Condensed Matter Intro

May 29, 2025

Phonons

1. Planes indicated by three points on-axis: $(1,0,0),(\overline{1},0,1)$ with basis $\mathbf{a},\mathbf{b},\mathbf{c}$, plane (u,v,w) is perpendicular to $\mathbf{r}=u\mathbf{a}+v\mathbf{b}+w\mathbf{c}$ (Passes through points $\frac{\mathbf{a}}{u},\frac{\mathbf{b}}{v},\frac{\mathbf{c}}{w}$)

2. The electron number density $n(x)=\sum_p n_p e^{i2\pi px/a}$, in 3D

$$n(\mathbf{r})=\sum_G n_G e^{i\mathbf{G}\cdot\mathbf{r}} \tag{1}$$

$$\mathbf{G}_{hkl}=h\mathbf{A}+k\mathbf{B}+l\mathbf{C} \tag{2}$$

$$\mathbf{A}=2\pi\frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}}\quad \mathbf{B}=2\pi\frac{\mathbf{c}\times\mathbf{a}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}}\quad \mathbf{C}=2\pi\frac{\mathbf{a}\times\mathbf{b}}{\mathbf{a}\cdot\mathbf{b}\times\mathbf{c}} \tag{3}$$

$$\mathbf{A}\cdot\mathbf{a}=2\pi\quad \mathbf{A}\cdot\mathbf{b}=0\quad \mathbf{A}\cdot\mathbf{c}=0 \tag{4}$$

$$f(\mathbf{r})=\sum_{h,k,l=-\infty}^{\infty} C_{hkl}e^{i\mathbf{G}_{hkl}\cdot\mathbf{r}} \tag{5}$$

where $\mathbf{G}$ and $\mathbf{A}$ are reciprocal lattice vectors.

Because of equation (4), the *atomic form factor* $f(\mathbf{r})=f(\mathbf{r}+\mathbf{r}'_{uvw})$ for integer u,v,w.

3.

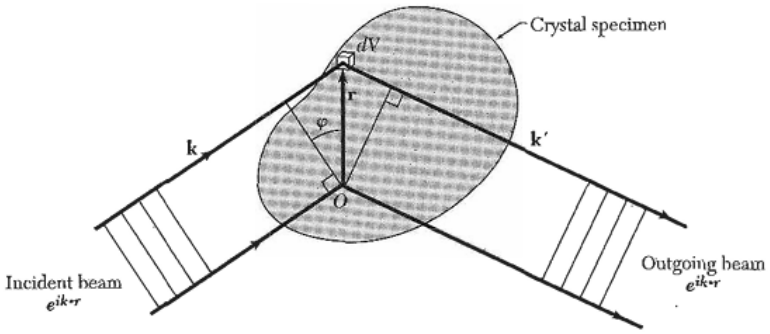
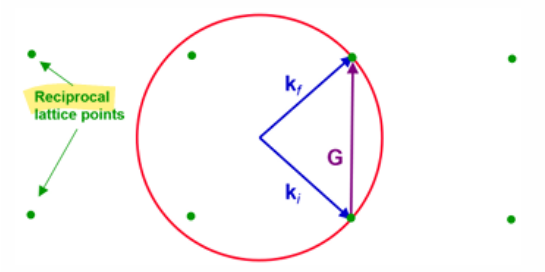


Figure 6 The difference in path length of the incident wave $\mathbf{k}$ at the points O, $\mathbf{r}$ is $r\sin\varphi$, and the difference in phase angle is $(2\pi r\sin\varphi)/\lambda$, which is equal to $\mathbf{k}\cdot\mathbf{r}$. For the diffracted wave the difference in phase angle is $-\mathbf{k}'\cdot\mathbf{r}$. The total difference in phase angle is $(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}$, and the wave scattered from dV at $\mathbf{r}$ has the phase factor $\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]$ relative to the wave scattered from a volume element at the origin O.

The scattering amplitude is $F=\int n(\mathbf{r})e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}\mathrm{d}V=\int n(\mathbf{r})e^{-i\Delta\mathbf{k}\cdot\mathbf{r}}\mathrm{d}V=\sum_G\int n_G e^{i(G-\Delta\mathbf{k})\cdot\mathbf{r}}\mathrm{d}V$

The scattering vector is $\Delta\mathbf{k}=\mathbf{k}'-\mathbf{k}$, for large (infinite) lattice, scattering happens if $\boxed{\Delta\mathbf{k}=\mathbf{G}}$. (Laue equation, Proof)

In elastic scattering, photon energy conserves, $k^2=k'^2=(\mathbf{k}+\mathbf{G})^2$, $2\mathbf{k}\cdot\mathbf{G}+G^2$, graphically using Ewald's sphere



4. The first Brillouin zone is the *Voronoi cell* around the *reciprocal lattice point* at origin in the *reciprocal lattice*. $\mathbf{k}$ on its edge satisfies $\mathbf{k} \cdot \mathbf{G} = \frac{1}{2}G^2$ and can be scattered.

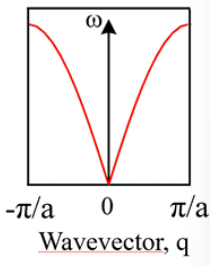
5.

	Name	Field
——→	Electron	—
~~→	Photon	Electromagnetic wave
⌇⌇⌇→	Phonon	Elastic wave
⊣⊢→	Plasmon	Collective electron wave
⌒⌒⌒→	Magnon	Magnetization wave
–	Polaron	Electron + elastic deformation
–	Exciton	Polarization wave

Figure 1 Important elementary excitations in solids.

6. Phonons are (quantized) normals modes in lattice vibration. *Inelastic* scattering involves phonons.

   - Dispersion relation of phonon (1D):★



$$\boxed{\omega(q) = \sqrt{\frac{4k}{m}}\left|\sin\left(\frac{qa}{2}\right)\right|}$$

where k is spring constant,
a is orignal length,
q is phonon wavevector(wavenumber).

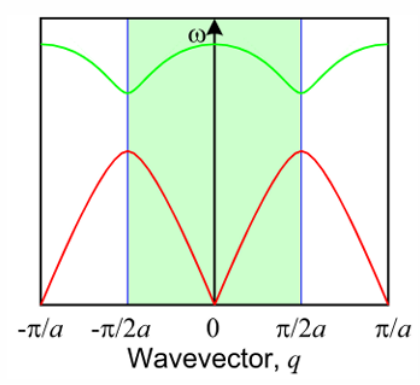
   - Long wavelength limit ($q \to 0$), $\omega(q) \approx \sqrt{\frac{k}{m}}qa$

     $v_p = \frac{\omega}{q} = \sqrt{\frac{ka}{m/a}} = \sqrt{\frac{Y}{\rho}}$

     where Y is Young's modulus.

