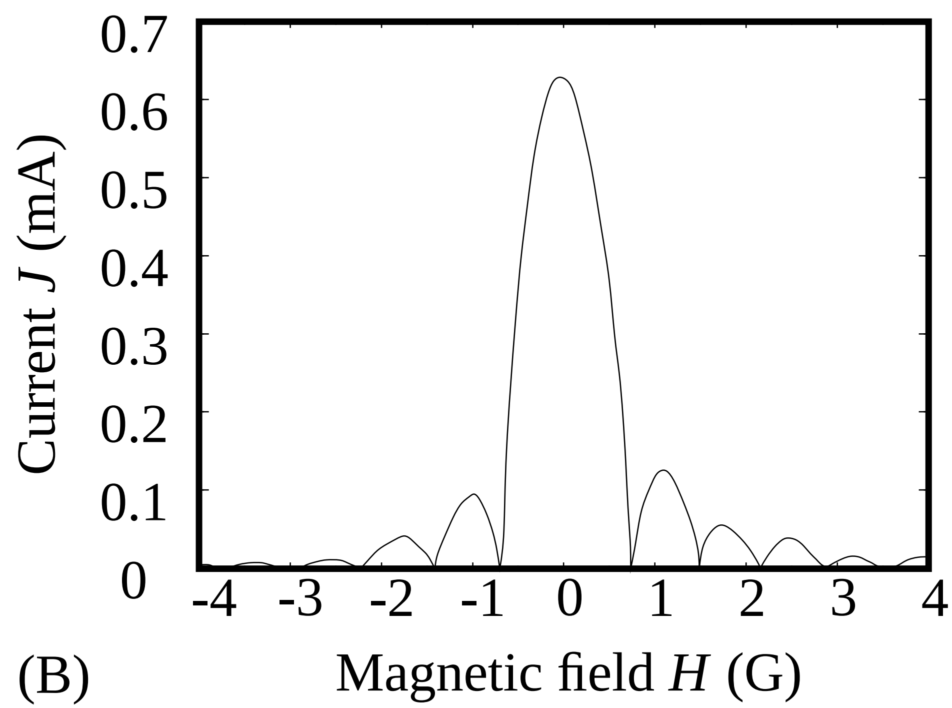


Figure 5: (A) Setting for Fraunhofer diffraction in a Josephson junction. (B) Measurement of J_c in an Sn–SnO–Sn junction at $T = 1.9$ K. [R. C Jaklevic, 1969]

$$\frac{V}{R} + J_0 \sin\phi + C\dot{V} = J, \tag{L69}$$

$$\dot{\phi} = 2eV/\hbar, \tag{L70}$$

$$J = \frac{\dot{\phi}\hbar}{2eR} + J_0 \sin\phi + \frac{C\hbar}{2e}\ddot{\phi} \tag{L71}$$

$$\Rightarrow \frac{\hbar C}{2e}\ddot{\phi} + \frac{\hbar}{2eR}\dot{\phi} = -\frac{\partial}{\partial\phi}\left[-\phi J - J_0 \cos\phi\right]. \tag{L72}$$

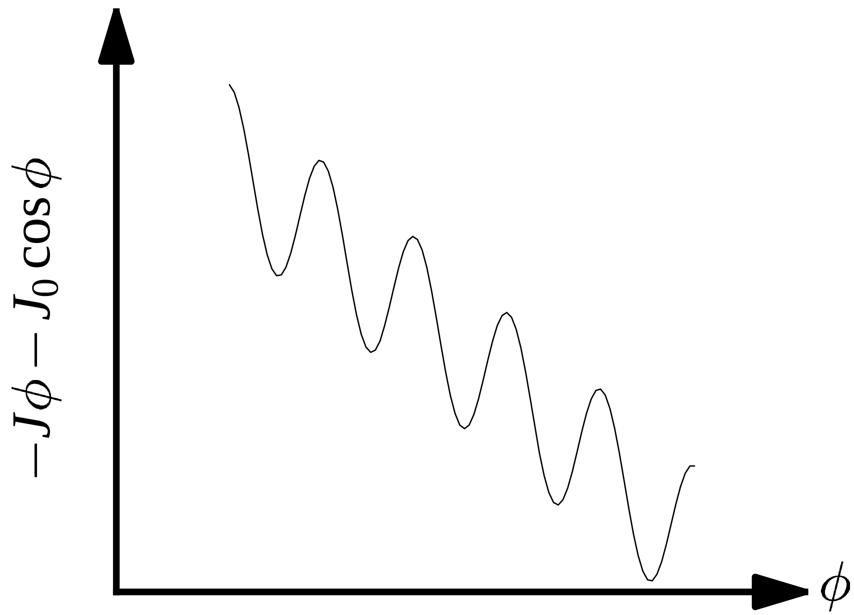


Figure 6: The washboard potential in Eq. (L72).

$$t_0 = \frac{\hbar}{2eJ_0R}, \tag{L73}$$

$$\beta\ddot{\phi} + \dot{\phi} = -\frac{\partial}{\partial\phi}\left[-\phi\frac{J}{J_0} - \cos\phi\right], \tag{L74}$$

$$\beta = \frac{J_0R^2C2e}{\hbar}. \tag{L75}$$

$$\oint d\vec{s}\cdot\vec{A} = \Phi = \int_4^1 d\vec{s}\cdot\vec{A} - \frac{\Phi_0}{4\pi}\int_1^2 d\vec{s}\cdot\vec{\nabla}\phi + \int_2^3 d\vec{s}\cdot\vec{A} - \frac{\Phi_0}{4\pi}\int_3^4 d\vec{s}\cdot\vec{\nabla}\phi \qquad \text{(L76)}$$

$$\Rightarrow \Phi = \frac{\Phi_0}{4\pi}\left(\gamma_{23} - \gamma_{14}\right), \qquad \text{(L77)}$$

where

$$\gamma_{14} = \phi_4 - \phi_1 + \frac{4\pi}{\Phi_0}\int_1^4 d\vec{s}\cdot\vec{A}. \qquad \text{(L78)}$$

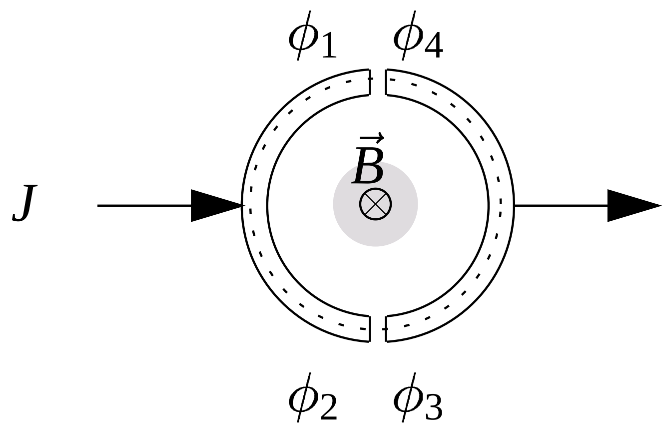


Figure 7: DC SQUID.

$$
\begin{aligned}
J &= J_0 \sin(\gamma_{14}) + J_0 \sin(\gamma_{23}) && \text{(L79)} \\
&= J_0 \Big[\sin(\gamma_{23} - 4\pi\Phi/\Phi_0) + \sin(\gamma_{23}) \Big]. && \text{(L80)}
\end{aligned}
$$

Origin of Josephson's Equations

$$\vec{j} = -\frac{|\Psi_0|^2 8\pi e\hbar}{m^\star \Phi_0}\left[\frac{\Phi_0}{4\pi}\vec{\nabla}\phi + \vec{A}\right]. \tag{L81}$$

$$L = \int d\vec{r}dt\,\mathcal{L} = \int d\vec{r}dt\left\{\frac{E^2 - B^2}{8\pi} - G(\vec{A} + \vec{\nabla}\chi, V - \dot{\chi}/c)\right\}. \tag{L82}$$

$$\vec{E} = -\vec{\nabla}V - \frac{1}{c}\frac{\partial\vec{A}}{\partial t}, \quad \text{and} \quad \vec{B} = \vec{\nabla}\times\vec{A}. \tag{L83}$$

$$\frac{\delta L}{\delta V} = 0 \Rightarrow \frac{\partial G}{\partial V} = -ne \tag{L84a}$$

$$\frac{\delta L}{\delta \vec{A}} = 0 \Rightarrow \frac{\partial G}{\partial \vec{A}} = -\frac{\vec{j}}{c}. \tag{L84b}$$

$$\frac{\delta L}{\delta \chi} = 0 \Rightarrow \vec{\nabla}\cdot\frac{\partial G}{\partial \vec{A}} - \frac{\partial}{\partial t}\frac{1}{c}\frac{\partial G}{\partial V} = 0 \tag{L85}$$

$$\Rightarrow \frac{\partial}{\partial t}[-ne] = -\vec{\nabla}\cdot\vec{j}. \tag{L86}$$

Origin of Josephson's Equations

$$\mathcal{H} = \dot{\vec{A}} \cdot \frac{\partial \mathcal{L}}{\partial \dot{\vec{A}}} + \dot{\chi} \frac{\partial \mathcal{L}}{\partial \dot{\chi}} - \mathcal{L}. \tag{L87}$$

$$\frac{\partial \mathcal{L}}{\partial \dot{\chi}} = -\frac{ne}{c}. \tag{L88}$$

$$\frac{\partial \mathcal{H}}{\partial \chi} = \frac{\dot{n}e}{c} \tag{L89a}$$

$$\frac{\partial \mathcal{H}}{\partial [-ne/c]} = \dot{\chi}. \tag{L89b}$$

$$\dot{\chi} = -\frac{c\mu}{e} \quad \Rightarrow \dot{\phi} = -\frac{2\mu}{\hbar} = \frac{2eV}{\hbar}. \tag{L90}$$

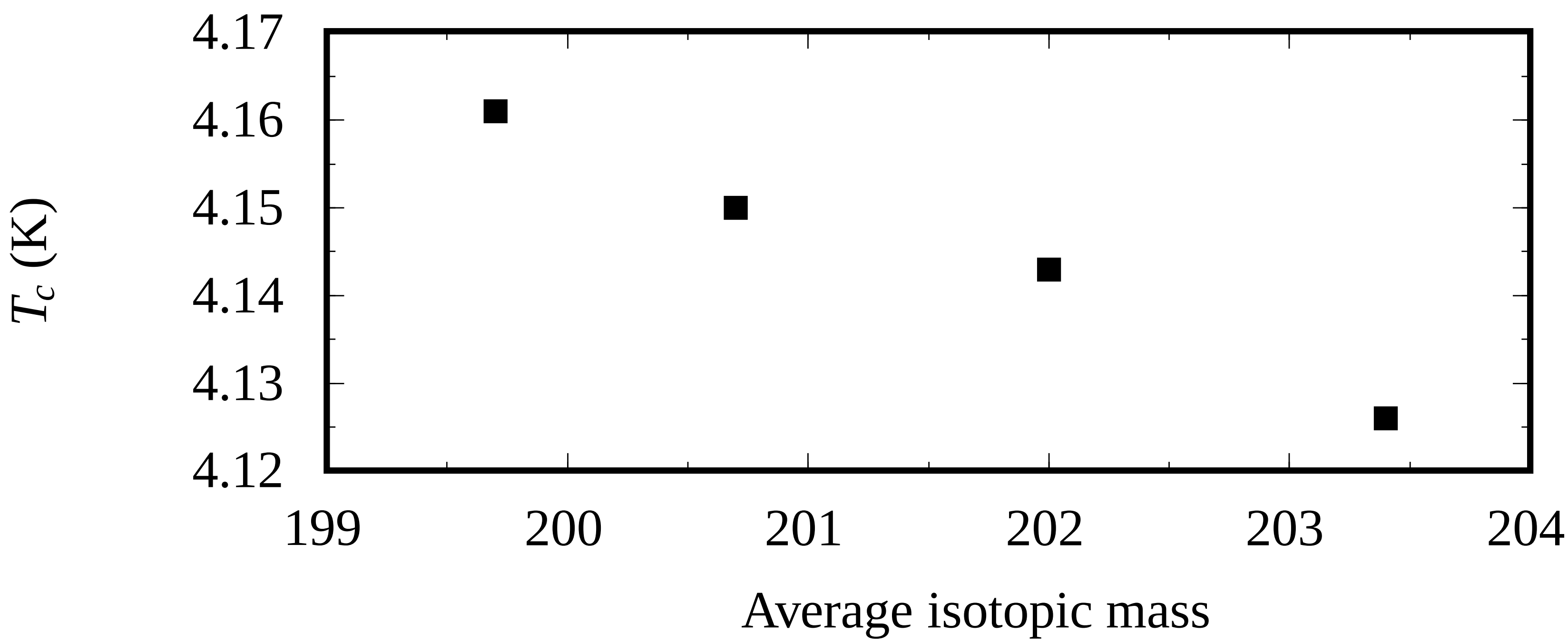


Figure 8: Superconducting transition temperature T_c versus average isotopic mass in four samples of mercury. [Reynolds et al. (1950).]

$$\sigma_{\text{el}} = \frac{i\omega\chi_{\text{c}}}{q^2}. \tag{L91}$$

$$\chi_{\text{c}} = -\frac{me^2}{\pi^2\hbar^2}\frac{(4k_F^2 - q^2)\log\left(\frac{q+2k_F}{2k_F-q}\right) + 4k_F q}{8q} \tag{L92}$$

$$\chi_{\text{c}} = -\frac{me^2 k_F}{\pi^2\hbar^2} \equiv -\frac{\kappa_{\text{c}}^2}{4\pi}. \tag{L93}$$

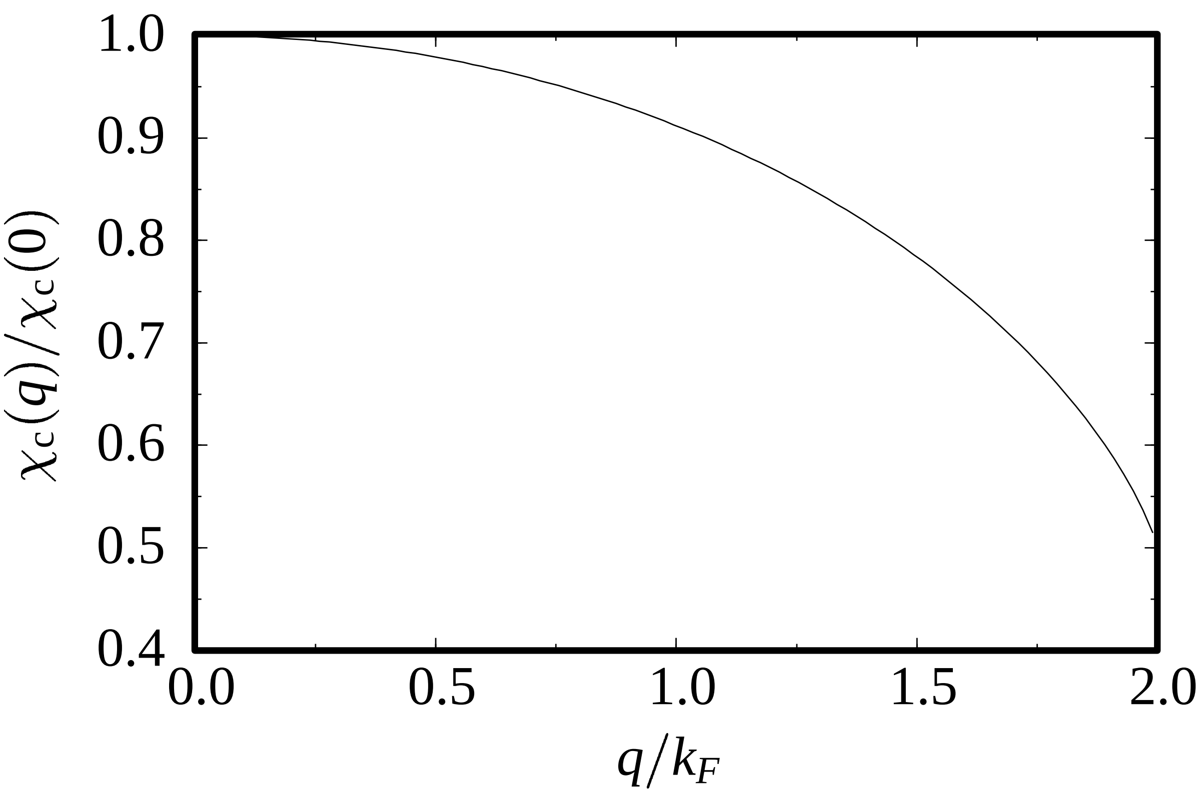


Figure 9: Charge susceptibility χ_c.

$$\sigma_{el} = \frac{\omega\kappa_c^2}{4\pi i q^2}. \tag{L94}$$

Electron–Ion Interaction

$$\vec{u} = \frac{-e^\star \vec{E}}{M(\omega^2 - \bar{\omega}_{\vec{q}}^2)}. \tag{L95}$$

$$\vec{j}_{\text{ion}}(\vec{q},\omega) = -i\omega n e^\star \vec{u} \tag{L96}$$

$$\omega_{\text{pi}}^2 = \frac{4\pi n e^{\star 2}}{M}, \tag{L97}$$

$$\sigma_{\text{ion}} = -\frac{\omega}{4\pi i}\frac{\omega_{\text{pi}}^2}{\omega^2 - \bar{\omega}_{\vec{q}}^2}. \tag{L98}$$

$$\sigma(\vec{q},\omega) = \frac{\omega}{4\pi i}\left[\frac{\kappa_{\text{c}}^2}{q^2} - \frac{\omega_{\text{pi}}^2}{\omega^2 - \bar{\omega}_{\vec{q}}^2}\right] \tag{L99}$$

$$\Rightarrow \epsilon(\vec{q},\omega) = 1 + \frac{\kappa_{\text{c}}^2}{q^2} - \frac{\omega_{\text{pi}}^2}{\omega^2 - \bar{\omega}_{\vec{q}}^2}. \tag{L100}$$

$$\omega_{\vec{q}}^2 = \bar{\omega}_{\vec{q}}^2 + \frac{q^2\omega_{\rm pi}^2}{q^2+\kappa_{\rm c}^2}. \tag{L101}$$

$$\frac{1}{\epsilon(\vec{q},\omega)} = \frac{q^2}{q^2+\kappa_{\rm c}^2}\left[\frac{\omega^2-\bar{\omega}_{\vec{q}}^2}{\omega^2-\omega_{\vec{q}}^2}\right]. \tag{L102}$$

$$|\psi_1 e^{i\vec{k}_1\cdot\vec{r}-\mathcal{E}_1 t/\hbar}+\psi_2 e^{i\vec{k}_2\cdot\vec{r}-\mathcal{E}_2 t/\hbar}|^2 \propto \text{const.}+\cos[(\vec{k}_1-\vec{k}_2)\cdot\vec{r}-(\mathcal{E}_1-\mathcal{E}_2)t/\hbar]. \tag{L103}$$

$$U_{\rm eff} = \frac{4\pi e^2}{\epsilon(\vec{q},\omega)q^2} = \frac{4\pi e^2}{q^2+\kappa_{\rm c}^2}\left[1+\frac{\omega_{\vec{q}}^2-\bar{\omega}_{\vec{q}}^2}{\omega^2-\omega_{\vec{q}}^2}\right] \tag{L104a}$$

with

$$\vec{q} = \vec{k}_1-\vec{k}_2 \quad \text{and} \quad \hbar\omega = \mathcal{E}_1-\mathcal{E}_2. \tag{L104b}$$

$$\hat{U}_{\mathrm{el-phon}} = \frac{1}{\sqrt{\mathcal{V}}}\sum_{\substack{\vec{q}''\vec{k}\\ \sigma}}[C^*_{\vec{k}}\hat{c}^\dagger_{\vec{q}''-\vec{k},\sigma}\hat{c}_{\vec{q}''\sigma}\hat{a}^\dagger_{\vec{k}} + C_{\vec{k}}\hat{c}^\dagger_{\vec{q}''+\vec{k},\sigma}\hat{c}_{\vec{q}'',\sigma}\hat{a}_{\vec{k}}] \quad \text{(L105)}$$

$$= \frac{1}{\sqrt{\mathcal{V}}}\sum_{\substack{\vec{q}'\vec{q}\\ \sigma}} C_{\vec{q}}[\hat{c}^\dagger_{\vec{q}'+\vec{q},\sigma}\hat{c}_{\vec{q}',\sigma}\hat{a}^\dagger_{-\vec{q}} + \hat{c}^\dagger_{\vec{q}'+\vec{q},\sigma}\hat{c}_{\vec{q}',\sigma}\hat{a}_{\vec{q}}]. \quad \text{(L106)}$$

$$\epsilon_{\mathrm{el}}(\vec{q},\omega) = \frac{q^2+\kappa_c^2}{q^2}, \quad \text{(L107)}$$

$$\hat{\mathcal{H}}_{\substack{\text{screened}\\ \text{Coulomb}}} = \frac{1}{\mathcal{V}}\sum_{\substack{\vec{q},\vec{k},\vec{k}'\\ \sigma,\sigma'}}\frac{1}{2}\frac{4\pi e^2}{q^2+\kappa_c^2}\hat{c}^\dagger_{\vec{k}'-\vec{q},\sigma'}\hat{c}^\dagger_{\vec{k}+\vec{q},\sigma}\hat{c}_{\vec{k},\sigma}\hat{c}_{\vec{k}',\sigma'}. \quad \text{(L108)}$$