     (In the limit of small a and large λ, v_p tends to the continuum speed of sound)
   - $\mathbf{K} = \mathbf{q} + \mathbf{G}$, because $\omega(\mathbf{q})$ has period $\mathbf{G}$
   - Energy conservation $\hbar\omega = \frac{\hbar^2}{2m}\left(k_i^2 - k_f^2\right)$ (TODO:Prove it)
   - Inelastic diffraction condition $\boxed{\mathbf{k} = \mathbf{k}' \pm \mathbf{K}}$ (Momentum conservation for creation/annihilation)

7. Diatomic lattice $\omega^2 = \frac{k}{m_A m_B}\left[(m_A + m_B) \pm \sqrt{(m_A + m_B)^2 - 4m_A m_B \sin^2(qa)}\right]$ ★



The two solutions are two modes. Optical mode due to EM radiation and acoustic mode due to sound-waves. Brillouin zone is halved. (a is half of the Wigner-Seitz unit cell width) (WLOG assume $m_A - m_B > 0$, m_A is heavier)

ω	optical	acoustic
$q = \pm\frac{\pi}{2a}$	$\sqrt{\frac{2k}{m_B}}$	$\sqrt{\frac{2k}{m_A}}$
$q \to 0$	$\omega = \frac{2k(m_A+m_B)}{m_A m_B} = \sqrt{\frac{2k}{\mu}}$	$\omega \approx \sqrt{\frac{2k}{m_A+m_B}}aq$

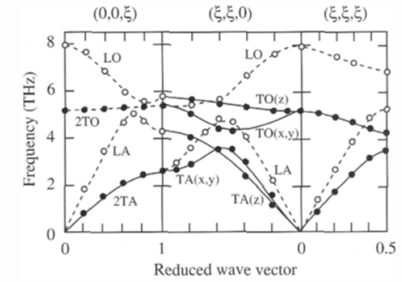
where μ is the reduced mass.

Plug into $(m_A\omega^2 - 2k)U_1 + 2k\cos(qa)U_2 = 0$

U_1/U_2	optical	acoustic
$q = \pm\frac{\pi}{2a}$	0	$\pm\infty$
$q \to 0$	$-m_B/m_A$	1

If $\lambda = \infty$, waves in optical mode out of phase with fixed CoM, in acoustic mode moves in phase; If $\lambda = 4a$, standing waves occur at the Brillouin zone boundary. In optical mode heavier atoms A fixed; In acoustic mode lighter atoms B fixed.

8. Phonons in 3D
   - Along 3 directions $(001), (110), (111)$
   - Longitudinal and transverse modes L and T. The latter is degenerate except for (110)
   - Diatomic have L, T combined with A, O, plus $T(x,y)$ and $T(z)$ for (110) (NaCl example:)



   - Van der Waals in Neon is weaker than ionic in NaCl, smaller k means lower ω

9. In insulating crystals, thermal energy is stored in the phonons; each mode has energy $E = (n + \frac{1}{2})\hbar\omega$, where n is the number of phonons in it.

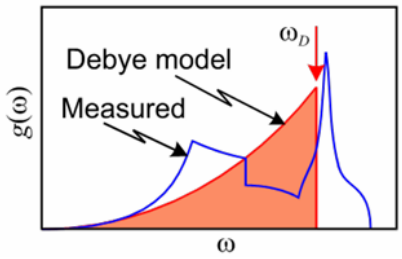
10. Heat capacity

- Each mode has energy $E = (n + \frac{1}{2})\hbar\omega$ with n phonons in it
- Zero phonon energy $\frac{1}{2}\hbar\omega$ can be ignored without harm
- Boltzmann factor $P_n = \exp\left(-\frac{E_n}{k_B T}\right)$ is the ratio of probabilities relative to that of 0 phonon.
- In the i-th mode, $E_i = \sum_{n=0}^{\infty} P_n E_n = \frac{\sum_{n=0}^{\infty} n\hbar\omega \exp\left(-\frac{n\hbar\omega_i}{k_B T}\right)}{\sum_{n=0}^{\infty} \exp\left(\frac{-n\hbar\omega_i}{k_B T}\right)} = \frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{k_B T}\right) - 1}$
- N atoms in 3D have $3N$ modes
- At high temperatures, $E_i \approx k_B T$, $U = 3Nk_B T$, $C = \frac{\partial U}{\partial T} = 3Nk_B$, Dulong-Petit Law: heat capacity at high temperature is $3R$
- At low temperatures, $E_i \approx \hbar\omega_i \exp\left(\frac{-\hbar\omega_i}{k_B T}\right)$
- At normal temperatures,

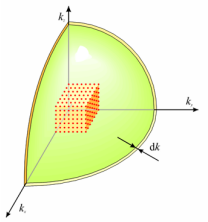
$$U = \sum_{i=1}^{N} \frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{k_B T}\right) - 1} \approx \int_0^{3N} \frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{k_B T}\right) - 1} \mathrm{d}N = \int_0^{\infty} \frac{\hbar\omega_i}{\exp\left(\frac{\hbar\omega_i}{k_B T}\right) - 1} g(\omega)\mathrm{d}\omega,$$

where $\mathrm{d}N = g(\omega)\mathrm{d}\omega$, $g(\omega) = \frac{\mathrm{d}N}{\mathrm{d}\omega}$ is the density of states.

- $3N = \int_0^{\omega_D} g(\omega)\mathrm{d}\omega$
- Debye model approximates $g(\omega)$



Assume standing waves in a box of sides A, B, C, $\mathbf{k} = (\frac{n_x\pi}{A}, \frac{n_y\pi}{B}, \frac{n_z\pi}{C})$.
In k space, $\mathbf{k}$ are the dots, number of such dots in $k < |\mathbf{k}| < k + \mathrm{d}k$ is approximately the volume of the shell$(\frac{1}{8}4\pi k^2\mathrm{d}k)$ $\times$ density of the dots $(\frac{ABC}{\pi^3})$. The number of states is the sum of number of dots in the 3 modes (2 transverse, 1 longitudinal).



$$\mathrm{d}N = g(k)\mathrm{d}k = \frac{3\pi k^2 \mathrm{d}k}{2\pi^3/ABC}$$
$$g(k) = \frac{3Vk^2}{2\pi^2}$$
$$g(\omega) = g(k)\frac{\mathrm{d}k}{\mathrm{d}\omega}$$

Assume k is small so phonon is not dispersive, $\omega = v_s k$, $g(\omega) = \frac{3V\omega^2}{2\pi^2 v_s^3}$

$3N = \int_0^{\omega_D} g(\omega)\mathrm{d}\omega \implies \boxed{\omega_D^3 = \frac{6\pi^2 v_s^3 N}{V}}$ is the Debye frequency

$$U = \frac{3V\hbar}{2\pi^2 v_s^3} \int_0^{\omega_D} \frac{\omega^3}{\exp(\hbar\omega/k_B T) - 1} \mathrm{d}\omega$$

Longitudinal and transverse wave velocities are different, so $\frac{1}{v_s^3} = \frac{1}{3}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)$

$$C = \frac{\partial U}{\partial T} = \frac{3V\hbar}{2\pi^2 v_s^3}\int_0^{\omega_D} \omega^3 \frac{\frac{\hbar\omega}{k_B T^2}\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T)-1]^2}\mathrm{d}\omega$$

$$\boxed{C = 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^4 e^x}{(e^x-1)^2}\mathrm{d}x}$$

where $\boxed{\theta_D = \frac{\hbar\omega_D}{k_B}}$ is Debye temperature, $x = \theta_D/T$.