Formal Derivation

$$\hat{\mathcal{H}} = \sum_{\vec{q},\sigma} \epsilon_{\vec{q}} \hat{c}^{\dagger}_{\vec{q}\sigma} \hat{c}_{\vec{q}\sigma} + \frac{1}{\mathcal{V}} \sum_{\substack{\vec{q},\vec{k},\vec{k}' \\ \sigma,\sigma'}} \frac{1}{2} \frac{4\pi e^2}{q^2+\kappa_c^2} \hat{c}^{\dagger}_{\vec{k}'-\vec{q},\sigma'} \hat{c}^{\dagger}_{\vec{k}+\vec{q},\sigma} \hat{c}_{\vec{k},\sigma} \hat{c}_{\vec{k}',\sigma'}$$
$$+ \sum_{\vec{k}} \hbar\omega_{\vec{k}} \hat{a}^{\dagger}_{\vec{k}} \hat{a}_{\vec{k}} + \frac{1}{\sqrt{\mathcal{V}}} \sum_{\substack{\vec{q},\vec{q}' \\ \sigma}} \hat{c}^{\dagger}_{\vec{q}+\vec{q}',\sigma} \hat{c}_{\vec{q}',\sigma} C_{\vec{q}} \left[\hat{a}_{\vec{q}} + \hat{a}^{\dagger}_{-\vec{q}}\right]. \tag{L109}$$

$$e^{-\hat{S}} \tilde{a}_{\vec{k}} e^{\hat{S}} = \hat{a}_{\vec{k}} \tag{L110}$$

$$e^{-\hat{S}} \tilde{c}_{\vec{k}\sigma} e^{\hat{S}} = \hat{c}_{\vec{k}\sigma}. \tag{L111}$$

$$\hat{\mathcal{H}} = e^{-\hat{S}} \tilde{\mathcal{H}} e^{\hat{S}}, \tag{L112}$$

$$e^{-\hat{S}} \tilde{\mathcal{H}} e^{\hat{S}} = \tilde{\mathcal{H}} + \left[\tilde{\mathcal{H}}, \hat{S}\right] + \frac{1}{2}\left[\left[\tilde{\mathcal{H}}, \hat{S}\right], \hat{S}\right] + \ldots. \tag{L113}$$

Formal Derivation

$$\hat{\mathcal{H}} \approx \tilde{\mathcal{H}}_0 + \left[\tilde{\mathcal{H}}_0, \hat{S}\right] + \tilde{\mathcal{H}}_1 + \frac{1}{2}\left[\left[\tilde{\mathcal{H}}_0, \hat{S}\right], \hat{S}\right] + \left[\tilde{\mathcal{H}}_1, \hat{S}\right] \quad \text{(L114)}$$

$$= \tilde{\mathcal{H}}_0 + \frac{1}{2}\left[\tilde{\mathcal{H}}_1, \hat{S}\right], \quad \text{(L115)}$$

just so long as

$$0 = \left[\tilde{\mathcal{H}}_0, \hat{S}\right] + \tilde{\mathcal{H}}_1. \quad \text{(L116)}$$

$$\hat{\mathcal{H}} = \frac{1}{2\mathcal{V}} \sum_{\substack{\vec{q}\vec{k}\vec{k}' \\ \sigma\sigma'}} \left[\frac{2|C_{\vec{q}}|^2 \hbar\omega_{\vec{q}}}{(\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}})^2 - \hbar^2\omega_{\vec{q}}^2} + \frac{4\pi e^2}{q^2 + \kappa_c^2} \right] \tilde{c}^{\dagger}_{\vec{k}'-\vec{q}\sigma'} \tilde{c}^{\dagger}_{\vec{k}+\vec{q}\sigma} \tilde{c}_{\vec{k}\sigma} \tilde{c}_{\vec{k}'\sigma'}. \quad \text{(L117)}$$

Cooper Problem

$$|G\rangle = \prod_{k<k_F} \hat{c}^{\dagger}_{\vec{k}} |\emptyset\rangle. \tag{L118}$$

$$\left[\frac{-\hbar^2\nabla_1^2}{2m} + \frac{-\hbar^2\nabla_2^2}{2m} + U(\vec{r}_1 - \vec{r}_2)\right]\Psi(\vec{r}_1, \vec{r}_2) = \mathcal{E}\Psi(\vec{r}_1, \vec{r}_2), \tag{L119}$$

$$\Psi(\vec{r}_1, \vec{r}_2) = \sum_{k'>k_F} \Psi_{\vec{k}'} e^{-i\vec{k}'\cdot(\vec{r}_1 - \vec{r}_2)}. \tag{L120}$$

$$(2\epsilon_{\vec{k}} - \mathcal{E})\Psi_{\vec{k}} + \sum_{k'>k_F} U_{\vec{k}\vec{k}'}\Psi_{\vec{k}'} = 0. \tag{L121}$$

$$U_{\vec{k}\vec{k}'} \quad = \quad -\frac{U_0}{\mathcal{V}}\theta(\hbar\omega - |\mathcal{E}_F - \epsilon_{\vec{k}}|)\theta(\hbar\omega - |\mathcal{E}_F - \epsilon_{\vec{k}'}|). \tag{L122}$$

Cooper Problem

$$(2\epsilon_{\vec{k}} - \mathcal{E})\Psi_{\vec{k}} = \frac{U_0}{\mathcal{V}} \sum_{k' > k_F}^{k_{\max}} \Psi_{\vec{k}'}. \tag{L123}$$

$$\mathcal{E} = 2\epsilon_{\vec{k}_a}, \tag{L124}$$

$$\Psi_{\vec{k}_a} = -\Psi_{\vec{k}_b} = \frac{1}{\sqrt{2}}. \tag{L125}$$

$$\sum_{\vec{k} > k_F}^{k_{\max}} \Psi_{\vec{k}} = \sum_{\vec{k} > k_F}^{k_{\max}} \frac{U_0}{\mathcal{V}} \frac{1}{(2\epsilon_{\vec{k}} - \mathcal{E})} \sum_{\vec{k}' > k_F}^{k_{\max}} \Psi_{\vec{k}'}. \tag{L126}$$

$$\Rightarrow 1 = \sum_{\vec{k}}^{k_{\max}} \frac{U_0}{(2\epsilon_{\vec{k}} - \mathcal{E})\mathcal{V}} \tag{L127}$$

$$\approx \int_{\mathcal{E}_F}^{\mathcal{E}_F + \hbar\omega} d\epsilon \, \frac{D(\mathcal{E}_F)}{2} \frac{U_0}{2\epsilon - \mathcal{E}} \tag{L128}$$

$$\Rightarrow 1 = \frac{1}{4}D(\mathcal{E}_F)U_0 \ln(\frac{2\mathcal{E}_F + 2\hbar\omega - \mathcal{E}}{2\mathcal{E}_F - \mathcal{E}}). \tag{L129}$$

$$\mathcal{E} = 2\mathcal{E}_F - (2\mathcal{E}_{\max} - 2\mathcal{E}_F)\exp\left[-\frac{4}{D(\mathcal{E}_F)U_0}\right]. \tag{L130}$$

$$\Psi_{\vec{k}} = \frac{U_0}{(2\epsilon_{\vec{k}} - \mathcal{E})\mathcal{V}} \sum_{\vec{k}' > k_F}^{k_{\max}} \Psi_{\vec{k}'}. \tag{L131}$$

$$|\Psi\rangle = \sum_{\vec{k}} \Psi_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow} |G\rangle. \tag{L132}$$

$$\mathcal{H} = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\sigma} \hat{c}_{\vec{k}\sigma} + \frac{1}{2\mathcal{V}} \sum_{\substack{\vec{q}\vec{k}\vec{k}' \\ \sigma\sigma'}} \left[\frac{2|C_{\vec{q}}|^2 \hbar\omega_{\vec{q}}}{(\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}})^2 - \hbar^2\omega_{\vec{q}}^2} + \frac{4\pi e^2}{q^2 + \kappa_c^2}\right] \hat{c}^{\dagger}_{\vec{k}'-\vec{q}\sigma'} \hat{c}^{\dagger}_{\vec{k}+\vec{q}\sigma} \hat{c}_{\vec{k}\sigma} \hat{c}_{\vec{k}'\sigma'} \tag{L133}$$

Cooper Problem

$$\langle\hat{K}\rangle = \sum_{\vec{k}_1\vec{k}_0\vec{q}\sigma} \Psi^*_{\vec{k}_1}\Psi_{\vec{k}_0}\langle G|\hat{c}_{-\vec{k}_1\downarrow}\hat{c}_{\vec{k}_1\uparrow}\,\epsilon_{\vec{q}}\hat{c}^\dagger_{\vec{q}\sigma}\hat{c}_{\vec{q}\sigma}\,\hat{c}^\dagger_{\vec{k}_0\uparrow}\hat{c}^\dagger_{-\vec{k}_0\downarrow}|G\rangle. \tag{L134}$$

$$\vec{k}_0 = \vec{k}_1. \tag{L135}$$

$$(2\sum_{q<k_F}\epsilon_{\vec{q}})(\sum_{k_0>k_F}|\Psi_{\vec{k}_0}|^2). \tag{L136}$$

$$\sigma = \uparrow \quad \text{and} \quad \vec{q} = \vec{k}_0 \quad \text{or} \quad \sigma = \downarrow \quad \text{and} \quad \vec{q} = -\vec{k}_0. \tag{L137}$$

$$\langle\hat{K}\rangle = (2\sum_{q<k_F}\epsilon_{\vec{q}})(\sum_{k_0>k_F}|\Psi_{\vec{k}_0}|^2) + \sum_{k_0>k_F} 2|\Psi_{\vec{k}_0}|^2\epsilon_{\vec{k}_0}. \tag{L138}$$

$$\hat{\mathcal{H}} = \sum_{\substack{\vec{q}\vec{k}\vec{k}' \\ \sigma\sigma'}} U^{\text{eff}}_{\vec{k}\vec{k}'}\hat{c}^\dagger_{-\vec{k}'+\vec{q},\sigma'}\hat{c}^\dagger_{\vec{k}',\sigma}\hat{c}_{\vec{k},\sigma}\hat{c}_{-\vec{k}+\vec{q},\sigma'}, \tag{L139}$$

$$U^{\text{eff}}_{\vec{k}\vec{k}'} = \frac{1}{2\mathcal{V}}\left[\frac{2|C_{\vec{k}-\vec{k}'}|^2\hbar\omega_{\vec{k}-\vec{k}'}}{(\epsilon_{\vec{k}}-\epsilon_{\vec{k}'})^2-\hbar^2\omega^2_{\vec{k}-\vec{k}'}}+\frac{4\pi e^2}{|\vec{k}-\vec{k}'|^2+\kappa_c^2}\right]. \tag{L140}$$

$$2\sum_{kk'>k_F} U^{\text{eff}}_{\vec{k},\vec{k}'}\Psi^*_{\vec{k}'}\Psi_{\vec{k}}, \tag{L141}$$

$$2\sum_{k>k_F}\epsilon^{\text{eff}}_{\vec{k}}|\Psi_{\vec{k}}|^2+2\sum_{kk'>k_F}\Psi^*_{\vec{k}'}\Psi_{\vec{k}}U^{\text{eff}}_{\vec{k}\vec{k}'}. \tag{L142}$$

$$2\epsilon^{\text{eff}}_{\vec{k}}\Psi_{\vec{k}}+2\sum_{k'>k_F}U^{\text{eff}}_{\vec{k}\vec{k}'}\Psi_{\vec{k}'}=\mathcal{E}\Psi_{\vec{k}}. \tag{L143}$$

$$\hat{\mathcal{H}}_{\mathrm{BCS}} = \sum_{\vec{k},\sigma} \epsilon_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\sigma} \hat{c}_{\vec{k}\sigma} + \sum_{\vec{k}\vec{k}'} U_{\vec{k}\vec{k}'} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow} \hat{c}_{-\vec{k}'\downarrow} \hat{c}_{\vec{k}'\uparrow}. \quad \text{(L144)}$$

$$|\Phi_N\rangle = \left[\sum_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow} g_{\vec{k}} \right]^N |\varnothing\rangle, \quad \text{(L145)}$$

$$|\Phi\rangle \equiv \sum_N \frac{1}{N!} |\Phi_N\rangle \quad \text{(L146)}$$

$$= \sum_N \frac{1}{N!} \left[\sum_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow} g_{\vec{k}} \right]^N |\varnothing\rangle. \quad \text{(L147)}$$

$$|\Phi\rangle = \exp[\sum_{\vec{k}} g_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow}] |\varnothing\rangle. \quad \text{(L148)}$$

$$|\Phi\rangle = \prod_{\vec{k}} \left[1 + g_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow}\right] |\varnothing\rangle \equiv \hat{\Phi}|\varnothing\rangle. \tag{L149}$$

$$\langle\Phi|\Phi\rangle = \prod_{\vec{k}} \left(1 + |g_{\vec{k}}|^2\right) = \mathcal{N}^2. \tag{L150}$$

$$b_{\vec{k}} = \frac{1}{\mathcal{N}^2} \langle\Phi|\hat{c}_{-\vec{k}\downarrow} \hat{c}_{\vec{k}\uparrow}|\Phi\rangle = \frac{g_{\vec{k}}}{1 + |g_{\vec{k}}|^2}, \tag{L151}$$

$$\frac{1}{\mathcal{N}^2} \langle\Phi|\hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow} \hat{c}_{-\vec{k}'\downarrow} \hat{c}_{\vec{k}'\uparrow}|\Phi\rangle = b^*_{\vec{k}} b_{\vec{k}'}. \tag{L152}$$

$$\left[\sum_{\sigma} \hat{n}_{\vec{k}\sigma}, \hat{\Phi}\right] = \left[g_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow} + g_{-\vec{k}} \hat{c}^{\dagger}_{-\vec{k}\uparrow} \hat{c}^{\dagger}_{\vec{k}\downarrow}\right] \hat{\Phi}. \tag{L153}$$

$$\frac{1}{\mathcal{N}^2} \langle\Phi| \sum_{\sigma} \hat{n}_{\vec{k}\sigma} |\Phi\rangle = \frac{1}{\mathcal{N}^2} \langle\Phi| \left(g_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}^{\dagger}_{-\vec{k}\downarrow} + g_{-\vec{k}} \hat{c}^{\dagger}_{-\vec{k}\uparrow} \hat{c}^{\dagger}_{\vec{k}\downarrow}\right) |\Phi\rangle \tag{L154}$$

$$\Rightarrow \sum_{\sigma} n_{\vec{k}\sigma} = g_{\vec{k}} b^*_{\vec{k}} + g_{-\vec{k}} b^*_{-\vec{k}}. \tag{L155}$$

$$\langle\Phi|\hat{\mathcal{H}}_{\rm BCS}-\mu N|\Phi\rangle = \sum_{\vec k} 2\left(\epsilon_{\vec k}-\mu\right) g_{\vec k} b^*_{\vec k} + \sum_{\vec k \vec k'} U_{\vec k \vec k'} b^*_{\vec k} b_{\vec k'}. \quad \text{(L156)}$$

$$\frac{\partial b^*_{\vec k}}{\partial g^*_{\vec k}} = \frac{1}{\left(1+|g_{\vec k}|^2\right)^2}; \; \frac{\partial b_{\vec k}}{\partial g^*_{\vec k}} = -\frac{g^2_{\vec k}}{\left(1+|g_{\vec k}|^2\right)^2}, \quad \text{(L157)}$$

$$\frac{2(\epsilon_{\vec q}-\mu)g_{\vec q}}{(1+|g_{\vec q}|^2)^2} + \sum_{\vec k \vec k'} \frac{U_{\vec k \vec k'}}{(1+|g_{\vec q}|^2)^2}\left[b_{\vec k'}\delta_{\vec k \vec q} - b^*_{\vec k} g^2_{\vec q} \delta_{\vec q \vec k'}\right] = 0. \quad \text{(L158)}$$

$$\Delta_{\vec k} = -\sum_{\vec k'} U_{\vec k \vec k'} b_{\vec k'}, \quad \text{(L159)}$$

$$0 = 2\left(\epsilon_{\vec q}-\mu\right) g_{\vec q} - \Delta_{\vec q} + g^2_{\vec q}\Delta^*_{\vec q} \quad \text{(L160)}$$

$$\Rightarrow g_{\vec k} = \frac{\mathcal{E}_{\vec k}-(\epsilon_{\vec k}-\mu)}{\Delta^*_{\vec k}}, \quad \text{(L161)}$$

with

$$\mathcal{E}_{\vec k} = \sqrt{(\epsilon_{\vec k}-\mu)^2+|\Delta_{\vec k}|^2}. \quad \text{(L162)}$$

$$b_{\vec{k}} = \frac{g_{\vec{k}}}{1+|g_{\vec{k}}|^2} = \frac{\Delta_{\vec{k}}}{2\mathcal{E}_{\vec{k}}}. \tag{L163}$$

$$N = 2\sum_{\vec{k}} \theta(\mathcal{E}_F - \epsilon_{\vec{k}}) = \int_0^{\mathcal{E}_F} d\epsilon D(\epsilon), \tag{L164}$$

$$N = \sum_{\vec{k}\sigma} g^*_{\vec{k}} b_{\vec{k}} = \sum_{\vec{k}\sigma} \frac{1}{2}\left[1 - \frac{\epsilon_{\vec{k}}-\mu}{\mathcal{E}_{\vec{k}}}\right] \tag{L165}$$

$$= \sum_{\vec{k}\sigma} \frac{1}{2}\left[1 - \frac{\epsilon_{\vec{k}}-\mu}{\sqrt{(\epsilon_{\vec{k}}-\mu)^2+|\Delta|^2}}\right] \tag{L166}$$

$$= \int d\epsilon \frac{D(\epsilon)}{2}\left[1 - \frac{\epsilon-\mu}{\sqrt{(\epsilon-\mu)^2+|\Delta|^2}}\right] \tag{L167}$$

$$= \int d\epsilon \left[\int^{\epsilon} d\epsilon' D(\epsilon')\right] \frac{1}{2}\frac{\partial}{\partial\epsilon} \frac{\epsilon-\mu}{\sqrt{(\epsilon-\mu)^2+|\Delta|^2}} \tag{L168}$$

$$= \int d\epsilon \left[\int^{\mu} d\epsilon' D(\epsilon')\right] \frac{1}{2}\frac{\partial}{\partial\epsilon} \frac{\epsilon-\mu}{\sqrt{(\epsilon-\mu)^2+|\Delta|^2}} + \mathcal{O}(\Delta/\mathcal{E}_F)^2 \tag{L169}$$

$$= \left[\int^{\mu} d\epsilon' D(\epsilon')\right] = N + D(\mathcal{E}_F)(\mu - \mathcal{E}_F) \quad \text{(L170)}$$

$$\Rightarrow \mu = \mathcal{E}_F . \quad \text{(L171)}$$

$$\Delta_{\vec{k}} = -\sum_{\vec{k}'} U_{\vec{k}\vec{k}'} \frac{\Delta_{\vec{k}'}}{2\mathcal{E}_{\vec{k}'}} . \quad \text{(L172)}$$

$$\Delta_{\vec{k}} = \theta(\hbar\omega - |\epsilon_{\vec{k}} - \mathcal{E}_F|) \frac{U_0}{\mathcal{V}} \sum_{\vec{k}'} \frac{\Delta_{\vec{k}'}}{2\sqrt{(\epsilon_{\vec{k}'} - \mu)^2 + |\Delta_{\vec{k}'}|^2}} . \quad \text{(L173)}$$

$$\Delta_{\vec{k}} = \Delta\theta(\hbar\omega - |\epsilon_{\vec{k}} - \mathcal{E}_F|) . \quad \text{(L174)}$$

$$1 = \sum_{\vec{k}} \frac{1}{\mathcal{V}} \theta(\hbar\omega - |\epsilon_{\vec{k}} - \mathcal{E}_F|) \frac{U_0}{2\sqrt{(\epsilon_{\vec{k}} - \mu)^2 + |\Delta|^2}} . \quad \text{(L175)}$$