- At high temperatures, Dulong-Petit Law:

$$C \approx 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T} x^2\mathrm{d}x = \boxed{3Nk_B}$$

- At low temperatures, Debye T^3 Law:

$$C = 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\infty} x^4\frac{e^x}{(e^x-1)^2}\mathrm{d}x = 9Nk_B\left(\frac{T}{\theta_D}\right)^3\frac{4\pi^4}{15} \propto T^3$$

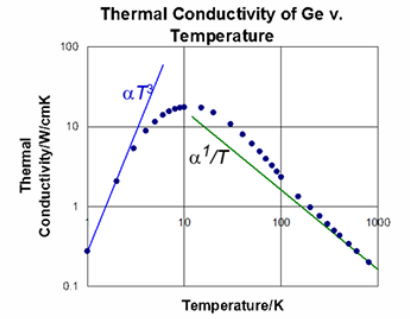
- Moving down groups in periodic table, v_s and θ_D decreases. (with some exceptions like carbon)
- Debye model works good only at low q (at high q, near Brillouin zone boundary, non-dispersive assumption fails). Measured $g(\omega)$ is complicated because transverse and longitudinal dispersion relations are different. the 3D 1st Brillouin zone has a complicated shape.

11. Thermal conductivity $\boxed{\kappa = \frac{1}{3}C\langle v\rangle l}$,★

where $C = 3\frac{N}{V}k_B$ is the heat capacity per unit volume,
$\langle v\rangle$ is the average speed,
l is the phonon mean free path.

12. Scattering reduces mean free path l, reduces thermal conductivity κ

- Geometric scattering - impurities, grain boundaries, sample boundaries,
  - dominant at low T, with long l, $l = D$ where D is size the of sample
  - κ is higher for pure crystals
  - $\boxed{\kappa \propto C \propto T^3}$
- Phonon-phonon scattering
  - anharmonic lattice only
  - dominant at high T, $C \approx 3nk_B$, $n \propto T$, $\boxed{\kappa \propto l \propto 1/T}$
  - *Normal* process N, $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$, phonon momentum $\mathbf{J} = \sum_{\mathbf{K}} n_{\mathbf{K}}\hbar\mathbf{K}$ conserved $\neq 0$, no effect on κ
  - *Umklapp* process U, $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}$ ($\mathbf{K}_1, \mathbf{K}_2$ near edge of Brillouin zone/high T), negative group velocity.
  - As temperature decrease from 1000K, κ gets slightly bigger than $1/T$ line, because lower temperature, less Umklapp, more normal. Less negative group velocity, higher average group velocity, higher thermal conductivity.



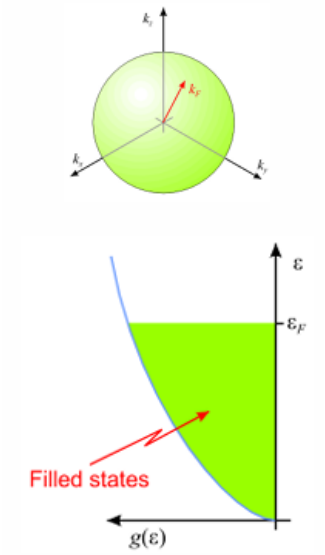
Free electrons

1. Classical Drude model, free electron are pinballs.

Can describe	Cannot describe
Electrical conductivity	Electron heat capacity C_{el}, too large
Optical reflectivity	Sign of Hall coefficient
Thermal conductivity	Existence and properties of conductors, semiconductors, insulators

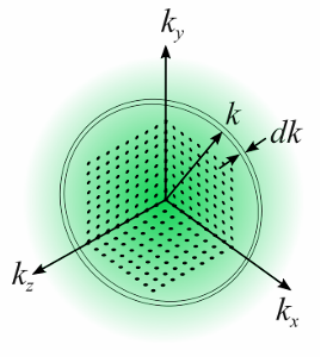
2. Hall coefficient and semiconductors are only explained using *nearly free electrons model*.

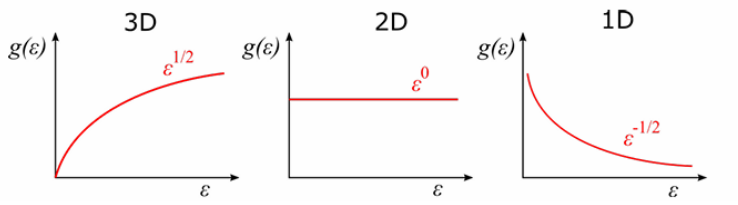
3. *Fermi energy* ϵ_F is the highest electron energy in the ground state (at $T = 0$) of the N electron system; or simply $\mu(T = 0)$. Electrons takes lowest possible energy states with Pauli exclusion principle, inside a sphere with radius k_F, the *Fermi wavevector*. The picture shows a *Fermi sphere*, a *Fermi surface*.



$$N = 2 \cdot \frac{4\pi k_F^3/3}{8\pi^3/V} = \frac{Vk_F^3}{3\pi^2}$$
$$k_F^3 = 3\pi^2 \frac{N}{V} = 3\pi^2 n$$
$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} \left(3\pi^2 n\right)^{2/3}$$

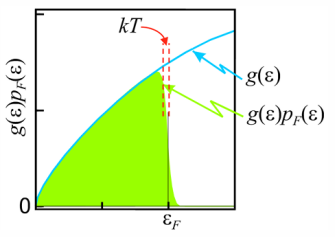
4. Free electron model, similarly,
   - not standing waves but cyclic travelling waves $\psi(x, y, z) \propto e^{ik_x x} e^{ik_y y} e^{ik_z z}$
   - $\mathbf{k} = (\pm\frac{2\pi n_x}{A}, \pm\frac{2\pi n_y}{B}, \pm\frac{2\pi n_z}{C})$
   - $\boxed{g(k) = \frac{Vk^2}{\pi^2}}$ (2 modes instead of 3 for two spins)
   - density of states wrt. energy $\boxed{\epsilon = \frac{mv^2}{2} = \frac{\hbar^2 k^2}{2m}}$, $\boxed{g(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2} = \frac{3N}{2\epsilon}}$
   - can confine electrons to 2D, 1D, even 0D, $g(\epsilon)$ also different