$$= \int_{\mathcal{E}_F - \hbar\omega}^{\mathcal{E}_F + \hbar\omega} d\epsilon \frac{D(\epsilon)}{2} \frac{U_0}{2\sqrt{(\epsilon - \mathcal{E}_F)^2 + |\Delta|^2}} \quad \text{(L176)}$$

$$
\begin{aligned}
&= U_0 \int_0^{\hbar\omega/\Delta} d\zeta \, \frac{D(\mathcal{E}_F)}{2\sqrt{\zeta^2+1}} && \text{(L177)}\\
&= \frac{U_0 D(\mathcal{E}_F)}{2} \sinh^{-1} \frac{\hbar\omega}{\Delta} && \text{(L178)}\\
\Rightarrow \Delta &= 2\hbar\omega \exp\left[-\frac{2}{D(\mathcal{E}_F)U_0}\right]. && \text{(L179)}
\end{aligned}
$$

$$Z_{\rm gr} = {\rm Tr} e^{-\beta[\hat{\mathcal{H}}_{\rm BCS} - \mu\hat{N}]}, \tag{L180}$$

$$\hat{c}_{-\vec{k}\downarrow}\hat{c}_{\vec{k}\uparrow} = b_{\vec{k}} + \left(\hat{c}_{-\vec{k}\downarrow}\hat{c}_{\vec{k}\uparrow} - b_{\vec{k}}\right), \tag{L181}$$

$$Z_{\rm gr} = {\rm Tr} e^{-\beta[\hat{\mathcal{H}}_{\rm eff} - \mu N]}, \tag{L182}$$

where

$$\begin{aligned} &\hat{\mathcal{H}}_{\rm eff} - \mu N \\ &= \sum_{\vec{k}\sigma} \hat{n}_{\vec{k}\sigma}(\epsilon_{\vec{k}} - \mu) + \sum_{\vec{k}\vec{k}'} b_{\vec{k}'} U_{\vec{k}\vec{k}'} \hat{c}^\dagger_{\vec{k}\uparrow}\hat{c}^\dagger_{-\vec{k}\downarrow} + b^*_{\vec{k}} U^*_{\vec{k}'\vec{k}} \hat{c}_{-\vec{k}'\downarrow}\hat{c}_{\vec{k}'\uparrow} - b^*_{\vec{k}} b_{\vec{k}'} U_{\vec{k}\vec{k}'} && \text{(L183)} \\ &\equiv \sum_{\vec{k}\sigma} \hat{n}_{\vec{k}\sigma}(\epsilon_{\vec{k}} - \mu) - \sum_{\vec{k}} [\Delta_{\vec{k}} \hat{c}^\dagger_{\vec{k}\uparrow}\hat{c}^\dagger_{-\vec{k}\downarrow} + \Delta^*_{\vec{k}} \hat{c}_{-\vec{k}\downarrow}\hat{c}_{\vec{k}\uparrow}] - \sum_{\vec{k}\vec{k}'} b^*_{\vec{k}} b_{\vec{k}'} U_{\vec{k}\vec{k}'}. && \text{(L184)} \end{aligned}$$

$$\begin{aligned} \hat{c}_{\vec{k}\uparrow} &= u_{\vec{k}}\hat{\gamma}_{\vec{k}\uparrow} + v^*_{\vec{k}}\hat{\gamma}^\dagger_{\vec{k}\downarrow} && \text{(L185a)} \\ \hat{c}^\dagger_{-\vec{k}\downarrow} &= -v_{\vec{k}}\hat{\gamma}_{\vec{k}\uparrow} + u^*_{\vec{k}}\hat{\gamma}^\dagger_{\vec{k}\downarrow}. && \text{(L185b)} \end{aligned}$$

$$|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1. \tag{L186}$$

$$\hat{\mathcal{H}}_{\text{eff}} - \mu N = \sum_{\vec{k}} \left[\begin{array}{ll} (\epsilon_{\vec{k}} - \mu) & \left\{ \begin{array}{l} [\quad u^*_{\vec{k}} \hat{\gamma}^\dagger_{\vec{k}\uparrow} + v_{\vec{k}} \hat{\gamma}_{\vec{k}\downarrow}] [\quad u_{\vec{k}} \hat{\gamma}_{\vec{k}\uparrow} + v^*_{\vec{k}} \hat{\gamma}^\dagger_{\vec{k}\downarrow}] \\ +[- \quad v_{\vec{k}} \hat{\gamma}_{\vec{k}\uparrow} + u^*_{\vec{k}} \hat{\gamma}^\dagger_{\vec{k}\downarrow}] [- \quad v^*_{\vec{k}} \hat{\gamma}^\dagger_{\vec{k}\uparrow} + u_{\vec{k}} \hat{\gamma}_{\vec{k}\downarrow}] \end{array} \right\} \\ - & \Delta_{\vec{k}} [u^*_{\vec{k}} \hat{\gamma}^\dagger_{\vec{k}\uparrow} + v_{\vec{k}} \hat{\gamma}_{\vec{k}\downarrow}] [-v_{\vec{k}} \hat{\gamma}_{\vec{k}\uparrow} + u^*_{\vec{k}} \hat{\gamma}^\dagger_{\vec{k}\downarrow}] \\ - & \Delta^*_{\vec{k}} [-v^*_{\vec{k}} \hat{\gamma}^\dagger_{\vec{k}\uparrow} + u_{\vec{k}} \hat{\gamma}_{\vec{k}\downarrow}] [u_{\vec{k}} \hat{\gamma}_{\vec{k}\uparrow} + v^*_{\vec{k}} \hat{\gamma}^\dagger_{\vec{k}\downarrow}] \\ - & \sum_{\vec{k}'} b^*_{\vec{k}} b_{\vec{k}'} U_{\vec{k}\vec{k}'}. \end{array} \right] \tag{L187}$$

$$2u_{\vec{k}} v_{\vec{k}} (\epsilon_{\vec{k}} - \mu) + \Delta_{\vec{k}} v^2_{\vec{k}} - \Delta^*_{\vec{k}} u^2_{\vec{k}} = 0. \tag{L188}$$

$$0 = 2\sqrt{1 - |v_{\vec{k}}|^2}\, v_{\vec{k}} (\epsilon_{\vec{k}} - \mu) + \Delta_{\vec{k}} v^2_{\vec{k}} - \Delta^*_{\vec{k}} (1 - |v_{\vec{k}}|^2). \tag{L189}$$

$$v_{\vec{k}} = \frac{g^*_{\vec{k}}}{\sqrt{1+|g_{\vec{k}}|^2}}, \tag{L190}$$

$$0 = 2(\epsilon_{\vec{k}} - \mu)g_{\vec{k}} - \Delta_{\vec{k}} + g^2_{\vec{k}}\Delta^*_{\vec{k}}. \tag{L191}$$

$$g_{\vec{k}} = \frac{\mathcal{E}_{\vec{k}} - (\epsilon_{\vec{k}} - \mu)}{\Delta^*_{\vec{k}}}. \tag{L192}$$

$$|v_{\vec{k}}|^2 = \frac{\mathcal{E}_{\vec{k}} - (\epsilon_{\vec{k}} - \mu)}{2\mathcal{E}_{\vec{k}}}, \quad |u_{\vec{k}}|^2 = \frac{\mathcal{E}_{\vec{k}} + \epsilon_{\vec{k}} - \mu}{2\mathcal{E}_{\vec{k}}}, \quad v_{\vec{k}}u^*_{\vec{k}} = \frac{\Delta^*_{\vec{k}}}{2\mathcal{E}_{\vec{k}}}. \tag{L193}$$

$$\hat{\mathcal{H}}_{\text{eff}} - \mu N = \sum_{\vec{k}} \mathcal{E}_{\vec{k}} \left[\hat{\gamma}^\dagger_{\vec{k}\uparrow}\hat{\gamma}_{\vec{k}\uparrow} + \hat{\gamma}^\dagger_{\vec{k}\downarrow}\hat{\gamma}_{\vec{k}\downarrow}\right] + \sum_{\vec{k}} \left[\epsilon_{\vec{k}} - \mu - \mathcal{E}_{\vec{k}} - \sum_{\vec{k}'} b^*_{\vec{k}} b_{\vec{k}'} U_{\vec{k}\vec{k}'}\right]. \tag{L194}$$

$$b^*_{-\vec{k}} = b^*_{\vec{k}} = \left\langle \hat{c}^\dagger_{\vec{k}\uparrow}\hat{c}^\dagger_{-\vec{k}\downarrow}\right\rangle = \left\langle v_{\vec{k}}u^*_{\vec{k}}\left(\hat{\gamma}_{\vec{k}\downarrow}\hat{\gamma}^\dagger_{\vec{k}\downarrow} - \hat{\gamma}^\dagger_{\vec{k}\uparrow}\hat{\gamma}_{\vec{k}\uparrow}\right)\right\rangle + \text{terms with } \gamma\gamma \text{ or } \gamma^\dagger\gamma^\dagger. \tag{L195}$$

$$b^*_{\vec{k}} = v_{\vec{k}} u^*_{\vec{k}} \left(1 - 2 f_{\vec{k}}\right), \tag{L196}$$

$$f_{\vec{k}} = \frac{1}{e^{\beta \mathcal{E}_{\vec{k}}} + 1} \tag{L197}$$

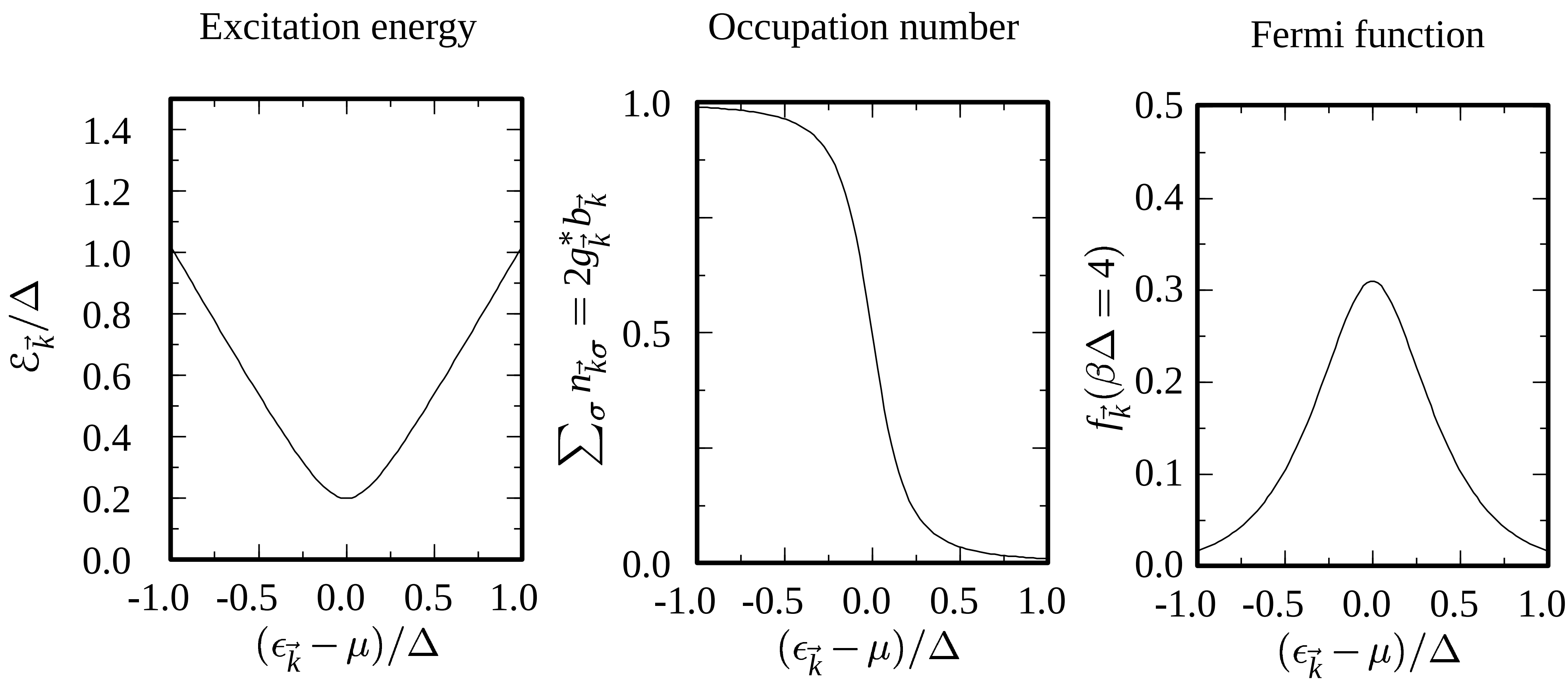


Figure 10: Sketches of the excitation energy, occupation number, and Fermi function for the BCS theory of superconductivity.

$$b_{\vec{k}} = \frac{\Delta_{\vec{k}}}{2\mathcal{E}_{\vec{k}}}\left(1 - 2f_{\vec{k}}\right) \tag{L198}$$

$$\Rightarrow \sum_{\vec{k}'} b_{\vec{k}'} U_{\vec{k}\vec{k}'} \quad = \quad -\Delta_{\vec{k}} = \sum_{\vec{k}'} \frac{\Delta_{\vec{k}'}}{2\mathcal{E}_{\vec{k}'}} \left(1 - 2f_{\vec{k}'}\right) U_{\vec{k}\vec{k}'}, \tag{L199}$$

$$\Delta \quad = \quad \sum_{\vec{k}} \theta(\hbar\omega - |\mathcal{E}_F - \epsilon_{\vec{k}}|) \frac{\Delta}{2|\epsilon_{\vec{k}} - \mu|} \frac{U_0}{\mathcal{V}} \left(1 - 2f_{\vec{k}}\right) \tag{L200}$$

$$\Rightarrow 1 \quad = \quad \int_0^{\beta\hbar\omega} U_0 \frac{D(\mathcal{E}_F)}{2} \frac{dx}{x} \left[1 - \frac{2}{e^x + 1}\right] \tag{L201}$$

$$\approx \quad \frac{U_0 D(\mathcal{E}_F)}{2} \left\{ \ln \beta\hbar\omega \left[1 - \frac{2}{e^{\beta\hbar\omega} + 1}\right] + 2\int_0^\infty dx \ln x \frac{\partial}{\partial x} \frac{1}{e^x + 1} \right\} \tag{L202}$$

$$\approx \quad \frac{U_0 D(\mathcal{E}_F)}{2} \left\{ \ln(\beta\hbar\omega) + \ln\left(\frac{2\gamma_E}{\pi}\right) \right\}, \tag{L203}$$

$$k_B T_c = \hbar\omega \frac{2\gamma_E}{\pi} \exp\left[-\frac{2}{U_0 D(\mathcal{E}_F)}\right], \tag{L204}$$

$$\Rightarrow \frac{2\Delta(T=0)}{k_B T_c} = \frac{2\pi}{\gamma_E} = 3.53. \tag{L205}$$

Thermodynamics of Superconductors

Element	$2\Delta/k_BT$	$(C_s - C_n)/C_n$	Element	$2\Delta/k_BT$	$(C_s - C_n)/C_n$
BCS	3.53	1.43			
Al	2.5–4.2	1.3–1.6	Pb	4.0–4.4	2.7
Cd	3.2–3.4	1.3–1.4	Sn	2.8–4.0	1.6
Ga	3.5	1.4	Ta	3.5–3.7	1.6
Hg	4.0–4.6	2.4	Tl	3.6–3.9	1.5
In	3.4–3.7	1.7	V	3.4–3.5	1.5
La	1.7–3.2	1.5	Zn	3.2–3.4	1.2–1.3
Nb	3.6–3.8	1.9–2.0			

$$\hat{\mathcal{H}} = \sum_{\vec{k}\vec{k}'\sigma} \epsilon_{\vec{k}\vec{k}'} \hat{c}^\dagger_{\vec{k}\sigma} \hat{c}_{\vec{k}'\sigma} - \sum_{\vec{k}\vec{q}\vec{k}'} \frac{U_0}{\mathcal{V}} \hat{c}^\dagger_{\vec{k}\uparrow} \hat{c}^\dagger_{\vec{q}-\vec{k}\downarrow} \hat{c}_{\vec{q}-\vec{k}'\downarrow} \hat{c}_{\vec{k}'\uparrow}. \tag{L206}$$

$$\Delta_{\vec{q}} = \sum_{\vec{k}'} \frac{U_0}{\mathcal{V}} \left\langle \hat{c}_{\vec{q}-\vec{k}'\downarrow} \hat{c}_{\vec{k}'\uparrow} \right\rangle. \tag{L207}$$

$$\hat{\mathcal{H}} - \mu N = \sum_{\vec{k}\vec{k}'\sigma} [\epsilon_{\vec{k}\vec{k}'} - \mu \delta_{\vec{k}\vec{k}'}] \hat{c}^\dagger_{\vec{k}\sigma} \hat{c}_{\vec{k}'\sigma} - \sum_{\vec{k}\vec{q}} [\Delta^*_{\vec{q}} \hat{c}_{\vec{q}-\vec{k}\downarrow} \hat{c}_{\vec{k}\uparrow} + \Delta_{\vec{q}} c^\dagger_{\vec{k}\uparrow} c^\dagger_{\vec{q}-\vec{k}\downarrow}]. \tag{L208}$$

$$\hat{c}_{\vec{r}\sigma} = \sum_{\vec{k}} \frac{e^{-i\vec{k}\cdot\vec{r}}}{\sqrt{N_k}} \hat{c}_{\vec{k}\sigma}, \quad \Delta_{\vec{k}} = \frac{1}{N_k} \sum_{\vec{r}} e^{i\vec{k}\cdot\vec{r}} \Delta_{\vec{r}}, \quad \epsilon_{\vec{k}\vec{k}'} = \frac{1}{N_k} \sum_{\vec{r}\vec{r}'} e^{i\vec{k}\cdot\vec{r} - i\vec{k}'\cdot\vec{r}'} \epsilon_{\vec{r}\vec{r}'}. \tag{L209}$$

$$\hat{\mathcal{H}} = \sum_{\vec{r}\vec{r}'\sigma} [\epsilon_{\vec{r}\vec{r}'} - \mu \delta_{\vec{r}\vec{r}'}] \hat{c}^\dagger_{\vec{r}\sigma} \hat{c}_{\vec{r}'\sigma} - \sum_{\vec{r}} [\Delta^*_{\vec{r}} \hat{c}_{\vec{r}\downarrow} \hat{c}_{\vec{r}\uparrow} + \Delta_{\vec{r}} \hat{c}^\dagger_{\vec{r}\uparrow} \hat{c}^\dagger_{\vec{r}\downarrow}]. \tag{L210}$$

$$\hat{\mathcal{H}} = \sum_l \mathcal{E}_l \left[\hat{\gamma}^\dagger_{l\uparrow}\hat{\gamma}_{l\uparrow} + \hat{\gamma}^\dagger_{l\downarrow}\hat{\gamma}_{l\downarrow}\right]. \tag{L211}$$

$$\begin{aligned} \hat{c}_{\vec{r}\uparrow} &= \frac{1}{\sqrt{N_k}} \sum_l u_l(\vec{r})\hat{\gamma}_{l\uparrow} + v^*_l(\vec{r})\hat{\gamma}^\dagger_{l\downarrow} \\ \hat{c}_{\vec{r}\downarrow} &= \frac{1}{\sqrt{N_k}} \sum_l u_l(\vec{r})\hat{\gamma}_{l\downarrow} - v^*_l(\vec{r})\hat{\gamma}^\dagger_{l\uparrow}. \end{aligned} \tag{L212}$$

$$\begin{aligned} [\mathcal{H}_B, \hat{\gamma}_{l\sigma}] &= -\mathcal{E}_l\hat{\gamma}_{l\sigma} \\ \left[\mathcal{H}_B, \hat{\gamma}^\dagger_{l\sigma}\right] &= \mathcal{E}_l\hat{\gamma}^\dagger_{l\sigma}. \end{aligned} \tag{L213}$$

$$\left[\mathcal{H}_B, \hat{c}^\dagger_{\vec{r}\uparrow}\right] = \sum_{\vec{r}'}[\epsilon^*_{\vec{r}\vec{r}'} - \mu\delta_{\vec{r}\vec{r}'}]\hat{c}^\dagger_{\vec{r}'\uparrow} - \Delta^*_{\vec{r}}\hat{c}_{\vec{r}\downarrow} \tag{L214a}$$

$$\left[\mathcal{H}_B, \hat{c}^\dagger_{\vec{r}\downarrow}\right] = \sum_{\vec{r}'}[\epsilon^*_{\vec{r}\vec{r}'} - \mu\delta_{\vec{r}\vec{r}'}]\hat{c}^\dagger_{\vec{r}'\downarrow} + \Delta^*_{\vec{r}}\hat{c}_{\vec{r}\uparrow} \tag{L214b}$$