5. Fermi Dirac distribution/function $p_F(\epsilon, T, \mu) = \dfrac{1}{1+\exp\left(\frac{\epsilon-\mu}{k_B T}\right)}$ (Proof)

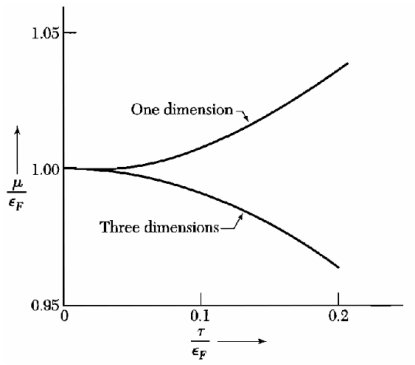
   - Step function $1 - u_\mu(\epsilon)$ at $T = 0$
   - $p_F(\mu) = 0.5$
   - At temperature $T \neq 0$, electron distribution is $g(\epsilon) \cdot p_F(\epsilon)$



   - The chemical potential is a function of temperature, $\mu = \mu(T)$, $\mu(T = 0) = \epsilon_F$

   $\boxed{\text{It varies to keep } \int_0^\infty p_F(\epsilon) g(\epsilon) \mathrm{d}\epsilon = N}$

   ($g(\epsilon) \propto \epsilon^{-1/2}, \epsilon^0, \epsilon^{1/2}$ for 1D, 2D, 3D, $p_F(\epsilon)$ is symmetrical about $\epsilon = \mu$
   as temperature increase, μ goes up/constant/down)



   In 3D, $\mu(T) \sim \epsilon_F - \alpha T^2$. For small T we assume $\mu(T) = \mu(0) = \epsilon_F$ ($\tau = k_B T$ in the picture)

   - For low T, $U_{el} = \int_0^\infty \dfrac{\epsilon g(\epsilon)}{\exp((\epsilon-\mu)/k_B T) + 1} \mathrm{d}\epsilon$ ★
   - $C_{el} = \dfrac{\partial U_{el}}{\partial T} \approx \boxed{\dfrac{\pi^2}{2} N k_B \dfrac{T}{T_F}}$, where $\boxed{T_F = \epsilon_F / k_B}$ is the Fermi temperature
   - $C_{el} \propto T$ at low T

6. At low T, $C_{tot} = C_{el} + C_{ph} = \gamma T + \beta T^3$

7. Electron pressure in metals is $P = -\dfrac{\partial U}{\partial V} = \dfrac{2}{5} n \epsilon_F$ ('smearing' of Fermi-Dirac distribution ignored) (Proof) ($n = N/V$)

8. The isothermal bulk modulus $K_T = -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{2}{3}n\epsilon_F$; contribute to a big part of bulk modulus K_{exp}; electron gas - short range, coulomb force between electrons and lattice - long range

9. Adding mean path length/mean time by adding rate of collision, like this: $\frac{1}{l} = \frac{1}{l_1} + \frac{1}{l_2}$, $\frac{1}{\tau} = \frac{1}{\tau_{phonon}} + \frac{1}{\tau_{defect}}$

10. Probability of no collision in a time t is $\boxed{e^{-t/\tau}}$

11. EoM for mean collison interval τ is $\boxed{m^*\left(\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t}+\frac{\mathbf{v}}{\tau}\right) = -e\mathbf{E} - e\mathbf{v}\times\mathbf{B}}$ (an additional damping/drag term $\frac{m^*\mathbf{v}}{\tau}$)

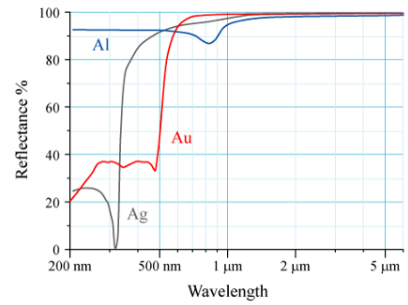
12. *Drift velocity* $\boxed{m^*\frac{\mathbf{v}_{drift}}{\tau} = -e\mathbf{E}}$

13. *Electron mobility* $\boxed{\mu = \frac{v_{drift}}{E} = \frac{e\tau}{m^*}}$

14. *Current density* $\mathbf{j} = n(-e)\mathbf{v}_{drift} = \frac{ne^2\tau}{m^*}\mathbf{E} = ne\mu\mathbf{E} = \sigma\mathbf{E}$, where $\boxed{\sigma = \frac{ne^2\tau}{m^*} = ne\mu}$ is conductivity.

15. Optical reflectivity

    - Optical frequency $\omega \gg \tau$, scattering ignored.
    - (Same as Phys B plasma, m^* instead of m_e)
    - $\epsilon = 1 + \chi = 1 + \frac{P}{\epsilon_0 E} = 1 - \frac{Ne^2}{\epsilon_0 m^*\omega^2} = 1 - \frac{\omega_p^2}{\omega^2}$, the plasma frequency is $\omega_p = \frac{Ne^2}{\epsilon_0 m^*}$, where N is unit volume electron density.
    - $n = \sqrt{\epsilon}$, below ω_p, n is imaginary, metal is reflective; above ω_p, metal is transparent. Examples:

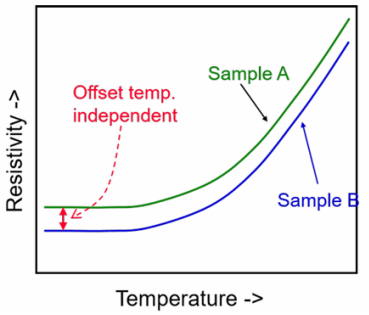


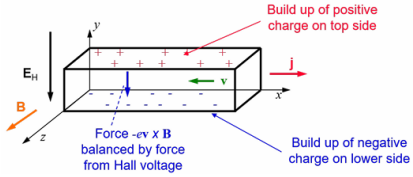
    (ω_p normally in UV range; for transparent metals (Indium tin oxide) near IR range, so visible light passes through)

16. Resistivity

    - Only electron states near the Fermi surface can be scattered. These are the only filled states with empty states at slightly different energies.
    - Electrons moved by $\mathbf{E}$ according to $\frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t} = -\frac{1}{\hbar}e\mathbf{E}$
    - Then scatter backwards due to phonons and defects. In average we have drift velocity $m^*v_{drift} = \hbar\Delta k$
    - $\boxed{\frac{1}{\tau} = \frac{1}{\tau_{phonons}} + \frac{1}{\tau_{defects}}}$ (Matthiessens's rule)

- At high temperatures, No. phonons $\propto T$, $\tau_{phonons} \ll \tau_{defects}$, $R \propto T$
- At low temperatures, $\tau_{phonons} \gg \tau_{defects}$, **offset** independent of T for different conductors



17. Thermal conductivity due to electrons (κ_{el})
    - $\kappa_{el} = \frac{1}{3} C_{el} \langle c \rangle l$
    - $\langle c \rangle = v_F$ (only electrons near Fermi surface are excited/moved)
    - $l = v_F \tau$
    - $T_F = \epsilon_F / k_B = \frac{m^* v_F^2}{2k_B}$
    - $\kappa_{el} = \frac{1}{3}\left(\frac{\pi^2}{2} n k_B \frac{T}{T_F}\right) v_F l = \frac{1}{3}\frac{\pi^2}{2} n k_B \frac{T}{m^* v_F^2 / 2k_B} v_F^2 \tau = \boxed{\frac{\pi^2 n k_B^2 T \tau}{3m^*}}$
    - At room temperature, $\kappa_{electron}$ much larger (100x) than κ_{phonon}, thermal conductivity of metal $\gg$ insulators
    - $\tau \propto 1/T$, k_{el} roughly constant with T
    - At high temperature, κ_{phonon} is dominant, κ_{el} is constant ($\tau \propto 1/T$ at high temp)
$\kappa \propto$, thermal conductivity	photon	electron
low temp	T^3	T
high temp	$1/T$	1
18. Wiedemann-Franz Law
    - A experimental observation, at not too low temperatures, $\frac{\kappa}{\sigma} = LT$, where L is teh Lorenz number
    - $\frac{\kappa}{\sigma} = \frac{\pi^2 k_B^2 n T \tau / 3m^*}{n e^2 \tau / m^*} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$
    - Theoretical values of $L = 2.45 \times 10^{-8} \mathrm{W\Omega K^{-2}}$
Element	Ag	Au	Cd	Cu	Ir	Mo	Pb	Pt	Sn	W
$L/\times 10^{-8}\mathrm{W\Omega K^{-2}}$	2.31	2.35	2.42	2.23	2.49	2.61	2.47	2.51	2.52	3.04
    - A strong support for the free electron model
19. Hall effect
    - 

    - $\mathbf{f} = m^* \frac{d v_{drift}}{dt} = -e\mathbf{E}_H + (-e)\mathbf{v}_{drift} \times \mathbf{B} = 0$, $\mathbf{j} = n(-e)\mathbf{v}_{drift}$, where n is the number of free electron density
    - $\mathbf{E}_H = \mathbf{B} \times \mathbf{v}_{drift} = -\frac{1}{ne}\mathbf{B} \times \mathbf{j} = R_H \mathbf{B} \times \mathbf{j}$

- $\boxed{R_H = \frac{E}{B} = \frac{1}{nq} = -\frac{1}{ne}}$
- The number of electrons per atom $\frac{n}{n_{atom}} = -\frac{1}{n_{atom} e R_H}$
-

Element	Na	K	Mg	Al	Be	Cd
n/n_{atom}	0.9	1.1	1.5	3.5	-0.2	-2.2

- Negative values, free electron model failed

The Nearly free electron model

1. Periodic potential as a series $V(x) = \sum_{n=-\infty}^{\infty} V_n \cos(nG_1 x)$
2. **Bloch's theorem**: the wavefunction of an electron with wavevector k is $\boxed{\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}}$ where $\mathbf{u_k}(\mathbf{r})$ has the periodicity of the potential
3. Bloch's theorem shows that $\mathbf{k}$ and $\mathbf{k} + \mathbf{G}$ describes the exact the same thing (link)

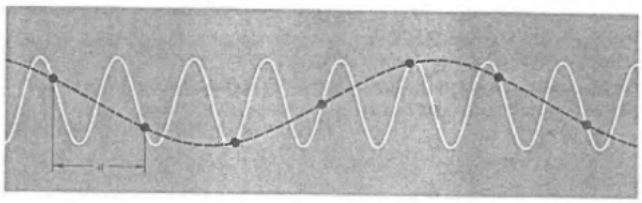
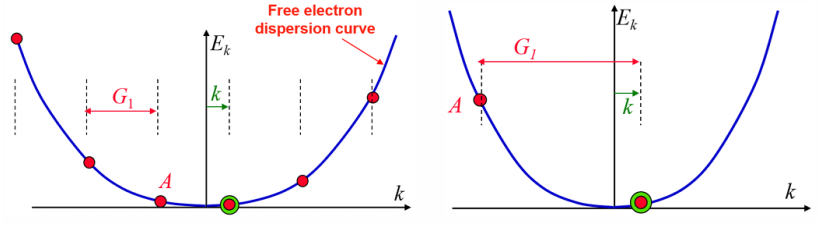


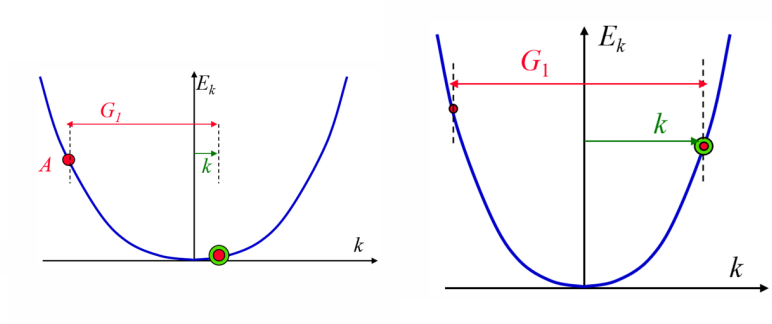
Figure 5 The wave represented by the solid curve conveys no information not given by the dashed curve. Only wavelengths longer than $2a$ are needed to represent the motion.

4. In 1D lattice with period a and total length A, $u_k(x) = \sum_{-\infty}^{\infty} C_{k,n} \frac{1}{\sqrt{A}} e^{inG_1 x}$, $G_1 = \frac{2\pi}{a}$
5. $\psi_k(x) = u_k(x) e^{ikx} = \sum_{-\infty}^{\infty} C_{k,n} \frac{1}{\sqrt{A}} e^{i(nG_1 + k)x} = \boxed{\sum_{-\infty}^{\infty} C_{k,n} |\phi_{k,n}\rangle}$, $\boxed{|\phi_{k,n}\rangle = \frac{1}{\sqrt{A}} e^{i(k+nG_1)x}}$
6.