$$[\mathcal{H}_B, \hat{c}_{\vec{r}\uparrow}] = -\sum_{\vec{r}'}[\epsilon_{\vec{r}\vec{r}'} - \mu\delta_{\vec{r}\vec{r}'}]\hat{c}_{\vec{r}'\uparrow} + \Delta_{\vec{r}}\hat{c}^\dagger_{\vec{r}\downarrow} \tag{L214c}$$

$$[\mathcal{H}_B, \hat{c}_{\vec{r}\downarrow}] = -\sum_{\vec{r}'}[\epsilon_{\vec{r}\vec{r}'} - \mu\delta_{\vec{r}\vec{r}'}]\hat{c}_{\vec{r}'\downarrow} - \Delta_{\vec{r}}\hat{c}^{\dagger}_{\vec{r}\uparrow}. \tag{L214d}$$

$$\begin{aligned} u_l(\vec{r})\mathcal{E}_l &= \sum_{\vec{r}'}[\epsilon_{\vec{r}\vec{r}'} - \mu\delta_{\vec{r}\vec{r}'}]u_l(\vec{r}') + v_l(\vec{r})\Delta_{\vec{r}} \\ v_l(\vec{r})\mathcal{E}_l &= -\sum_{\vec{r}'}[\epsilon^*_{\vec{r}\vec{r}'} - \mu\delta_{\vec{r}\vec{r}'}]v_l(\vec{r}') + u_l(\vec{r})\Delta^*_{\vec{r}}. \end{aligned} \tag{L215}$$

$$\Delta_{\vec{r}} = \frac{U_0}{\mathcal{V}} N_k \langle \hat{c}_{\vec{r}\downarrow}\hat{c}_{\vec{r}\uparrow}\rangle = \sum_l \frac{U_0}{\mathcal{V}} u_l(\vec{r})v_l^*(\vec{r}). \tag{L216}$$

$$u^{(0)}_{\vec{k}}(\vec{r}) = u_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}}, \quad v^{(0)}_{\vec{k}}(\vec{r}) = v_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}}. \tag{L217}$$

$$u_{\vec{k}}(\vec{r})\mathcal{E}_{\vec{k}} = \left\{\frac{1}{2m}\left(-i\hbar\vec{\nabla} + \frac{e\vec{A}}{c}\right)^2 - \mu\right\}u_{\vec{k}}(\vec{r}) + v_{\vec{k}}(\vec{r})\Delta_{\vec{r}} \tag{L218a}$$

$$v_{\vec{k}}(\vec{r})\mathcal{E}_{\vec{k}} = -\left\{\frac{1}{2m}\left(i\hbar\vec{\nabla} + \frac{e\vec{A}}{c}\right)^2 - \mu\right\}v_{\vec{k}}(\vec{r}) + u_{\vec{k}}(\vec{r})\Delta^*_{\vec{r}}. \tag{L218b}$$

$$u_{\vec{k}}(\vec{r}) = u^{(0)}_{\vec{k}}(\vec{r}) + u^{(1)}_{\vec{k}}(\vec{r}) = u_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}} + \sum_{\vec{k}'} e^{-i\vec{k}'\cdot\vec{r}} u^{(1)}_{\vec{k}}(\vec{k}') \quad \text{(L219a)}$$

$$v_{\vec{k}}(\vec{r}) = v^{(0)}_{\vec{k}}(\vec{r}) + v^{(1)}_{\vec{k}}(\vec{r}) = v_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}} + \sum_{\vec{k}'} e^{-i\vec{k}'\cdot\vec{r}} v^{(1)}_{\vec{k}}(\vec{k}'). \quad \text{(L219b)}$$

$$\left(\mathcal{E}_{\vec{k}} - \frac{\hbar^2}{2m}\nabla^2 - \mu\right) v^{(1)}_{\vec{k}}(\vec{r}) - \Delta^* u^{(1)}_{\vec{k}}(\vec{r}) = -\frac{ie\hbar}{2mc}\left(\vec{A}\cdot\vec{\nabla} + \vec{\nabla}\cdot\vec{A}\right) v^{(0)}_{\vec{k}}(\vec{r}) \quad \text{(L220a)}$$

$$\left(\mathcal{E}_{\vec{k}} + \frac{\hbar^2}{2m}\nabla^2 + \mu\right) u^{(1)}_{\vec{k}}(\vec{r}) - \Delta\, v^{(1)}_{\vec{k}}(\vec{r}) = -\frac{ie\hbar}{2mc}\left(\vec{A}\cdot\vec{\nabla} + \vec{\nabla}\cdot\vec{A}\right) u^{(0)}_{\vec{k}}(\vec{r}). \quad \text{(L220b)}$$

$$\left(\mathcal{E}_{\vec{k}} + \zeta_{\vec{k}'}\right) v^{(1)}_{\vec{k}}(\vec{k}') - \Delta^* u^{(1)}_{\vec{k}}(\vec{k}') = F_{\vec{k}'\vec{k}} v^{(0)}_{\vec{k}} \quad \text{(L221a)}$$

$$\left(\mathcal{E}_{\vec{k}} - \zeta_{\vec{k}'}\right) u^{(1)}_{\vec{k}}(\vec{k}') - \Delta v^{(1)}_{\vec{k}}(\vec{k}') = F_{\vec{k}'\vec{k}} u^{(0)}_{\vec{k}}, \quad \text{(L221b)}$$

$$\zeta_{\vec{k}} = \frac{\hbar^2 k^2}{2m} - \mu, \text{ so that } \mathcal{E}_{\vec{k}} = \sqrt{\zeta^2_{\vec{k}} + |\Delta|^2}, \quad \text{(L222)}$$

$$F_{\vec{k}'\vec{k}} = -\frac{e\hbar}{2mc}\int \frac{d\vec{r}'}{\mathcal{V}}\, e^{i(\vec{k}'-\vec{k})\cdot\vec{r}'}\,(\vec{k}+\vec{k}')\cdot\vec{A}(\vec{r}') = F^{*}_{\vec{k}\vec{k}'}. \quad \text{(L223)}$$

$$v^{(1)}_{\vec{k}}(\vec{k}') = \frac{F_{\vec{k}'\vec{k}}}{\mathcal{E}^2_{\vec{k}}-\mathcal{E}^2_{\vec{k}'}}\left[(\mathcal{E}_{\vec{k}}-\zeta_{\vec{k}'})v_{\vec{k}}+\Delta^* u_{\vec{k}}\right] \quad \text{(L224a)}$$

$$u^{(1)}_{\vec{k}}(\vec{k}') = \frac{F_{\vec{k}'\vec{k}}}{\mathcal{E}^2_{\vec{k}}-\mathcal{E}^2_{\vec{k}'}}\left[(\mathcal{E}_{\vec{k}}+\zeta_{\vec{k}'})u_{\vec{k}}+\Delta v_{\vec{k}}\right]. \quad \text{(L224b)}$$

$$\vec{j} = -2e\frac{N_k}{\mathcal{V}}\mathrm{Re}\left\langle \hat{c}^\dagger_{\vec{r}\uparrow}\left(\frac{\hat{P}}{m}+\frac{e\vec{A}}{mc}\right)\hat{c}_{\vec{r}\uparrow}\right\rangle \tag{L225}$$

$$= \frac{-e}{\mathcal{V}}\sum_{\vec{k}\vec{k}'}\left\langle \left(u^*_{\vec{k}'}(\vec{r})\hat{\gamma}^\dagger_{\vec{k}'\uparrow}+v_{\vec{k}'}(\vec{r})\hat{\gamma}_{\vec{k}\downarrow}\right)\left(\frac{\hat{P}}{m}+\frac{e\vec{A}}{mc}\right)\left(u_{\vec{k}}(\vec{r})\hat{\gamma}_{\vec{k}\uparrow}+v^*_{\vec{k}}(\vec{r})\hat{\gamma}^\dagger_{\vec{k}\downarrow}\right)\right\rangle$$

$$+\mathrm{c.c.} \tag{L226}$$

$$= \frac{-e}{\mathcal{V}}\sum_{\vec{k}}v_{\vec{k}}(\vec{r})\left[\frac{\hbar\vec{\nabla}}{im}+\frac{e\vec{A}}{mc}\right]v^*_{\vec{k}}(\vec{r})+\mathrm{c.c.}. \tag{L227}$$

$$\sum_{\vec{k}}v_{\vec{k}}v^*_{\vec{k}} = \frac{1}{2}\sum_{\vec{k}}\frac{\mathcal{E}_{\vec{k}}-\zeta_{\vec{k}}}{\mathcal{E}_{\vec{k}}} = N/2, \tag{L228}$$

$$\vec{j} = \vec{j}^1 - \frac{ne^2\vec{A}}{mc}, \tag{L229}$$

$$\vec{j}^1 = -e\frac{1}{\mathcal{V}}\sum_{\vec{k}}v_{\vec{k}}\frac{\hbar\vec{\nabla}}{im}v^*_{\vec{k}}(\vec{r})+\mathrm{c.c.} \tag{L230}$$

Derivation of Meissner Effect

$$\vec{j}^1 = -\frac{e\hbar}{\mathcal{V}m}\sum_{\vec{k}\vec{k}'} v_{\vec{k}} v_{\vec{k}}^{(1)*}(\vec{k}')\left(\vec{k}+\vec{k}'\right)e^{i(\vec{k}'-\vec{k})\cdot\vec{r}} + v_{\vec{k}}^* v_{\vec{k}}^{(1)}(\vec{k}')\left(\vec{k}+\vec{k}'\right)e^{-i(\vec{k}'-\vec{k})\cdot\vec{r}}. \quad \text{(L231)}$$

$$\begin{aligned}\vec{j}^1 \quad = \quad & \frac{-e\hbar}{m\mathcal{V}}\sum_{\vec{k}\vec{k}'} \quad \left(\vec{k}+\vec{k}'\right)e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}\frac{F_{\vec{k}'\vec{k}}}{\mathcal{E}_{\vec{k}}^2-\mathcal{E}_{\vec{k}'}^2}\left[(\mathcal{E}_{\vec{k}}-\zeta_{\vec{k}'})\left(\frac{\mathcal{E}_{\vec{k}}-\zeta_{\vec{k}}}{2\mathcal{E}_{\vec{k}}}\right)+\frac{\Delta^*\Delta}{2\mathcal{E}_{\vec{k}}}\right] \\ & + \quad \left(\vec{k}+\vec{k}'\right)e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}}\frac{F^*_{\vec{k}'\vec{k}}}{\mathcal{E}_{\vec{k}}^2-\mathcal{E}_{\vec{k}'}^2}\left[(\mathcal{E}_{\vec{k}}-\zeta_{\vec{k}'})\left(\frac{\mathcal{E}_{\vec{k}}-\zeta_{\vec{k}}}{2\mathcal{E}_{\vec{k}}}\right)+\frac{\Delta\Delta^*}{2\mathcal{E}_{\vec{k}}}\right]\end{aligned} \quad \text{(L232)}$$

$$= \quad \frac{-e\hbar}{m\mathcal{V}}\sum_{\vec{k}\vec{k}'}\left(\vec{k}+\vec{k}'\right)e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}F_{\vec{k}'\vec{k}}L(\zeta_{\vec{k}},\zeta_{\vec{k}'}), \quad \text{(L233)}$$

$$L(\zeta_{\vec{k}},\zeta_{\vec{k}'}) = \frac{\mathcal{E}_{\vec{k}}\mathcal{E}_{\vec{k}'}-\zeta_{\vec{k}}\zeta_{\vec{k}'}-\Delta^*\Delta}{2(\mathcal{E}_{\vec{k}}+\mathcal{E}_{\vec{k}'})\mathcal{E}_{\vec{k}}\mathcal{E}_{\vec{k}'}}. \quad \text{(L234)}$$

Derivation of Meissner Effect

$$\sigma_{\alpha\beta}(\zeta,\zeta',\vec{R}) = \frac{2\pi\hbar}{2\mathcal{V}^2}\left(\frac{e\hbar}{m}\right)^2 \sum_{\vec{k}\vec{k}'} \delta(\zeta_{\vec{k}}-\zeta)\delta(\zeta_{\vec{k}'}-\zeta')\,(k_\alpha+k'_\alpha)\,(k_\beta+k'_\beta)\,e^{i(\vec{k}-\vec{k}')\cdot\vec{R}}. \tag{L235}$$

$$\vec{j}^1_\alpha(\vec{r}) = \frac{1}{2\pi\hbar c}\sum_\beta \int d\vec{r}'\,d\zeta\,d\zeta'\,L(\zeta,\zeta')\sigma_{\alpha\beta}(\zeta,\zeta',\vec{r}-\vec{r}')A_\beta(\vec{r}'). \tag{L236}$$

$$Q(\zeta,\vec{r}) \quad = \quad \frac{1}{\mathcal{V}}\sum_{\vec{k}} \delta(\zeta_{\vec{k}}-\zeta)e^{-i\vec{k}\cdot\vec{r}} \approx \frac{D(\mathcal{E}_F)\sin\sqrt{2m\zeta/\hbar^2}r}{2k_F r}, \tag{L237}$$

$$\sigma_{\alpha\beta}(\zeta,\zeta',\vec{R}) \quad = \quad -\frac{2\pi\hbar}{2}\left(\frac{e\hbar}{m}\right)^2 \frac{\partial}{\partial a_\alpha}\frac{\partial}{\partial a_\beta} Q(\zeta,\vec{R}-\vec{a})Q(\zeta',-(\vec{R}+\vec{a})\Big|_{\vec{a}=0} \tag{L238}$$

$$\approx \quad e^2\frac{v_F}{2\pi}D(\mathcal{E}_F)\frac{R_\alpha R_\beta}{R^4}\cos\left[\frac{(\zeta-\zeta')R}{\hbar v_F}\right]. \tag{L239}$$

$$j^1_\alpha(\vec r) = \sum_\beta \int d\vec r' S^1_{\alpha\beta}(\vec r - \vec r')A_\beta(\vec r'), \tag{L240}$$

$$S^1_{\alpha\beta}(\vec R) = \frac{3ne^2}{4\pi^2 mc\hbar v_F}\frac{R_\alpha R_\beta}{R^4}\int d\zeta\, d\zeta' L(\zeta,\zeta')\cos\left[\frac{(\zeta-\zeta')R}{\hbar v_F}\right]. \tag{L241}$$

$$\xi = \frac{\hbar v_F}{\pi\Delta}. \tag{L242}$$

$$j_\alpha(\vec r) \;=\; \sum_\beta \int d\vec r'\, S_{\alpha\beta}(\vec r - \vec r')A_\beta(\vec r') \tag{L243a}$$

with

$$S_{\alpha\beta}(\vec R) \;=\; \frac{-3ne^2}{4\pi mc\xi}\frac{R_\alpha R_\beta}{R^4} I(R) \tag{L243b}$$

and

Derivation of Meissner Effect

$$I(R) = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{dy'}{\cosh y'} \exp\left[-\frac{2R}{\pi\xi}\cosh y'\right]. \quad \text{(L243c)}$$

$$\vec{j}(\vec{r}) = \frac{-ne^2}{mc}\vec{A}(\vec{r}). \quad \text{(L244)}$$

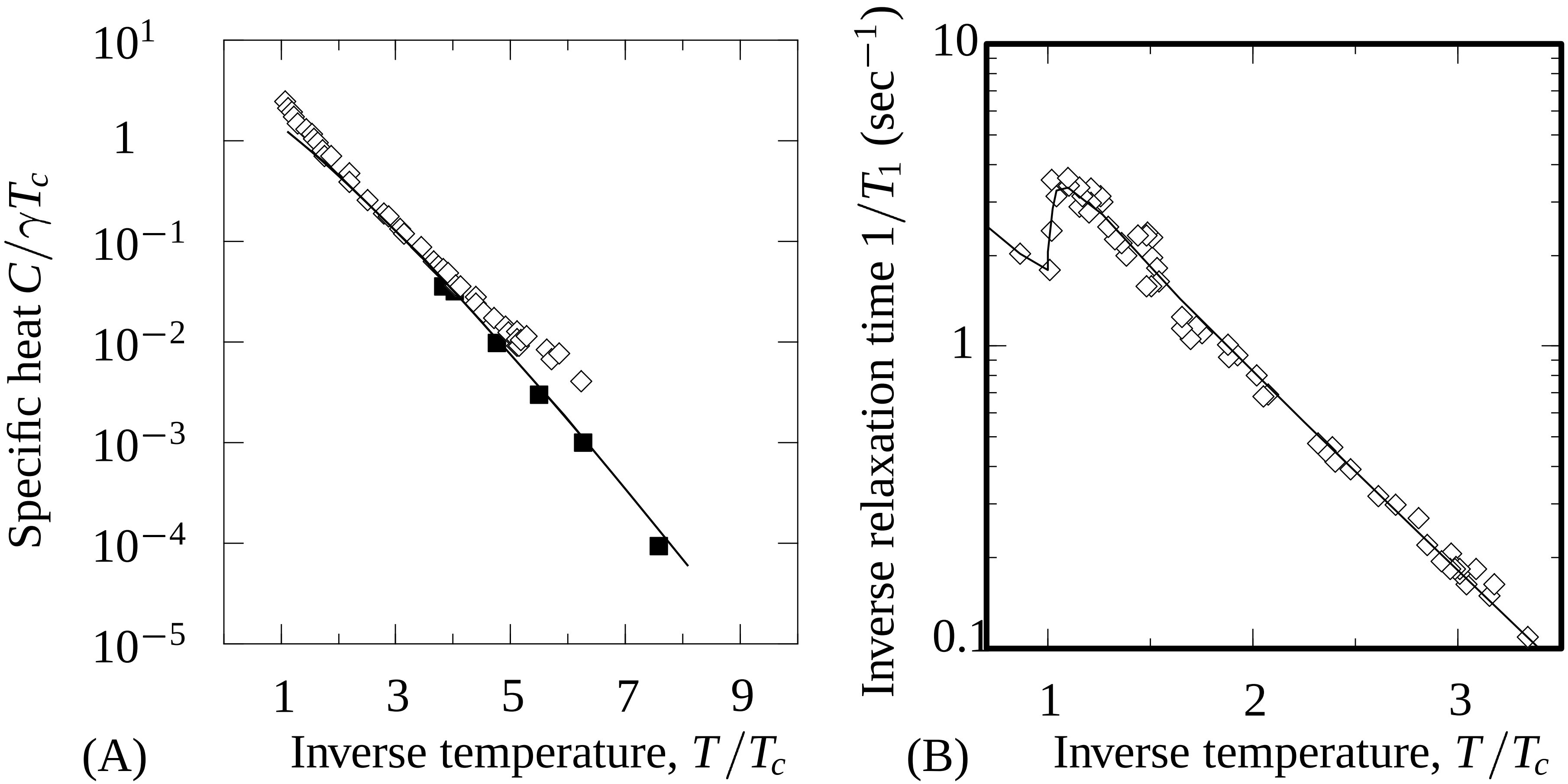


Figure 11: (A) Specific heat of aluminum and vanadium, relative to γT_c, where γ is the Sommerfeld parameter. [Boorse (1959)] (B) Inverse nuclear spin relaxation in aluminum compared with prediction of Bardeen, Cooper, and Schrieffer. [Masuda and Redfield (1962),]

Comparison with Experiment

$$\lambda_{\rm ep} = -D(\mathcal{E}_F)\left\langle \frac{2|C_{\vec{k}-\vec{k}'}|^2\hbar\omega_{\vec{k}-\vec{k}'}}{(\epsilon_{\vec{k}}-\epsilon_{\vec{k}'})^2-\hbar^2\omega^2_{\vec{k}-\vec{k}'}}\right\rangle, \quad \mu^* = D(\mathcal{E}_F)\left\langle \frac{4\pi e^2}{|\vec{k}-\vec{k}'|^2+\kappa_{\rm c}^2}\right\rangle. \qquad \text{(L245)}$$

$$T_c = \frac{\Theta_D}{1.45}\exp\left\{-\left[\frac{(1+\lambda_{\rm ep})}{\lambda_{\rm ep}-\mu^*(1+0.62\lambda_{\rm ep})}\right]\right\}, \qquad \text{(L246)}$$