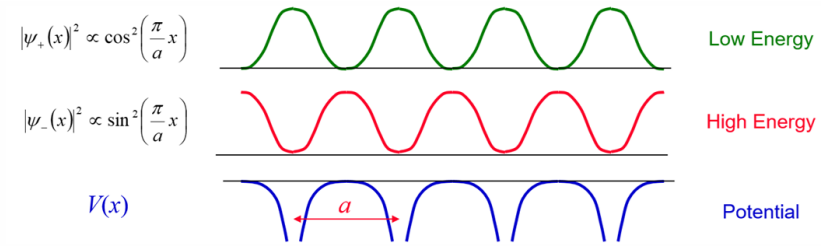
$$\hat{H}\psi(x) = \epsilon\psi(x)$$
$$\sum_m C_{k,m} \hat{H} |\phi\rangle_{k,m} = \epsilon \sum_p C_{k,p} |\phi_{k,p}\rangle$$
$$\sum_m C_{k,m} \langle\phi_{k,n}| \hat{H} |\phi_{k,m}\rangle = \sum_m H_{nm} C_{k,m} = \epsilon C_{k,n}$$
$$\underline{\mathbf{H}}\mathbf{C} = \epsilon\mathbf{C}$$
$$(\underline{\mathbf{H}} - \epsilon\mathbf{I})\mathbf{C} = 0$$

7. *2 states approximation*
   - Small potential $\implies$ great central basis-state contribution
   - 

   - $\psi_k(x) \approx C_{k,0} |\phi_{k,0}\rangle + C_{k,-1} |\phi_{k,-1}\rangle$



-
- For small k, $\psi_k(x) \sim |\phi_{k,0}\rangle$



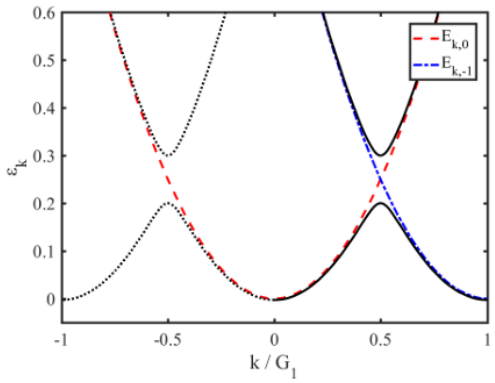
- The two new states, ψ_+ and ψ_- have different energies, so the degeneracy in the dispersion relationship is lifted; the two branches split apart in energy.
- For large k, $k \approx G_1/2$.

$$\psi_+(x) = \frac{1}{2}(|\phi_{G_1/2}\rangle + |\phi_{-G_1/2}\rangle) \propto \cos\left(\frac{\pi}{a}x\right)$$
$$\psi_-(x) = \frac{1}{2}(|\phi_{G_1/2}\rangle - |\phi_{-G_1/2}\rangle) \propto \sin\left(\frac{\pi}{a}x\right)$$

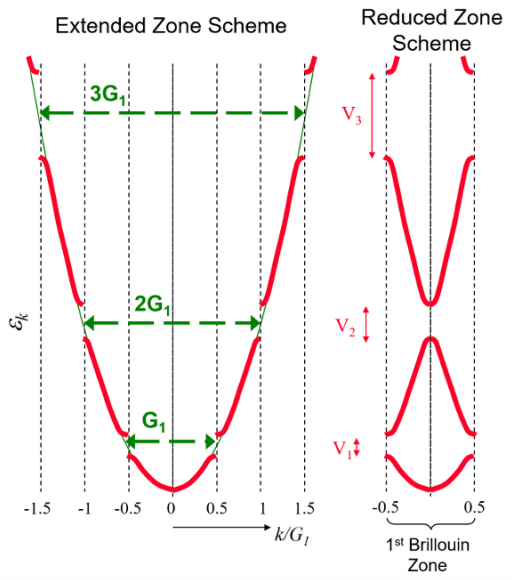
8.

$$\begin{aligned}
H_{nm} &= \langle\phi_{k,n}|\,\hat{H}\,|\phi_{k,m}\rangle \\
&= \int_0^A \left(\frac{1}{\sqrt{A}}e^{-i(nG_1+k)x}\right)\left(-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2} + V(x)\right)\left(\frac{1}{\sqrt{A}}e^{i(mG_1+k)x}\right)\mathrm{d}x \\
&= \frac{1}{A}\int_0^A e^{-inG_1x}\frac{\hbar^2(mG_1+k)^2}{2m_e}e^{imG_1x}\mathrm{d}x + \frac{1}{A}\int_0^A e^{-i(nG_1+k)x}\sum_p \frac{V_p}{2}(e^{-ipG_1x} + e^{ipG_1x})e^{i(mG_1+k)x}\mathrm{d}x \\
&= \frac{\hbar^2(mG_1+k)^2}{2m_e}\delta_{n,m} + \sum_{p=-\infty}^{\infty}\frac{V_p}{2}(\delta_{n,m+p} + \delta_{n,m-p})
\end{aligned}$$

9. For *2 states approximation*
   - $\psi_k(x) = C_{k,0}\,|\phi_{k,0}\rangle + C_{k,-1}\,|\phi_{k,-1}\rangle$
   - Let $V_0 = 0$, so $H_{00} = E_{k,0} = \frac{\hbar^2k^2}{2m_e}$, $H_{\bar{1}\bar{1}} = E_{k,-1} = \frac{\hbar^2(k-G_1)^2}{2m_e}$, $H_{0\bar{1}} = H_{\bar{1}0} = \frac{V_1}{2}$
   - $\begin{pmatrix} H_{00} & H_{0\bar{1}} \\ H_{\bar{1}0} & H_{\bar{1}\bar{1}} \end{pmatrix}\begin{pmatrix} C_{k,0} \\ C_{k,\bar{1}} \end{pmatrix} = \begin{pmatrix} E_{k,0} & V_1/2 \\ V_1/2 & E_{k,-1} \end{pmatrix}\begin{pmatrix} C_{k,0} \\ C_{k,\bar{1}} \end{pmatrix} = \epsilon_k \begin{pmatrix} C_{k,0} \\ C_{k,\bar{1}} \end{pmatrix}$
   - Solve for eigenvalues $\epsilon_k = \frac{1}{2}(E_{k,-1} + E_{k,0}) \pm \sqrt{\frac{1}{4}(E_{k,-1} - E_{k,0})^2 + \left(\frac{V_1}{2}\right)^2}$
   - Graph of ϵ_k, $E_{k,-1}$, $E_{k,0}$, band gap at $k = G_1/2$ is $\epsilon_g = V_1$ (according to equation)

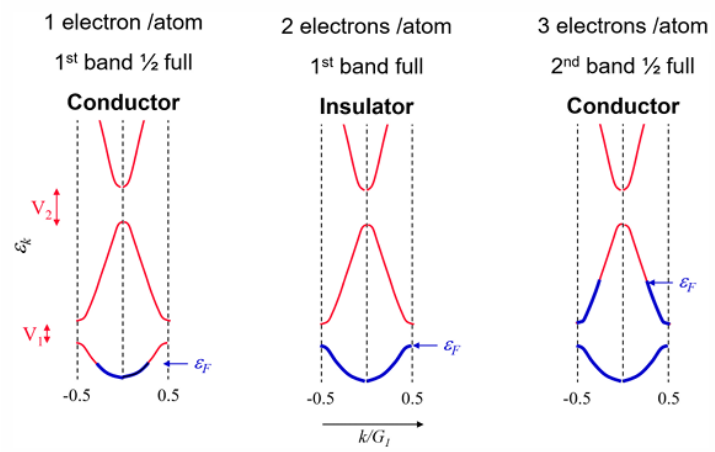


- Now consider more than 2 states, states further away with more G offset will fall inside Brillouin zone
  Note that the band gap at $k = G_1/2$ are $\epsilon_g = V_1, V_2, V_3, \ldots$
  The min and max of adjacent bands are at the same $k = G_1/2$, therefore we have *direct band gaps*.

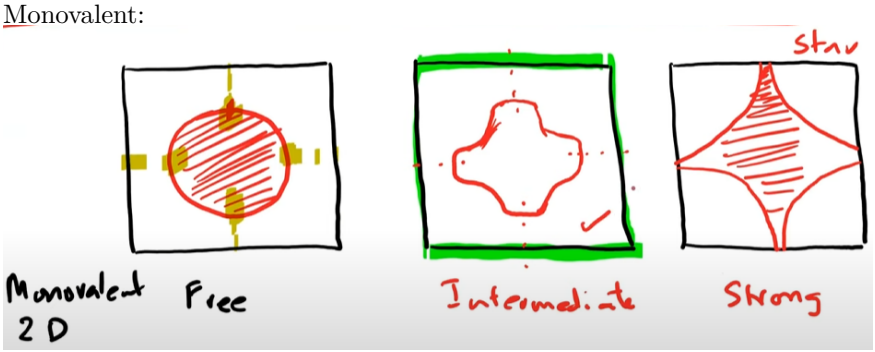


10. To form current, electrons need to move, so they must be in *partially filled bands*

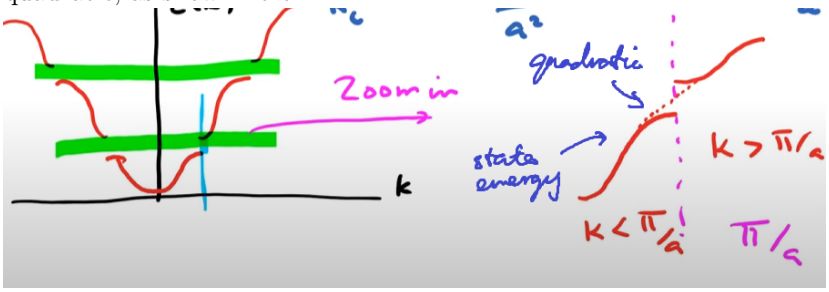
- In k space electrons separated by $2\pi/A$ (they're standing waves)
- 1st Brillouin zone's width $2\pi/a$
- No. states/energy bands in a zone $A/a = N$
- Electron has two spins, 2 electrons in each k-point
- Monovalent - N electrons, 1st state half filled, **conductor** (electrons near Fermi surface have nearby empty k-points to move to); Divalent - $2N$ electrons, 1st state fully filled, insulator (electrons need to overcome ϵ_g, band gap energy to conduct)
- Filling in electrons in 1D



11. 2D Fermi surfaces allow divalent elements to be conductors. Let's fill electrons from lowest energy for 0 potential, weak V_1 and strong V_1.
Monovalent:

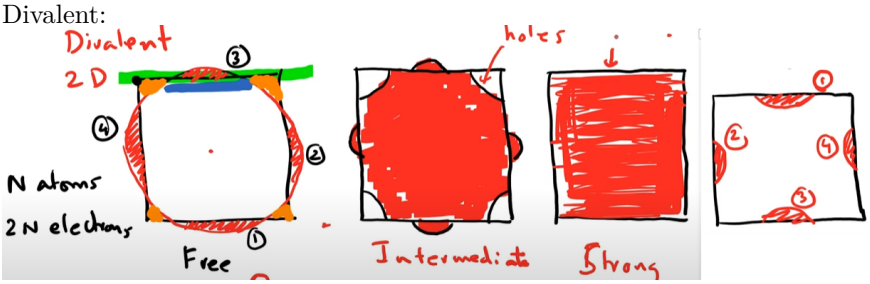


- If $V_1 = 0$, state energy is quadratic, Fermi surface is a cirlce. (N states each contain 2 electrons max, N electrons because monovalent, circle area is half square area ($(2\pi/a)^2/2 = \pi k_F^2$))
- If $V_1 \neq 0$ and small, parts near edge filled more because state energy there is lower than quadratic, as shown here:



- If V_1 is big, more dramatic

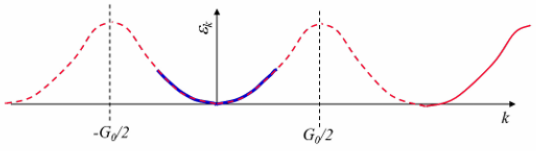
Divalent:



- $V_1 = 0$, parts outside 1st BZ, fold back like in 4th figure (*conduction bands*); parts inside are *valency bands*
- $V_1 \neq 0$ and small, less in higher state, more in lower state
- V_1/band gap very large, all electrons in 1st state

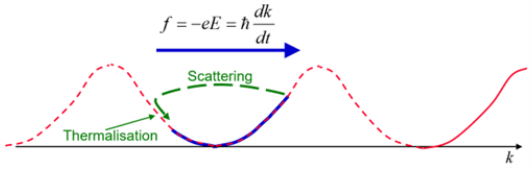
12. 3D Fermi surfaces website

No electric field:



- Electrons in ground state
- Equal numbers moving forwards and backwards
- No net current

Electric field, E, pushing electrons to the right:

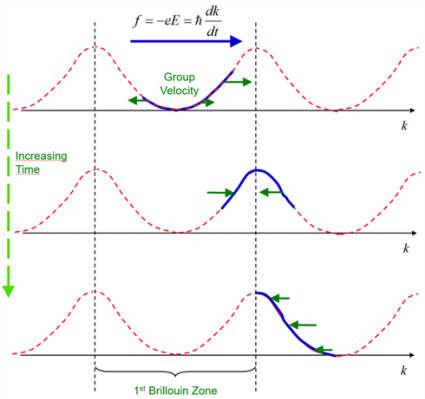


- E field causes electrons move to higher k-states (greater momentum).
- Phonons and defects scatter electrons into empty states of comparable energy.