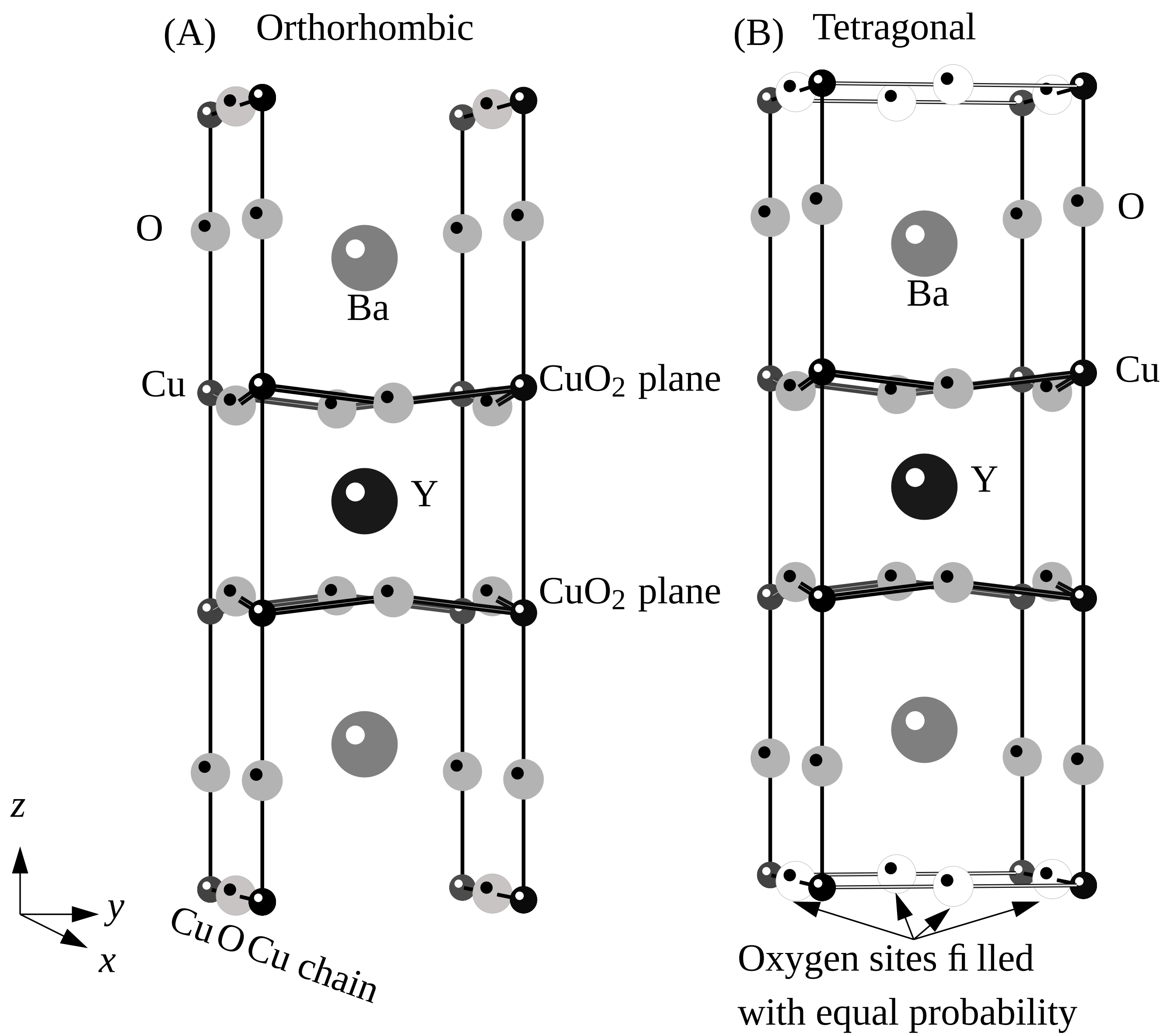


Figure 12: Structure of $YBa_2Cu_3O_x$, [Poole et al. (1988)] (A) Orthorhombic structure. (B) Tetragonal structure.

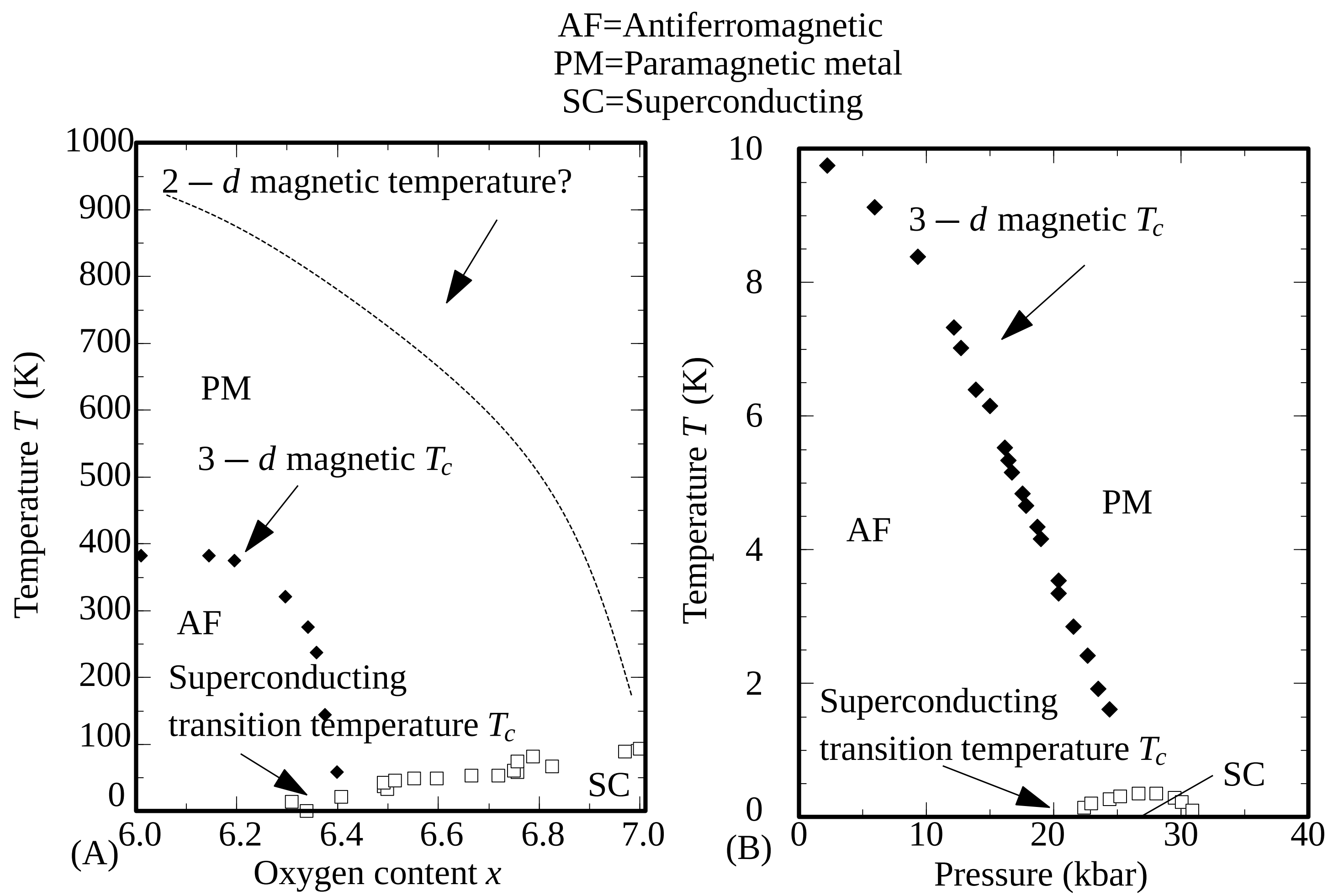


Figure 13: (A) Phase diagram for YBCO [Rossat-Mignod et al. (1990) and Greene and Bagley (1990)] (B) Heavy-fermion compound $CePd_2Si_2$.[Mathur et al. (1998).]

$$\vec{A} \to \vec{A} + \vec{\nabla}\chi \text{ as } \Psi \to \Psi e^{-2ie\chi/\hbar c}. \tag{L247}$$

$$u_{\vec{k}}(\vec{r}) \to u_{\vec{k}}(\vec{r})e^{-ie\chi/\hbar c}, v_{\vec{k}}(\vec{r}) \to v_{\vec{k}}(\vec{r})e^{ie\chi/\hbar c}, \quad \text{and} \quad \Delta_{\vec{r}} \to \Delta_{\vec{r}}e^{-2ie\chi/\hbar c}. \tag{L248}$$

$$\Delta_{\vec{k}\vec{q}} = \sum_{\vec{k}'} \frac{U_{\vec{k}\vec{k}'}}{\mathcal{V}} \left\langle \hat{c}_{\vec{q}-\vec{k}'\downarrow}\hat{c}_{\vec{k}'\uparrow} \right\rangle. \tag{L249}$$

$$\Delta_{\vec{r}\vec{r}'} = \sum_{\vec{r}''} \frac{U_{\vec{r}\vec{r}''}}{\mathcal{V}} \left\langle \hat{c}_{-\vec{r}'\downarrow}\hat{c}_{\vec{r}''-\vec{r}'\uparrow} \right\rangle. \tag{L250}$$

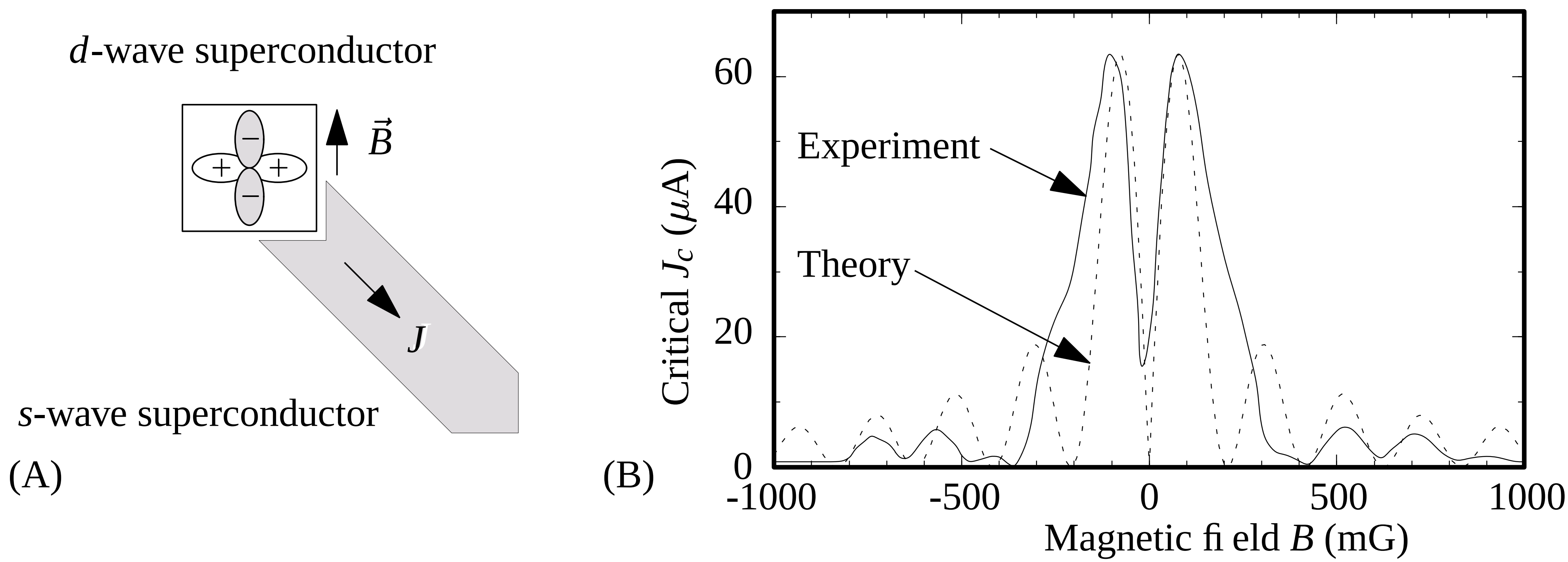
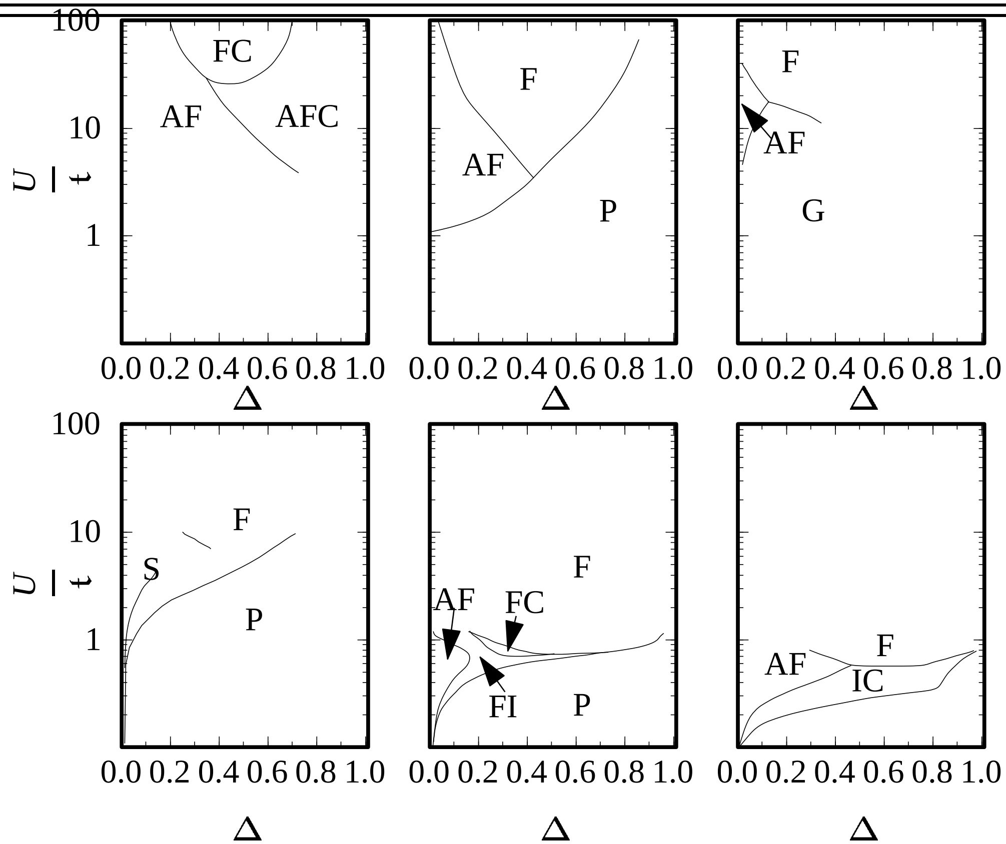


Figure 14: *d*–wave pairing. (A) Sketch of the experiment (B) Diffraction pattern. [Wollman et al. (1995)]

Quantum Mechanics of Interacting Magnetic Moments



F=Ferromagnetic

FC=Short-range ferromagnetic correlations

AF=Antiferromagnetic

AFC=Short-range antiferromagnetic correlations

P=Paramagnetic

FI=Ferrimagnetic

IC=Incommensurate, S=Spiral

G=Correlated state of Gutzwiller type

Definitions

- Heitler–London Calculation for Ferromagnetism
- Heisenberg Model of Ferromagnets
- Néel State
- Indirect Exchange
- Spin Waves
- Schwinger Bosons
- Holstein–Primakoff Transformation
- Stoner Model
- Anderson Model
- Kondo Effect and Scaling Theory
- Hubbard Model

Weakness of Magnetic Dipole Moments

$$\vec{B} = \vec{\nabla}\left[\vec{m}_1 \cdot \vec{\nabla}\frac{1}{r}\right] = \frac{3\hat{r}(\vec{m}_1 \cdot \hat{r}) - \vec{m}_1}{r^3}, \tag{L1}$$

$$\frac{\vec{m}_1 \cdot \vec{m}_2 - 3(\vec{m}_2 \cdot \hat{r}_{12})(\vec{m}_1 \cdot \hat{r}_{12})}{r_{12}^3}, \tag{L2}$$

$$\frac{1}{4}\frac{m_1}{\mu_B}\frac{m_2}{\mu_B}\left(\frac{2a_0}{r_{12}}\right)^3 \frac{\mu_B^2}{a_0^3} = 0.9 \cdot 10^{-4}\,\text{eV} \cdot \frac{m_1}{\mu_B}\frac{m_2}{\mu_B}\left(\frac{2a_0}{r_{12}}\right)^3. \tag{L3}$$

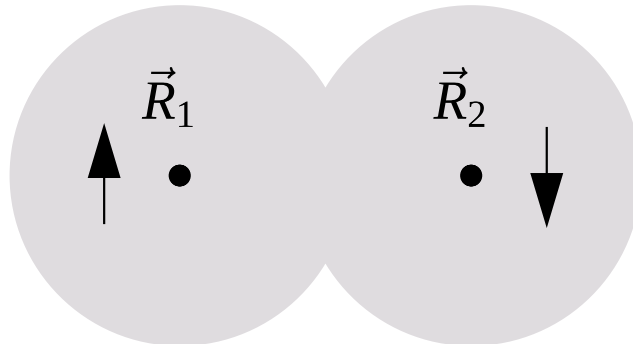


Figure 1: Setting for the calculation of Heitler and London (1927).

$$l \equiv \| \int d\vec{r}\, \phi_1^*(\vec{r})\phi_2(\vec{r}) \| \tag{L4}$$

Singlet:

$$\frac{1}{\sqrt{2}}\left(\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2) - \chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)\right), \tag{L5a}$$

Triplet:

$$\begin{aligned} &\chi_\uparrow(\sigma_1)\chi_\uparrow(\sigma_2) && S=1 \quad ;S_z=1 \\ &\frac{1}{\sqrt{2}}\left(\chi_\uparrow(\sigma_1)\chi_\downarrow(\sigma_2)+\chi_\downarrow(\sigma_1)\chi_\uparrow(\sigma_2)\right) && S=1 \quad ;S_z=0 \\ &\chi_\downarrow(\sigma_1)\chi_\downarrow(\sigma_2) && S=1 \quad ;S_z=-1. \end{aligned} \tag{L6a}$$

$$\phi_s(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2+2l^2}}[\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)+\phi_1(\vec{r}_2)\phi_2(\vec{r}_1)], \tag{L7a}$$

$$\phi_t(\vec{r}_1,\vec{r}_2) = \frac{1}{\sqrt{2-2l^2}}[\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)-\phi_1(\vec{r}_2)\phi_2(\vec{r}_1)]. \tag{L7b}$$

$$\left[\frac{\hat{P}_1^2}{2m}-\frac{e^2}{|\vec{r}_1-\vec{R}_1|}\right]\phi_1(\vec{r}_1)=\mathcal{E}_0\phi_1(\vec{r}_1). \tag{L8}$$

$$\hat{\mathcal{H}} = \frac{\hat{P}_1^2}{2m} - \frac{e^2}{|\vec{r}_1 - \vec{R}_1|} + \frac{\hat{P}_2^2}{2m} - \frac{e^2}{|\vec{r}_2 - \vec{R}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{|\vec{R}_1 - \vec{R}_2|} - \frac{e^2}{|\vec{r}_1 - \vec{R}_2|} - \frac{e^2}{|\vec{r}_2 - \vec{R}_1|}. \quad \text{(L9)}$$

$$\int d\vec{r}_1 d\vec{r}_2\, \phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2)\hat{\mathcal{H}}\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)$$

$$= \int d\vec{r}_1 d\vec{r}_2\, \phi_2^*(\vec{r}_1)\phi_1^*(\vec{r}_2)\hat{\mathcal{H}}\phi_2(\vec{r}_1)\phi_1(\vec{r}_2) \quad \text{(L10)}$$

$$= 2\mathcal{E}_0 + U, \quad \text{(L11)}$$

where

$$U = \int d\vec{r}_1 d\vec{r}_2 \begin{bmatrix} |\phi_1(\vec{r}_1)|^2 \\ |\phi_2(\vec{r}_2)|^2 \end{bmatrix} \left[\frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{|\vec{R}_1 - \vec{R}_2|} - \frac{e^2}{|\vec{r}_1 - \vec{R}_2|} - \frac{e^2}{|\vec{r}_2 - \vec{R}_1|}\right], \quad \text{(L12)}$$

and

$$\begin{aligned}
& \int d\vec{r}_1 d\vec{r}_2\, \phi_2^*(\vec{r}_1)\phi_1^*(\vec{r}_2)\hat{\mathcal{H}}\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) \\
= & \int d\vec{r}_1 d\vec{r}_2\, \phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2)\hat{\mathcal{H}}\phi_2(\vec{r}_1)\phi_1(\vec{r}_2) \quad \text{(L13)} \\
= & \; 2\mathcal{E}_0 l^2 + V, \quad \text{(L14)}
\end{aligned}$$

with

$$V = \int d\vec{r}_1 d\vec{r}_2 \left[\begin{array}{c} \phi_1^*(\vec{r}_1)\phi_2^*(\vec{r}_2) \\ \phi_2(\vec{r}_1)\phi_1(\vec{r}_2) \end{array} \right] \left[\frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \frac{e^2}{|\vec{R}_1 - \vec{R}_2|} - \frac{e^2}{|\vec{r}_1 - \vec{R}_1|} - \frac{e^2}{|\vec{r}_2 - \vec{R}_2|} \right]. \quad \text{(L15)}$$

$$\mathcal{E}_s = \langle \phi_s | \hat{\mathcal{H}} | \phi_s \rangle = 2 \frac{2\mathcal{E}_0 + U + 2l^2\mathcal{E}_0 + V}{2 + 2l^2} = 2\mathcal{E}_0 + \frac{U + V}{1 + l^2} \quad \text{(L16a)}$$

and

Heitler–London Calculation

$$\mathcal{E}_t = \langle\phi_t|\hat{\mathcal{H}}|\phi_t\rangle = 2\frac{2\mathcal{E}_0 + U - 2l^2\mathcal{E}_0 - V}{2-2l^2} = 2\mathcal{E}_0 + \frac{U-V}{1-l^2} \quad \text{(L16b)}$$

$$\mathcal{E}_t - \mathcal{E}_s = \frac{2l^2U - 2V}{1-l^4} \equiv -J. \quad \text{(L17)}$$

$$\mathcal{F}\{\phi\} = \frac{\int d\vec{r}_1 d\vec{r}_2 \, \frac{\hbar^2}{2m}|\nabla_1\phi|^2 + \frac{\hbar^2}{2m}|\nabla_2\phi|^2 + U(\vec{r}_1,\vec{r}_2)|\phi(\vec{r}_1,\vec{r}_2)|^2}{\int d\vec{r}_1 d\vec{r}_2 \, |\phi(\vec{r}_1,\vec{r}_2)|^2}. \quad \text{(L18)}$$

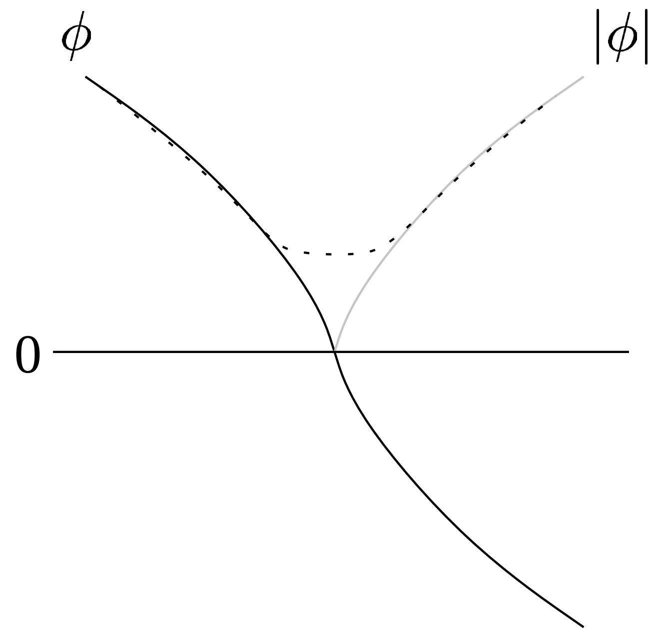


Figure 2: The energy of a wave function with a cusp is always lowered by smoothing out the cusp.

$$\hat{\mathcal{H}} = a + b\hat{S}_1 \cdot \hat{S}_2 \tag{L19}$$

$$= a + b\left(\hat{S}_1^z \hat{S}_2^z + \frac{1}{2}[\hat{S}_1^+ \hat{S}_2^- + \hat{S}_2^+ \hat{S}_1^-]\right). \tag{L20}$$

$$\hat{\mathcal{H}} = 2\mathcal{E}_0 + \frac{U-V}{1-l^2} + \left(\frac{1}{4} - \hat{S}_1 \cdot \hat{S}_2\right) J. \tag{L21}$$

Heisenberg Model

$$\hat{\mathcal{H}} = -\sum_{\langle ll' \rangle} J_{ll'} \hat{S}_l \cdot \hat{S}_{l'}. \tag{L22}$$

$$\sum_{l=1}^{N} \frac{\hat{P}_l^2}{2m} + \hat{U} = \hat{\mathcal{H}}_{\text{kinetic}} + \hat{\mathcal{H}}_{\text{int}}, \tag{L23}$$

$$\hat{\mathcal{H}}_{\text{int}} = \sum_{\substack{ll'l''l''' \\ \sigma\sigma'}} \langle \vec{R}_l \vec{R}_{l'} | \hat{U} | \vec{R}_{l''} \vec{R}_{l'''} \rangle \hat{c}^\dagger_{l\sigma} \hat{c}^\dagger_{l'\sigma'} \hat{c}_{l'''\sigma'} \hat{c}_{l''\sigma}. \tag{L24}$$

$$\hat{\mathcal{H}}_{\text{int}} = \sum_{\substack{ll' \\ \sigma\sigma'}} \begin{array}{l} \langle \vec{R}_l \vec{R}_{l'} | \hat{U} | \vec{R}_l \vec{R}_{l'} \rangle \hat{c}^\dagger_{l\sigma} \hat{c}^\dagger_{l'\sigma'} \hat{c}_{l'\sigma'} \hat{c}_{l\sigma} \\ + \; \langle \vec{R}_l \vec{R}_{l'} | \hat{U} | \vec{R}_{l'} \vec{R}_l \rangle \hat{c}^\dagger_{l\sigma} \hat{c}^\dagger_{l'\sigma'} \hat{c}_{l\sigma'} \hat{c}_{l'\sigma} \end{array} \tag{L25}$$

$$= \sum_{\substack{ll' \\ \sigma\sigma'}} \begin{array}{l} \langle \vec{R}_l \vec{R}_{l'} | \hat{U} | \vec{R}_l \vec{R}_{l'} \rangle \hat{c}^\dagger_{l\sigma} \hat{c}^\dagger_{l'\sigma'} \hat{c}_{l'\sigma'} \hat{c}_{l\sigma} \\ + \; \langle \vec{R}_l \vec{R}_{l'} | \hat{U} | \vec{R}_{l'} \vec{R}_l \rangle [\hat{n}_{l\sigma} \delta_{ll'} - \hat{c}^\dagger_{l\sigma} \hat{c}_{l\sigma'} \hat{c}^\dagger_{l'\sigma'} \hat{c}_{l'\sigma}]. \end{array} \tag{L26}$$

Heisenberg Model

$$\hat{S}^z = \frac{1}{2}[\hat{c}^\dagger_\uparrow \hat{c}_\uparrow - \hat{c}^\dagger_\downarrow \hat{c}_\downarrow] = \frac{1}{2}[\hat{n}_\uparrow - \hat{n}_\downarrow] \tag{L27a}$$

$$\hat{S}^+ = \hat{c}^\dagger_\uparrow c_\downarrow; \;\; \hat{S}^- = \hat{c}^\dagger_\downarrow c_\uparrow. \tag{L27b}$$

$$\hat{n}_{l\uparrow}\hat{n}_{l'\uparrow} + \hat{n}_{l\downarrow}\hat{n}_{l'\downarrow} \tag{L28}$$

$$= \frac{1}{2}\left\{(\hat{n}_{l\uparrow} + \hat{n}_{l\downarrow})(\hat{n}_{l'\uparrow} + \hat{n}_{l'\downarrow}) + (\hat{n}_{l\uparrow} - \hat{n}_{l\downarrow})(\hat{n}_{l'\uparrow} - \hat{n}_{l'\downarrow})\right\} \tag{L29}$$

$$= \frac{1}{2}\left\{1 + 4\hat{S}^z_l \cdot \hat{S}^z_{l'}\right\}. \tag{L30}$$

$$\hat{\mathcal{H}}_{\text{exch}} = -\langle \vec{R}_l \vec{R}_{l'} | \hat{U} | \vec{R}_{l'} \vec{R}_l \rangle \left\{ \begin{array}{rl} & \hat{n}_{l\uparrow}\hat{n}_{l'\uparrow} + \hat{c}^\dagger_{l\uparrow}\hat{c}_{l\downarrow} c^\dagger_{l'\downarrow}\hat{c}_{l'\uparrow} \\ + & \hat{c}^\dagger_{l\downarrow}\hat{c}_{l\uparrow} c^\dagger_{l'\uparrow}\hat{c}_{l'\downarrow} + \hat{n}_{l\downarrow}\hat{n}_{l'\downarrow} \end{array} \right\} \tag{L31}$$

$$= -2\langle \vec{R}_l \vec{R}_{l'} | \hat{U} | \vec{R}_{l'} \vec{R}_l \rangle \left\{ \frac{1}{4} + \hat{S}^z_l \hat{S}^z_{l'} + \frac{1}{2}[\hat{S}^+_l \hat{S}^-_{l'} + \hat{S}^-_l \hat{S}^+_{l'}] \right\} \tag{L32}$$

$$= \quad -2\langle \vec{R}_l \vec{R}_{l'} | \hat{U} | \vec{R}_{l'} \vec{R}_l \rangle \left\{ \frac{1}{4} + \hat{S}_l \cdot \hat{S}_{l'} \right\}, \tag{L33}$$

$$-4 \sum_{\langle ll' \rangle} \langle \vec{R}_l \vec{R}_{l'} | \hat{U} | \vec{R}_{l'} \vec{R}_l \rangle \hat{S}_l \cdot \hat{S}_{l'} \tag{L34}$$

Ground State

$$\langle \uparrow\uparrow\uparrow \ldots | \hat{\mathcal{H}} | \uparrow\uparrow\uparrow \ldots \rangle = -\sum_{\langle ll' \rangle} \frac{J_{ll'}}{4}. \tag{L35}$$

$$\hat{S}^{\alpha} = \frac{1}{2}\sum_{ll'} a_l^{\dagger}\sigma_{ll'}^{\alpha}a_{l'}. \tag{L36}$$

$$\hat{S}^{z} = \frac{1}{2}\left(\hat{a}_1^{\dagger}\hat{a}_1 - \hat{a}_2^{\dagger}\hat{a}_2\right) \tag{L37a}$$

$$\hat{S}^{x} = \frac{1}{2}\left(\hat{a}_1^{\dagger}\hat{a}_2 + \hat{a}_2^{\dagger}\hat{a}_1\right) \tag{L37b}$$

$$\hat{S}^{y} = i\frac{1}{2}\left(\hat{a}_2^{\dagger}\hat{a}_1 - \hat{a}_1^{\dagger}\hat{a}_2\right). \tag{L37c}$$

$$\begin{aligned} \left[\hat{S}^x, \hat{S}^y\right] &= i\frac{1}{4}\left[\hat{a}_1^{\dagger}\hat{a}_2 + \hat{a}_2^{\dagger}\hat{a}_1, \hat{a}_2^{\dagger}\hat{a}_1 - \hat{a}_1^{\dagger}\hat{a}_2\right] \\ &= i\hat{S}^z. \end{aligned} \tag{L38}$$

$$\hat{S}^{+} = \hat{a}_1^{\dagger}\hat{a}_2;\ \hat{S}^{-} = \hat{a}_2^{\dagger}\hat{a}_1. \tag{L39}$$

$$\frac{1}{2}\left(\hat{a}_1^\dagger \hat{a}_1 + \hat{a}_2^\dagger \hat{a}_2\right) = S. \tag{L40}$$

$$\hat{a}_2^\dagger \hat{a}_2 = 2S - \hat{a}_1^\dagger \hat{a}_1 \tag{L41}$$

$$\hat{a}_2 = \sqrt{2S - \hat{a}_1^\dagger \hat{a}_1}. \tag{L42}$$

$$\hat{S}^+ = a_1^\dagger \sqrt{2S - \hat{a}_1^\dagger \hat{a}_1} \tag{L43a}$$

$$\hat{S}^- = \sqrt{2S - \hat{a}_1^\dagger \hat{a}_1}\,\hat{a}_1 \tag{L43b}$$

$$\hat{S}^z = (\hat{a}_1^\dagger \hat{a}_1 - S). \tag{L43c}$$

$$[\hat{S}^+, \hat{S}^-] = 2\hat{S}^z. \tag{L44}$$

$$\hat{S}_l \cdot \hat{S}_{l'} = \frac{1}{2}\left(\hat{S}_l^+ \hat{S}_{l'}^- + \hat{S}_{l'}^+ \hat{S}_l^-\right) + \hat{S}_l^z \hat{S}_{l'}^z \quad \text{(L45)}$$

$$\begin{aligned} &= \frac{1}{2}\hat{a}_l^\dagger \sqrt{2S - \hat{a}_l^\dagger \hat{a}_l}\sqrt{2S - \hat{a}_{l'}^\dagger \hat{a}_{l'}}\hat{a}_{l'} \\ &+ \frac{1}{2}\hat{a}_{l'}^\dagger \sqrt{2S - \hat{a}_{l'}^\dagger \hat{a}_{l'}}\sqrt{2S - \hat{a}_l^\dagger \hat{a}_l}\hat{a}_l + (S - \hat{a}_l^\dagger \hat{a}_l)(S - \hat{a}_{l'}^\dagger \hat{a}_{l'}). \end{aligned} \quad \text{(L46)}$$

$$\hat{a}_l = \sqrt{S} b_l + \left(\hat{a}_l - \sqrt{S} b_l\right), \quad \text{(L47)}$$

$$\hat{\mathcal{H}} = -\sum_{ll'} J_{ll'} S^2 \left[\begin{array}{r} \frac{1}{2}\left(b_l b_{l'}^* + b_{l'} b_l^*\right)\sqrt{2 - |b_l|^2}\sqrt{2 - |b_{l'}|^2} \\ +\left(1 - |b_l|^2\right)\left(1 - |b_{l'}|^2\right) \end{array} \right]. \quad \text{(L48)}$$

$$\mathcal{E}_0 = -JNzS^2\left(|b|^2(2 - |b|^2) + (1 - |b|^2)^2\right) = -JNzS^2, \quad \text{(L49)}$$

$$\hat{\mathcal{H}} \approx -NJzS^2 - 2J\sum_{\langle ll' \rangle} S\left(\hat{a}_l^\dagger \hat{a}_{l'} + \hat{a}_{l'}^\dagger \hat{a}_l - \hat{a}_l^\dagger \hat{a}_l - \hat{a}_{l'}^\dagger \hat{a}_{l'}\right). \quad \text{(L50)}$$

$$\hat{a}_l = \frac{1}{\sqrt{N}} \sum_{\vec{k}} \hat{a}_k e^{-i\vec{k}\cdot\vec{r}_l} \tag{L52}$$

$$\hat{\mathcal{H}} = -NJzS^2 - 2JS \sum_{\vec{k}} \sum_{\vec{\delta}} \left[\cos\left(\vec{k}\cdot\vec{\delta}\right) - 1\right] \hat{a}^{\dagger}_{\vec{k}} \hat{a}_{\vec{k}} \tag{L53}$$

$$= -NJzS^2 + \sum_{\vec{k}} \hbar\omega_{\vec{k}} \hat{n}_{\vec{k}}, \tag{L54}$$

where

$$\hbar\omega = 2SJ \sum_{\vec{\delta}} \left(1 - \cos(\vec{\delta}\cdot\vec{k})\right), \tag{L55}$$

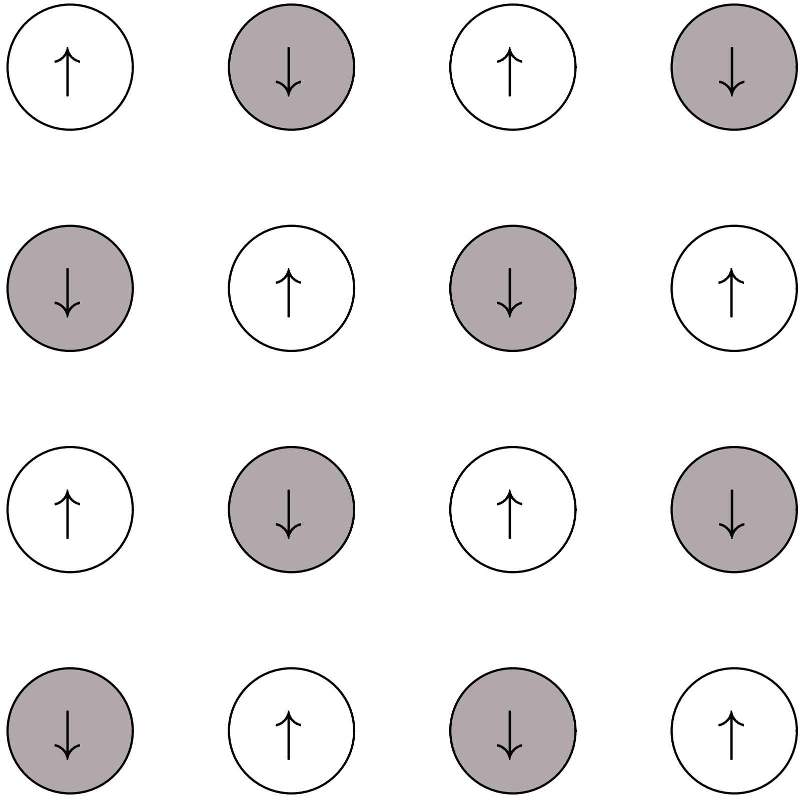


Figure 3: The Néel state.

$$S_{l'}^{\pm} \rightarrow S_{l'}^{\mp} \quad S_{l'}^{z} \rightarrow -S_{l'}^{z}. \tag{L56}$$

$$\hat{\mathcal{H}} = 2|J| \sum_{\langle ll' \rangle} \tfrac{1}{2} \left[\hat{S}_l^+ \hat{S}_{l'}^+ + \hat{S}_l^- \hat{S}_{l'}^- \right] - \hat{S}_l^z \hat{S}_{l'}^z \tag{L57}$$

$$= 2|J| \sum_{\langle ll' \rangle} \begin{array}{l} \tfrac{1}{2} \hat{a}_l^\dagger \sqrt{2S - \hat{a}_l^\dagger \hat{a}_l} \hat{a}_{l'}^\dagger \sqrt{2S - \hat{a}_{l'}^\dagger \hat{a}_{l'}} \\ + \tfrac{1}{2} \sqrt{2S - \hat{a}_l^\dagger \hat{a}_l} \hat{a}_l \sqrt{2S - \hat{a}_{l'}^\dagger \hat{a}_{l'}} \hat{a}_{l'} - (\hat{a}_l^\dagger \hat{a}_l - S)(\hat{a}_{l'}^\dagger \hat{a}_{l'} - S). \end{array} \tag{L58}$$

$$\hat{\mathcal{H}} \approx -Nz|J|S^2 \left[\left(1 - b^2\right)^2 - b^2 \left(2 - b^2\right) \right], \tag{L59}$$

$$b = 0. \tag{L60}$$

$$\hat{\mathcal{H}} \approx 2|J| \sum_{\langle ll' \rangle} \left[-S^2 + S \left\{ \hat{a}_l^\dagger \hat{a}_l + \hat{a}_{l'}^\dagger \hat{a}_{l'} + \hat{a}_l^\dagger \hat{a}_{l'}^\dagger + \hat{a}_l \hat{a}_{l'} \right\} \right]. \tag{L61}$$

$$\hat{a}_{\vec{k}} = \frac{1}{\sqrt{N}} \sum_l e^{i\vec{k}\cdot\vec{R}_l} \hat{a}_l \tag{L62}$$

$$\hat{\mathcal{H}} = -|J|NzS^2 + |J|S\sum_{\vec{k}\vec{\delta}}\left[\left(\hat{a}^\dagger_{\vec{k}}\hat{a}^\dagger_{-\vec{k}} + \hat{a}_{\vec{k}}\hat{a}_{-\vec{k}}\right)\cos(\vec{k}\cdot\vec{\delta}) + 2\hat{a}^\dagger_{\vec{k}}\hat{a}_{\vec{k}}\right]. \tag{L63}$$

$$\hat{a}_{\vec{k}} = \cosh\alpha_{\vec{k}}\,\hat{\gamma}_{\vec{k}} + \sinh\alpha_{\vec{k}}\,\hat{\gamma}^\dagger_{-\vec{k}}, \tag{L64}$$

$$\tanh 2\alpha_{\vec{k}} = -\frac{1}{z}\sum_{\vec{\delta}}\cos(\vec{k}\cdot\vec{\delta}). \tag{L65}$$

$$\hat{\mathcal{H}} = -Nz|J|S(S+1) + 2|J|zS\sum_{\vec{k}}\left(\hat{\gamma}^\dagger_{\vec{k}}\hat{\gamma}_{\vec{k}} + \frac{1}{2}\right)\sqrt{1-\tanh^2 2\alpha_{\vec{k}}}. \tag{L66}$$

$$-NS^2|J|z\left(1+\frac{\Gamma}{zS}\right). \tag{L67}$$

$$\mathcal{E}_{\vec{k}} = 2|J|S\sqrt{z^2 - (\textstyle\sum_{\vec{\delta}}\cos\vec{k}\cdot\vec{\delta})^2}. \tag{L68}$$

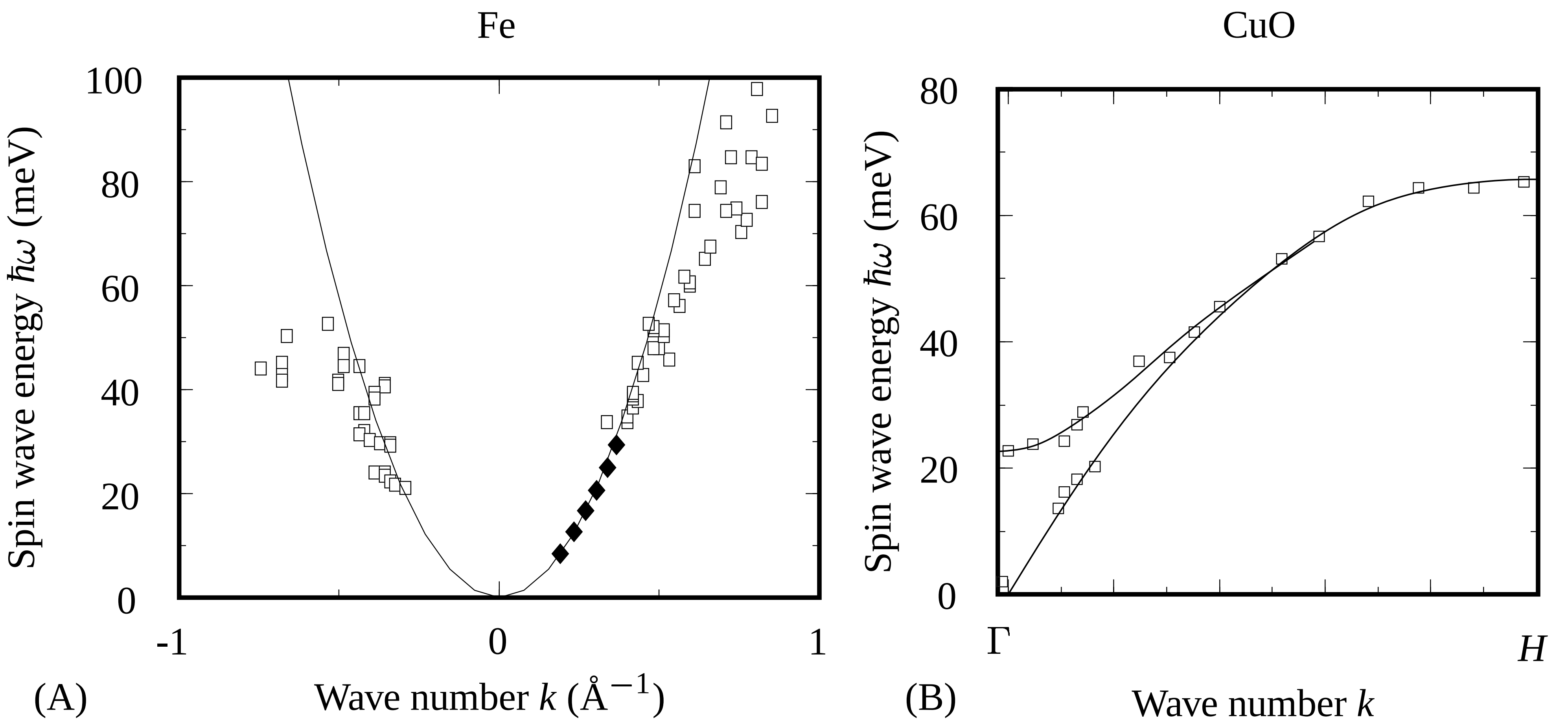


Figure 4: (A) Dispersion relation for ferromagnetic magnons in iron. [Yethiraj et al. (1991), and Lynn (1975),.] (B) Dispersion relation for antiferromagnetic magnons in CuO. [Aïn et al. (1989).]

Stoner Model

$$\mathcal{E} = \int_0^{\mathcal{E}_F - \Delta} d\mathcal{E}' D(\mathcal{E}')\mathcal{E}' + \frac{1}{2}\int_{\mathcal{E}_F-\Delta}^{\mathcal{E}_F+\Delta} d\mathcal{E}' D(\mathcal{E}')\mathcal{E}' - \frac{1}{2} nJ \langle S \rangle^2, \tag{L69}$$

$$\langle S \rangle = \frac{1}{2n}\int_{\mathcal{E}_F-\Delta}^{\mathcal{E}_F+\Delta} d\mathcal{E}' \frac{1}{2} D(\mathcal{E}') = \frac{1}{2n} D(\mathcal{E}_F)\Delta. \tag{L70}$$

$$\left.\frac{\partial \mathcal{E}}{\partial \Delta}\right|_{\mathcal{E}_F} = \Delta D(\mathcal{E}_F) - \frac{J}{4n} D(\mathcal{E}_F)^2 \Delta, \tag{L71}$$

$$\left.\frac{\partial \mathcal{E}}{\partial \Delta}\right|_{\mathcal{E}_F} = 0 \Rightarrow \frac{J}{n} D(\mathcal{E}_F) = 4. \tag{L72}$$

$$\mathcal{E} = \int_0^{\mathcal{E}_F - \Delta_1} d\mathcal{E}' D(\mathcal{E}')\mathcal{E}' + \frac{1}{2}\int_{\mathcal{E}_F-\Delta_1}^{\mathcal{E}_F+\Delta_2} d\mathcal{E}' D(\mathcal{E}')\mathcal{E}' - \frac{1}{2} Jn \langle S \rangle^2, \tag{L73}$$

$$\frac{\partial \Delta_2}{\partial \Delta_1} = \frac{D(\mathcal{E}_F - \Delta_1)}{D(\mathcal{E}_F + \Delta_2)}, \tag{L74}$$

$$\frac{\partial \mathcal{E}}{\partial \Delta_1} \leq 0 \tag{L75}$$

$$\Rightarrow \Delta_1 + \Delta_2 \leq \frac{J}{4n} \int_{\mathcal{E}_F - \Delta_1}^{\mathcal{E}_F + \Delta_2} d\mathcal{E}' D(\mathcal{E}'). \tag{L76}$$

$$\mathcal{E} = \mathcal{E}_\uparrow + \mathcal{E}_\downarrow \tag{L77}$$

where

$$\mathcal{E}_\uparrow = N_\uparrow \left[\frac{3}{5}\mathcal{E}_{F\uparrow} - \frac{3}{4}\frac{e^2 k_{F\uparrow}}{\pi} \right], \tag{L78}$$

$$\mathcal{E}_{F\uparrow} = \frac{\hbar^2 k_{F\uparrow}^2}{2m}, \text{ and } \frac{4\pi}{3}\frac{1}{(2\pi)^3} k_{F\uparrow}^3 = \frac{N_\uparrow}{\mathcal{V}}. \tag{L79}$$

$$\mathcal{E}_{\text{polarized}} = N \left[\frac{3}{5}\frac{\hbar^2}{2m}\left(6\pi^2 n\right)^{2/3} - \frac{3}{4\pi} e^2 \left(6\pi^2 n\right)^{1/3} \right], \tag{L80}$$

$$\mathcal{E}_{\text{unpolarized}} = N \left[\frac{3}{5}\frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3} - \frac{3}{4\pi} e^2 \left(3\pi^2 n\right)^{1/3} \right]. \tag{L81}$$

$$\frac{2\pi\hbar^2}{5m}\left(\frac{1}{2^{1/3}} + 1\right) < e^2 (6\pi^2 n)^{-1/3} \tag{L82}$$

$$\Rightarrow \quad \frac{r_W}{a_0} > \frac{2\pi}{5}\left(\frac{1}{2^{1/3}}+1\right)\left(\frac{9\pi}{2}\right)^{1/3} = 5.45. \tag{L83}$$

Element:	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Calculated m/μ_B (bcc):	0	0	0	0	0.70	2.15	1.68	0.38
Experimental m/μ_B (bcc):				0		2.12		
Calculated m/μ_B (fcc):	0	0	0	0	0	0	1.56	0.60
Experimental m/μ_B (fcc):							1.61	0.61

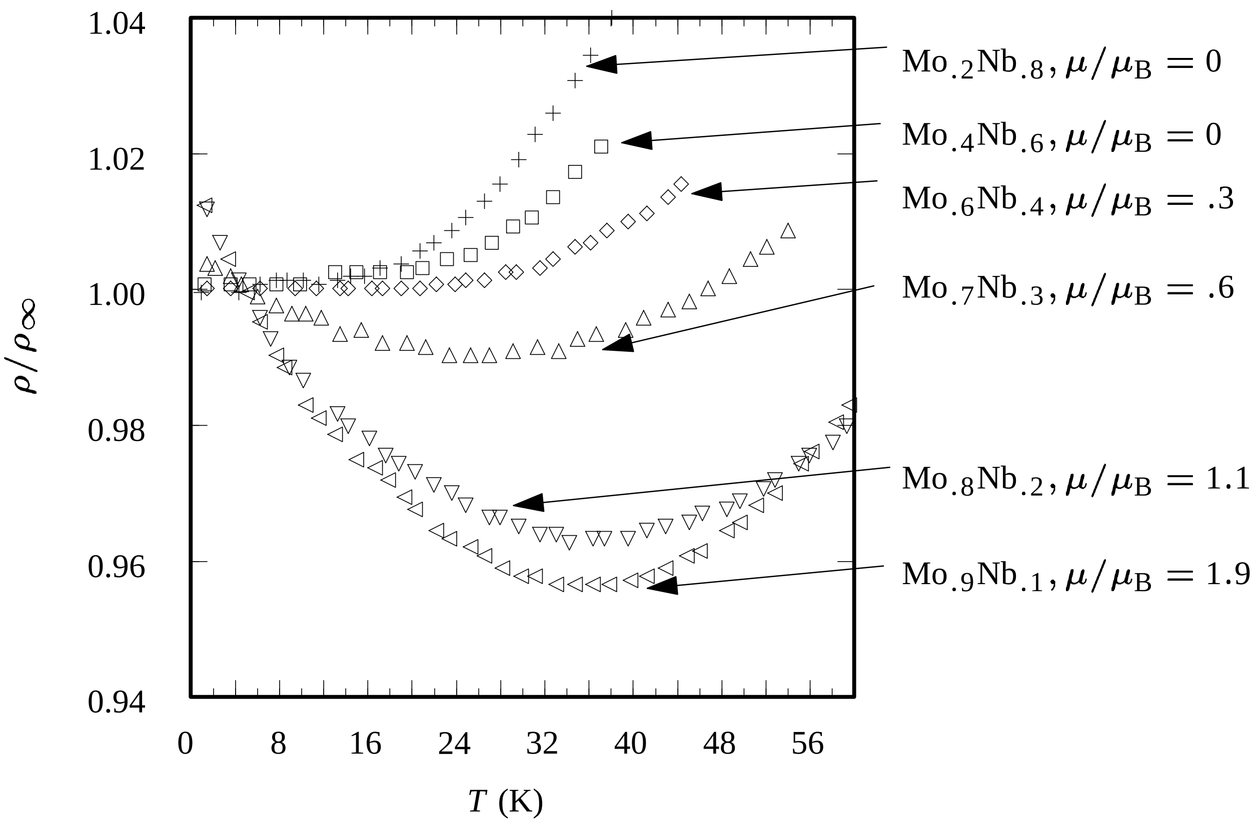


Figure 5: Resistivity data for Mo_xNb_{1-x} alloys. [Source: Sarachik et al. (1964).]

$$\hat{\mathcal{H}} = \epsilon_0[\hat{n}_{0\uparrow} + \hat{n}_{0\downarrow}] + U\hat{n}_{0\uparrow}\hat{n}_{0\downarrow} + \sum_{\vec{k}\sigma}[\epsilon_{\vec{k}}\hat{c}^\dagger_{\vec{k}\sigma}\hat{c}_{\vec{k}\sigma} + v_{\vec{k}}\hat{c}^\dagger_{0\sigma}\hat{c}_{\vec{k}\sigma} + v^*_{\vec{k}}\hat{c}^\dagger_{\vec{k}\sigma}\hat{c}_{0\sigma}]. \quad \text{(L84)}$$

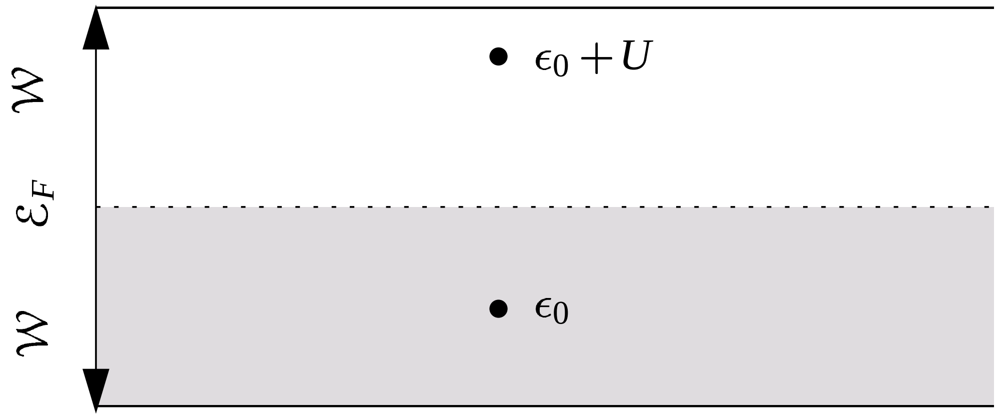


Figure 6: Conduction electrons placed in contact with an impurity site.

$$\hat{P}_0 = (1 - \hat{n}_{0\downarrow})(1 - \hat{n}_{0\uparrow}), \quad \text{(L85)}$$

$$|\psi_0\rangle = \hat{P}_0|\psi\rangle, \; |\psi_1\rangle = \hat{P}_1|\psi\rangle, \text{and} |\psi_2\rangle = \hat{P}_2|\psi\rangle. \quad \text{(L86)}$$

$$\hat{\mathcal{H}}_{ll'} = \hat{P}_l\hat{\mathcal{H}}\hat{P}_{l'} \quad \text{(L87)}$$

so $\hat{\mathcal{H}}|\psi\rangle = \mathcal{E}|\psi\rangle$ can be rewritten as

$$\begin{pmatrix} \hat{\mathcal{H}}_{00} & \hat{\mathcal{H}}_{01} & 0 \\ \hat{\mathcal{H}}_{10} & \hat{\mathcal{H}}_{11} & \hat{\mathcal{H}}_{12} \\ 0 & \hat{\mathcal{H}}_{21} & \hat{\mathcal{H}}_{22} \end{pmatrix} \begin{pmatrix} |\psi_0\rangle \\ |\psi_1\rangle \\ |\psi_2\rangle \end{pmatrix} = \mathcal{E} \begin{pmatrix} |\psi_0\rangle \\ |\psi_1\rangle \\ |\psi_2\rangle \end{pmatrix} \tag{L88}$$

$$\hat{\mathcal{H}}_{00}|\psi_0\rangle + \hat{\mathcal{H}}_{01}|\psi_1\rangle = \mathcal{E}|\psi_0\rangle \tag{L89}$$

$$\Rightarrow \qquad |\psi_0\rangle = \left(\mathcal{E} - \hat{\mathcal{H}}_{00}\right)^{-1} \hat{\mathcal{H}}_{01}|\psi_1\rangle \tag{L90}$$

$$\text{and} \qquad |\psi_2\rangle = \left(\mathcal{E} - \hat{\mathcal{H}}_{22}\right)^{-1} \hat{\mathcal{H}}_{21}|\psi_1\rangle; \tag{L91}$$

$$\left\{\hat{\mathcal{H}}_{10}\left(\mathcal{E} - \hat{\mathcal{H}}_{00}\right)^{-1}\hat{\mathcal{H}}_{01} + \left(\hat{\mathcal{H}}_{11} - \mathcal{E}\right) + \hat{\mathcal{H}}_{12}\left(\mathcal{E} - \hat{\mathcal{H}}_{22}\right)^{-1}\hat{\mathcal{H}}_{21}\right\}|\psi_1\rangle = 0. \tag{L92}$$

$$\sum_{\vec{k}\sigma} v_{\vec{k}} \hat{c}^{\dagger}_{0\sigma} \hat{c}_{\vec{k}\sigma}. \tag{L93}$$

$$\hat{\mathcal{H}}_{10} = \sum_{\vec{k}\sigma} v_{\vec{k}} \hat{c}^{\dagger}_{0\sigma} \hat{c}_{\vec{k}\sigma} \hat{P}_0 \tag{L94}$$

$$= \sum_{\vec{k}\sigma} v_{\vec{k}} \hat{c}^{\dagger}_{0\sigma} \hat{c}_{\vec{k}\sigma} (1 - \hat{n}_{0\downarrow})(1 - \hat{n}_{0\uparrow}) \tag{L95}$$

$$= \sum_{\vec{k}\sigma} v_{\vec{k}} \hat{c}^{\dagger}_{0\sigma} \hat{c}_{\vec{k}\sigma} (1 - \hat{n}_{0,-\sigma}). \tag{L96}$$

$$\hat{\mathcal{H}}_{01} = \hat{\mathcal{H}}^*_{10} = \sum_{\vec{k}\sigma} (1 - \hat{n}_{0,-\sigma}) v^*_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\sigma} \hat{c}_{0\sigma}. \tag{L97}$$

$$\hat{\mathcal{H}}_{11} = \hat{P}_1 [\epsilon_0 + \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\sigma} \hat{c}_{\vec{k}\sigma}]; \; \hat{\mathcal{H}}_{00} = \hat{P}_0 \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\sigma} \hat{c}_{\vec{k}\sigma} \tag{L98}$$

and

$$\hat{\mathcal{H}}_{21} = \hat{\mathcal{H}}^*_{12} = \sum_{\vec{k}\sigma} v_{\vec{k}} \hat{c}^{\dagger}_{0\sigma} \hat{c}_{\vec{k}\sigma} \hat{n}_{0,-\sigma}. \tag{L99}$$

$$\hat{\mathcal{H}}_{10}\left(\mathcal{E}-\hat{\mathcal{H}}_{00}\right)^{-1}\hat{\mathcal{H}}_{01}|\psi_1\rangle \tag{L100}$$

$$= \hat{\mathcal{H}}_{10}\sum_{\vec{k}\sigma}(1-\hat{n}_{0,-\sigma})v^*_{\vec{k}}\hat{c}^\dagger_{\vec{k}\sigma}\hat{c}_{0\sigma}\left(\mathcal{E}-[\hat{\mathcal{H}}_{11}-\epsilon_0+\epsilon_{\vec{k}}]\right)^{-1}|\psi_1\rangle. \tag{L101}$$

$$\frac{\hat{\mathcal{H}}_{10}}{\epsilon_0-\mathcal{E}_F}\sum_{\vec{k}\sigma}v^*_{\vec{k}}(1-\hat{n}_{0,-\sigma})\hat{c}^\dagger_{\vec{k}\sigma}\hat{c}_{0\sigma}|\psi_1\rangle \tag{L102}$$

$$= \sum_{\vec{k}\vec{k}'\sigma\sigma'}\frac{v_{\vec{k}'}v^*_{\vec{k}}}{\epsilon_0-\mathcal{E}_F}\hat{c}^\dagger_{0\sigma'}\hat{c}_{\vec{k}'\sigma'}(1-\hat{n}_{0,-\sigma'})(1-\hat{n}_{0,-\sigma})\hat{c}^\dagger_{\vec{k}\sigma}\hat{c}_{0\sigma}|\psi_1\rangle \tag{L103}$$

$$= \sum_{\vec{k}\vec{k}'\sigma\sigma'}\frac{v_{\vec{k}'}v^*_{\vec{k}}}{\mathcal{E}_F-\epsilon_0}\hat{c}^\dagger_{0\sigma'}\hat{c}^\dagger_{\vec{k}\sigma}\hat{c}_{\vec{k}'\sigma'}\hat{c}_{0\sigma}|\psi_1\rangle. \tag{L104}$$

$$\hat{n}_{0\uparrow}\hat{c}^\dagger_{\vec{k}\uparrow}\hat{c}_{\vec{k}'\uparrow}+\hat{n}_{0\downarrow}\hat{c}^\dagger_{\vec{k}\downarrow}\hat{c}_{\vec{k}'\downarrow} \tag{L105}$$

$$= \frac{1}{2}(\hat{n}_{0\uparrow} - \hat{n}_{0\downarrow})(\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{k}'\uparrow} - \hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{k}'\downarrow})$$

$$+\frac{1}{2}(\hat{n}_{0\uparrow} + \hat{n}_{0\downarrow})(\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{k}'\uparrow} + \hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{k}'\downarrow}) \quad \text{(L106)}$$

$$= \hat{S}^z(\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{k}'\uparrow} - \hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{k}'\downarrow}) + \frac{1}{2}\sum_{\sigma}\hat{c}^{\dagger}_{\vec{k}\sigma}\hat{c}_{\vec{k}'\sigma}. \quad \text{(L107)}$$

$$\sum_{\vec{k}\vec{k}'}\frac{v_{\vec{k}'}v^*_{\vec{k}}}{\mathcal{E}_F - \epsilon_0}\left[\hat{S}^+\hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{k}'\uparrow} + \hat{S}^-\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{k}'\downarrow} + \hat{S}^z(\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{k}'\uparrow} - \hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{k}'\downarrow}) + \frac{1}{2}\sum_{\sigma}\hat{c}^{\dagger}_{\vec{k}\sigma}\hat{c}_{\vec{k}'\sigma}\right]|\psi_1\rangle. \quad \text{(L108)}$$

$$\hat{\mathcal{H}}_{\text{eff}} = \hat{\mathcal{H}}_{11} + \sum_{\vec{k}\vec{k}'} J_{\vec{k}\vec{k}'}\left[\hat{S}^+\hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{k}'\uparrow} + \hat{S}^-\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{k}'\downarrow} + \hat{S}^z(\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{k}'\uparrow} - \hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{k}'\downarrow})\right]$$

$$+K_{\vec{k}\vec{k}'}\sum_{\sigma}\hat{c}^{\dagger}_{\vec{k}\sigma}\hat{c}_{\vec{k}'\sigma} \quad \text{(L109a)}$$

$$J_{\vec{k}\vec{k}'} = v_{\vec{k}'}v^*_{\vec{k}}\left[\frac{1}{\mathcal{E}_F - \epsilon_0} + \frac{1}{U + \epsilon_0 - \mathcal{E}_F}\right]. \quad \text{(L109b)}$$

$$\hat{\mathcal{H}} = \sum_{\substack{\vec{k}\sigma \\ \epsilon_{\vec{k}} < \mathcal{W}}} \epsilon_{\vec{k}} \hat{c}^{\dagger}_{\vec{k}\sigma} \hat{c}_{\vec{k}\sigma} + \sum_{\vec{k}\vec{k}'} J \left\{ \hat{S}^{-} \hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}_{\vec{k}'\downarrow} + \hat{S}^{+} \hat{c}^{\dagger}_{\vec{k}\downarrow} \hat{c}_{\vec{k}'\uparrow} + \hat{S}^{z} \left[\hat{c}^{\dagger}_{\vec{k}\uparrow} \hat{c}_{\vec{k}'\uparrow} - \hat{c}^{\dagger}_{\vec{k}\downarrow} \hat{c}_{\vec{k}'\downarrow} \right] \right\}. \quad \text{(L110)}$$

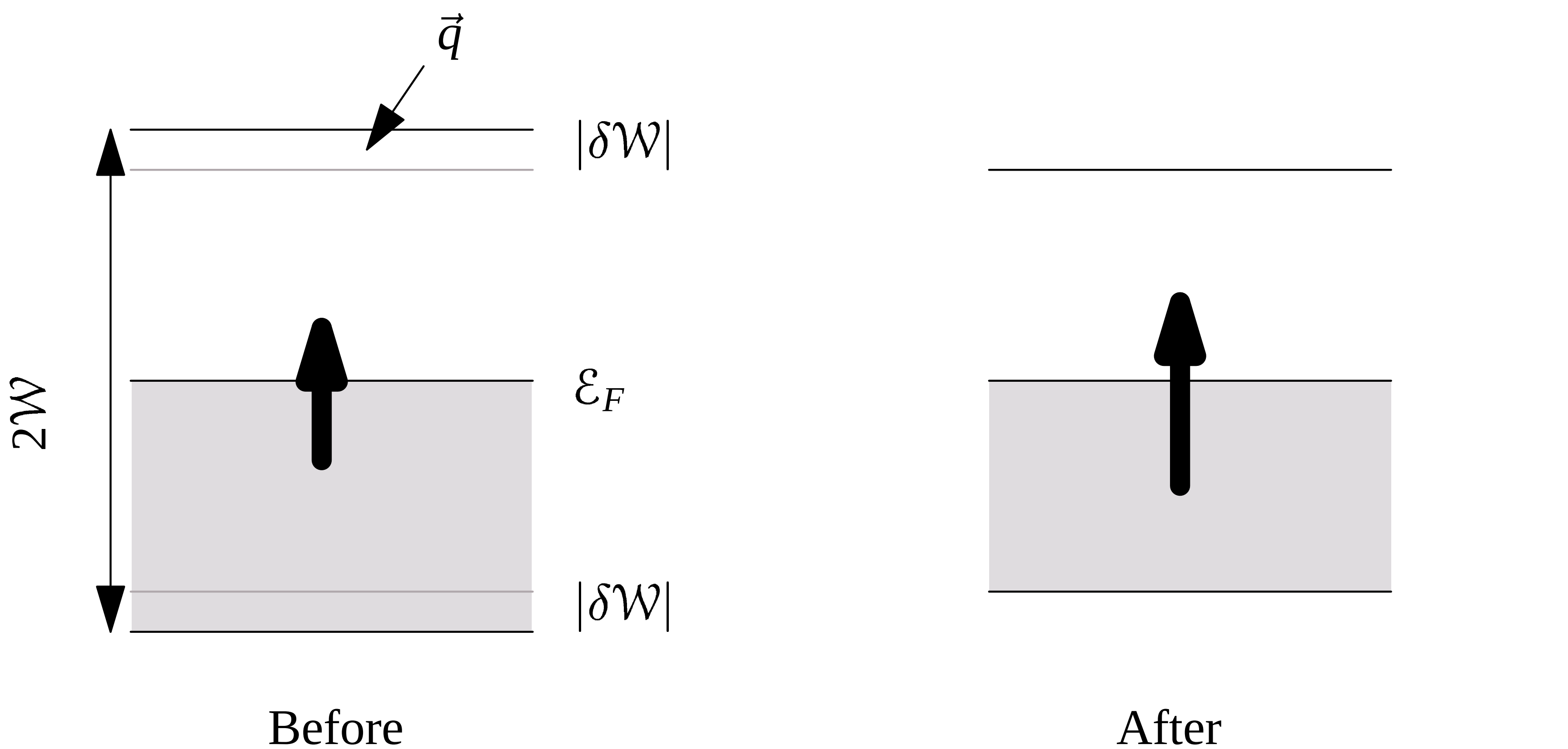


Figure 7: A small band of states, of width $|\delta\mathcal{W}|$ is eliminated from the upper and lower band edges.

$$\hat{\mathcal{H}}_{12} = J\sum_{\vec{k}\vec{q}} \hat{S}^{-}\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{q}\downarrow} + \hat{S}^{+}\hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{q}\uparrow} + \hat{S}^{z}\left[\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{q}\uparrow} - \hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{q}\downarrow}\right], \quad \text{(L111a)}$$

$$\hat{\mathcal{H}}_{21} = J\sum_{\vec{k}'\vec{q}'} \hat{S}^{-}\hat{c}^{\dagger}_{\vec{q}'\uparrow}\hat{c}_{\vec{k}\downarrow} + \hat{S}^{+}\hat{c}^{\dagger}_{\vec{q}'\downarrow}\hat{c}_{\vec{k}'\uparrow} + \hat{S}^{z}\left[\hat{c}^{\dagger}_{\vec{q}'\uparrow}\hat{c}_{\vec{k}'\uparrow} - \hat{c}^{\dagger}_{\vec{q}'\downarrow}\hat{c}_{\vec{k}'\downarrow}\right]. \quad \text{(L111b)}$$

$$\hat{\mathcal{H}}_{12}(\mathcal{E} - \hat{\mathcal{H}}_{22})^{-1}\hat{\mathcal{H}}_{21}|\psi_1\rangle \quad \text{(L112)}$$

$$\approx \hat{\mathcal{H}}_{12}\hat{\mathcal{H}}_{21}(\mathcal{E} - \hat{\mathcal{H}}_{22} - [\mathcal{W} - \mathcal{E}_F])^{-1}|\psi_1\rangle \quad \text{(L113)}$$

$$\approx \hat{\mathcal{H}}_{12}\hat{\mathcal{H}}_{21}(-\mathcal{W})^{-1}|\psi_1\rangle. \quad \text{(L114)}$$

$$\hat{\mathcal{H}}_{12}\hat{\mathcal{H}}_{21} = J^2 D(\mathcal{W})[-\delta\mathcal{W}]\sum_{\vec{k}\vec{k}'}\frac{3}{4}\sum_{\sigma}\hat{c}^{\dagger}_{\vec{k}\sigma}\hat{c}_{\vec{k}'\sigma} - \begin{array}{l}\Big\{\hat{S}^{-}\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{k}'\downarrow} + \hat{S}^{+}\hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{k}'\uparrow} \\ +\hat{S}^{z}\left[\hat{c}^{\dagger}_{\vec{k}\uparrow}\hat{c}_{\vec{k}'\uparrow} - \hat{c}^{\dagger}_{\vec{k}\downarrow}\hat{c}_{\vec{k}'\downarrow}\right]\Big\}.\end{array} \quad \text{(L115)}$$

$$J + \delta J = J - 2\frac{J^2}{\mathcal{W}} D(\mathcal{W}) \delta \mathcal{W}, \tag{L116}$$

$$\frac{3}{2} J^2 D(\mathcal{W}) \frac{\delta \mathcal{W}}{\mathcal{W}} \sum_{\vec{k}\vec{k}'\sigma} \hat{c}^{\dagger}_{\vec{k}\sigma} \hat{c}_{\vec{k}'\sigma}. \tag{L117}$$

$$\frac{dJ}{d\mathcal{W}} = -2\frac{J^2}{\mathcal{W}} D(\mathcal{W}). \tag{L118}$$

$$\mathcal{W} \exp\left[-\frac{1}{2D_0 J}\right] = \text{constant} \equiv k_B T_K, \tag{L119}$$

$$\rho = \mathcal{F}\left(\frac{T}{T_K}\right). \tag{L120}$$

$$\mathcal{F}(x) \quad = \quad \left[\frac{1}{\ln(x)}\right]^2 \tag{L121}$$

Scaling Theory

$$\Rightarrow \mathcal{F}\left(\frac{T}{T_K}\right) = \rho = \left[\frac{2D_0J}{1+2D_0J\ln(k_BT/\mathcal{W})}\right]^2 \quad \text{(L122)}$$

$$\sim 4D_0^2J^2\left(1-4D_0J\ln(k_BT/\mathcal{W})\right). \quad \text{(L123)}$$

$$\rho \sim \mathcal{A}T^5 - \mathcal{B}n_{\text{mi}}\ln(k_BT/\mathcal{W}), \quad \text{(L124)}$$

$$\frac{d\rho}{dT} = 0 \Rightarrow T_{\text{min}} = \left(\frac{\mathcal{B}n_{\text{mi}}}{5\mathcal{A}}\right)^{1/5}. \quad \text{(L125)}$$

$$\mathcal{F}\left(\frac{T}{T_K}\right) = \left[\frac{1}{\cosh^{-1}(T/T_K)}\right]^2, \quad \text{(L126)}$$

$$C_\mathcal{V} \propto n\frac{T}{T_K} = n\frac{k_BT}{\mathcal{W}}\exp\left[\frac{1}{2D_0J}\right]. \quad \text{(L127)}$$

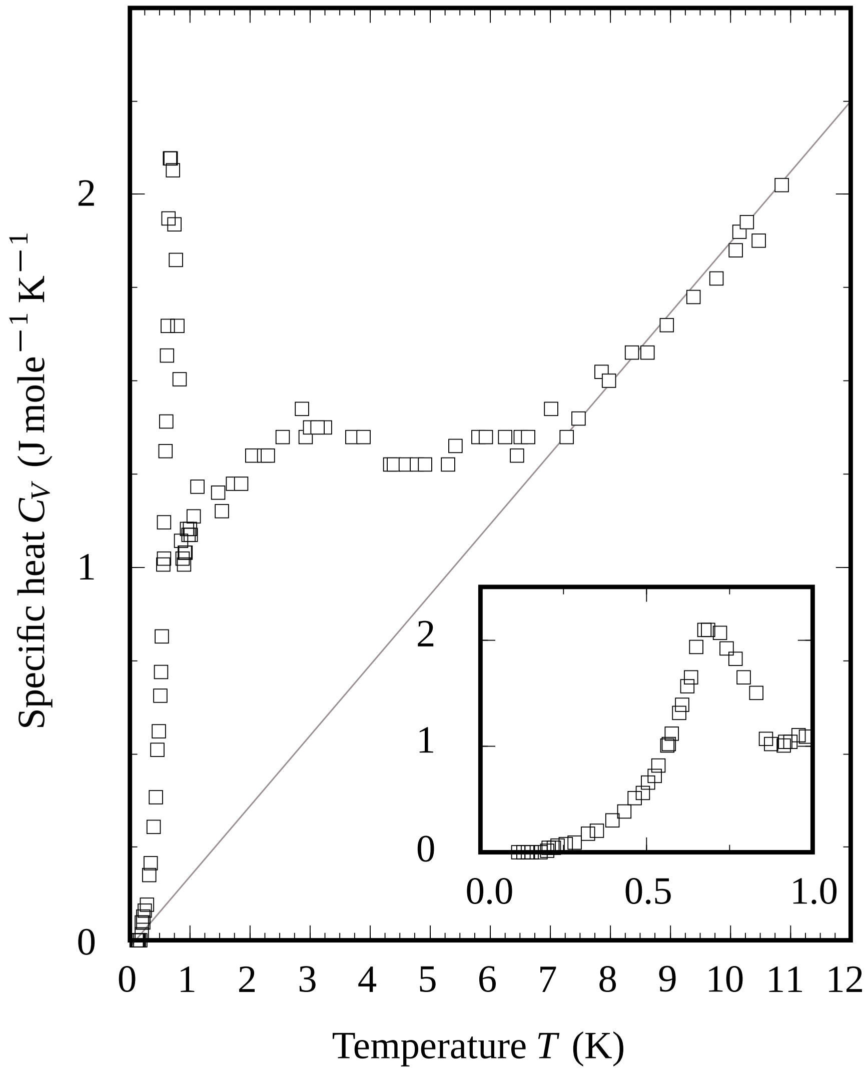


Figure 8: Low-temperature specific heat of the heavy fermion compound UBe_{13}. [Source Ott et al. (1983, 1984).]

$$\hat{\mathcal{H}} = \sum_{\substack{\langle ll' \rangle \\ \sigma}} -\mathfrak{t}\left[\hat{c}^{\dagger}_{l\sigma}\hat{c}_{l'\sigma} + \hat{c}^{\dagger}_{l'\sigma}\hat{c}_{l\sigma}\right] + U\sum_{l}\hat{c}^{\dagger}_{l\uparrow}\hat{c}_{l\uparrow}\hat{c}^{\dagger}_{l\downarrow}\hat{c}_{l\downarrow}, \tag{L128}$$

Mean-Field Solution

$$\hat{\mathcal{H}} = \sum_{\substack{\langle ll' \rangle \\ \sigma}} -\mathfrak{t}\left[\hat{c}^{\dagger}_{l\sigma}\hat{c}_{l'\sigma} + \hat{c}^{\dagger}_{l'\sigma}\hat{c}_{l\sigma}\right] + U\sum_{l}\hat{n}_{l\uparrow}\hat{n}_{l\downarrow}. \tag{L129}$$

$$\hat{n}_{l\sigma} = n_{\sigma} + (\hat{n}_{l\sigma} - n_{\sigma}). \tag{L130}$$

$$\hat{\mathcal{H}} \approx \sum_{\substack{\langle ll' \rangle \\ \sigma}} -\mathfrak{t}\left[\hat{c}^{\dagger}_{l\sigma}\hat{c}_{l'\sigma} + \hat{c}^{\dagger}_{l'\sigma}\hat{c}_{l\sigma}\right] + U\sum_{l}\hat{n}_{l\uparrow}n_{\downarrow} + n_{\uparrow}\hat{n}_{l\downarrow} - n_{\uparrow}n_{\downarrow}. \tag{L131}$$

$$\sum_{\vec{k}\vec{\delta}\sigma} -\mathfrak{t}\hat{c}^{\dagger}_{\vec{k}\sigma}\hat{c}_{\vec{k}\sigma}\cos\vec{\delta}\cdot\vec{k} + U\sum_{\vec{k}}\hat{n}_{\vec{k}\uparrow}n_{\downarrow} + n_{\uparrow}\hat{n}_{\vec{k}\downarrow} - n_{\uparrow}n_{\downarrow}. \tag{L132}$$

$$Nn_{\uparrow} = Na\int_{-k_{F\uparrow}}^{k_{F\uparrow}} \frac{dk}{2\pi} \tag{L133}$$

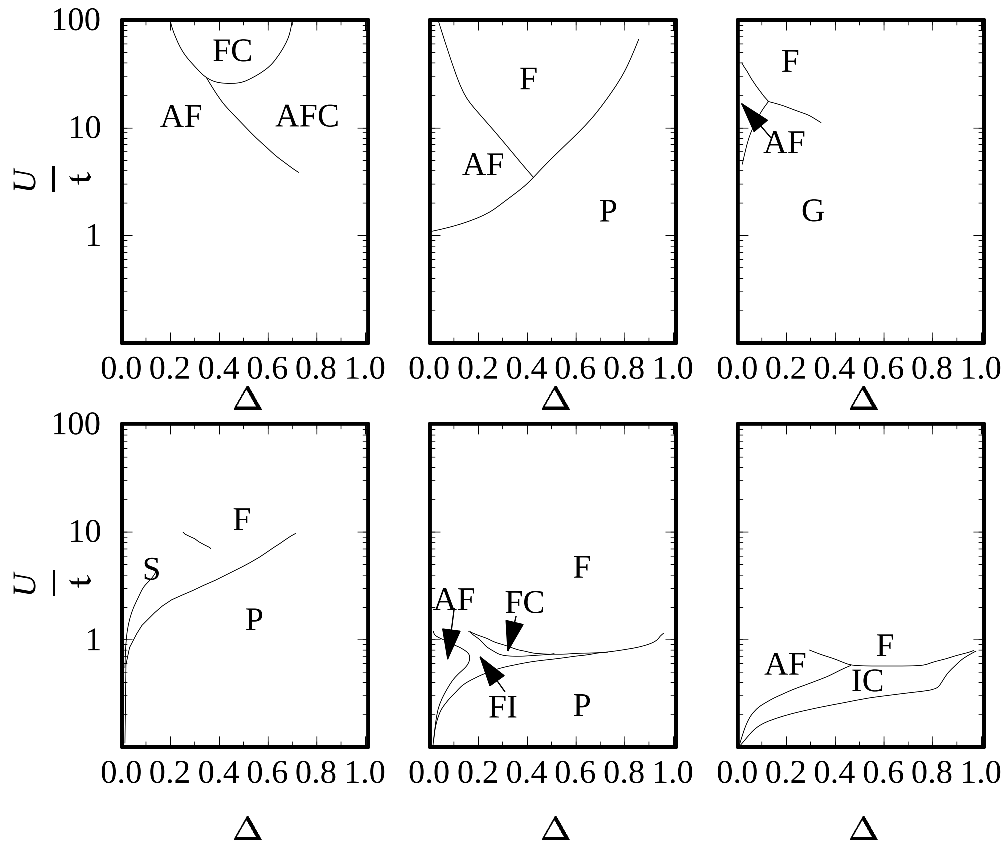
$$\Rightarrow \pi n_{\uparrow} = ak_{F\uparrow}. \tag{L134}$$

$$\mathcal{E}_0 = \frac{N}{\pi}\left[-2\mathfrak{t}\right]\left[\sin\pi n_{\uparrow} + \sin\pi n_{\downarrow}\right] + NUn_{\uparrow}n_{\downarrow}. \tag{L135}$$

$$\mathcal{E}_0 = \frac{-4\mathfrak{t}N}{\pi}\sin\pi n_{\uparrow} + NUn_{\uparrow}\left(1 - n_{\uparrow}\right). \tag{L136}$$

$$\frac{U}{\mathfrak{t}} > \frac{16}{\pi}, \tag{L137}$$

An Unsolved Problem...



F=Ferromagnetic

FC=Short-range ferromagnetic correlations

AF=Antiferromagnetic

AFC=Short-range antiferromagnetic correlations

P=Paramagnetic

FI=Ferrimagnetic

IC=Incommensurate, S=Spiral

G=Correlated state of Gutzwiller type

Figure 9: Six representative phase diagrams of the two-dimensional Hubbard model