- Scattered electrons thermalise (lose energy) by further phonon-interactions, until they reach the occupied states.
- Result is a net current; more electrons are moving forwards than backwards.[5]

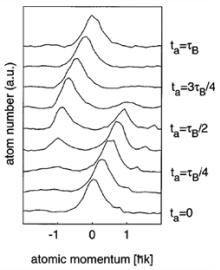
[5] Remember, it is the group velocity that is relevant, which is given by the gradient of the dispersion relation.

13. If the **electric field is strong** and the **scattering processes are weak**, an extreme situation can be reached - occupied states move continuously through k-space.



- Strong E field and weak scattering causes occupied states to steadily increase in k.
- Filled states cross into 2nd BZ.
- Direction of electron group velocity reverses.
- Backfolding means process is continuous.

- Group velocity, and hence position of electrons, oscillates.
- Effect is known as '**Bloch oscillation**'.



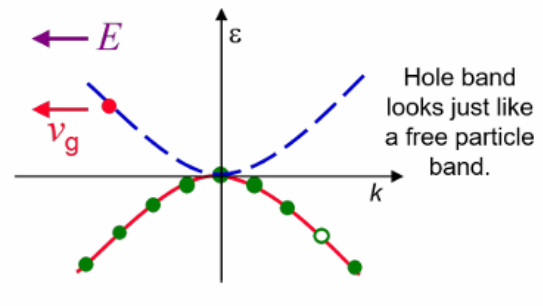
14.

15. Holes are "absence of electrons". $\epsilon_h = -\epsilon_e$, $k_h = -k_e$

16. **Effective mass** as in classical equations

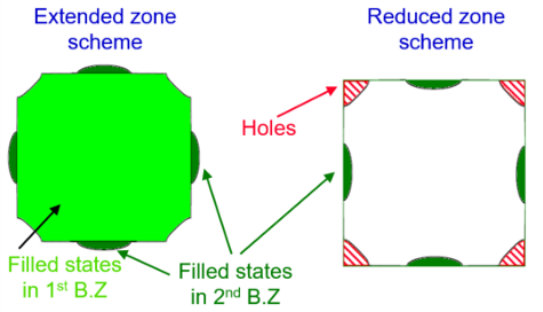
- $f = m^* \dfrac{\mathrm{d}v}{\mathrm{d}t}$
- $f = \dfrac{\mathrm{d}\hbar k}{\mathrm{d}t} = \hbar \dfrac{\mathrm{d}k}{\mathrm{d}t}$
- $v = v_g = \dfrac{\mathrm{d}\omega}{\mathrm{d}k}$
- $\epsilon = \hbar\omega$
- $f = m^* \dfrac{\mathrm{d}}{\mathrm{d}t}\dfrac{\mathrm{d}\omega}{\mathrm{d}k} = \dfrac{\mathrm{d}^2\omega}{\mathrm{d}k^2}\dfrac{\mathrm{d}k}{\mathrm{d}t} = \dfrac{1}{\hbar}\dfrac{\mathrm{d}^2\epsilon}{\mathrm{d}k^2}\dfrac{\mathrm{d}k}{\mathrm{d}t}$
- $\boxed{m^* = \hbar^2 / \dfrac{\mathrm{d}^2\epsilon}{\mathrm{d}k^2}}$
- Measurements: Hall effect, Cyclotron resonance

17. For an almost full ground state, curvature $\dfrac{\mathrm{d}^2\epsilon}{\mathrm{d}k^2} < 0$. $\boxed{m^* < 0}$



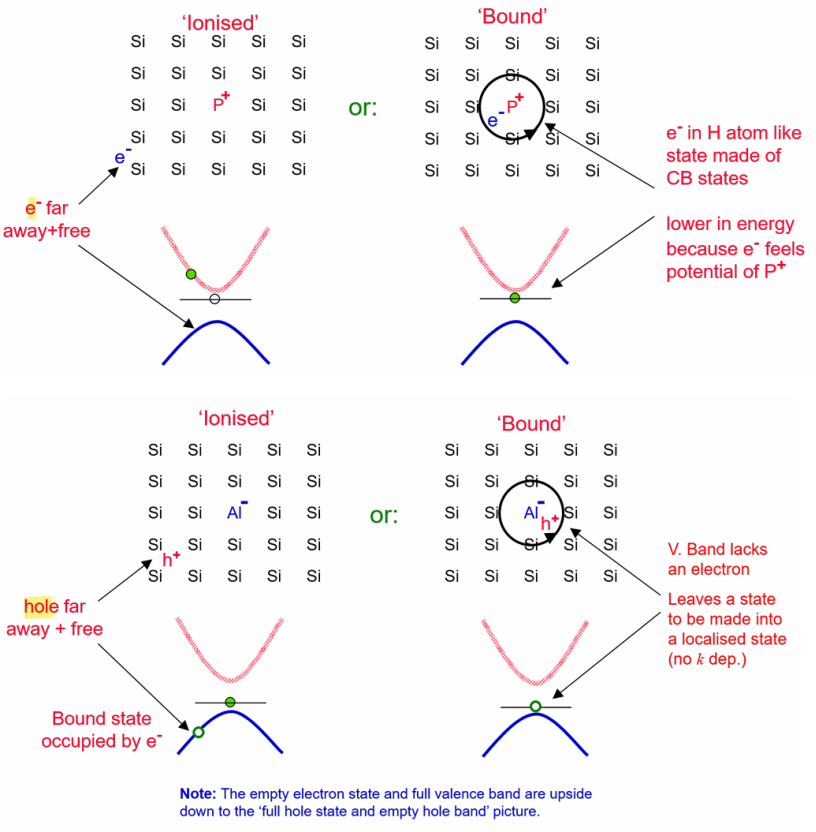
18. $\epsilon_h = -\epsilon_e$, $k_h = -k_e$

19. 2D holes

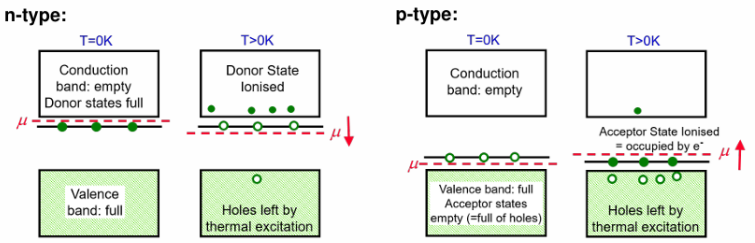


Semiconductors

1. n-type doping (P) creates electrons, p-type doping (Al) creates holes



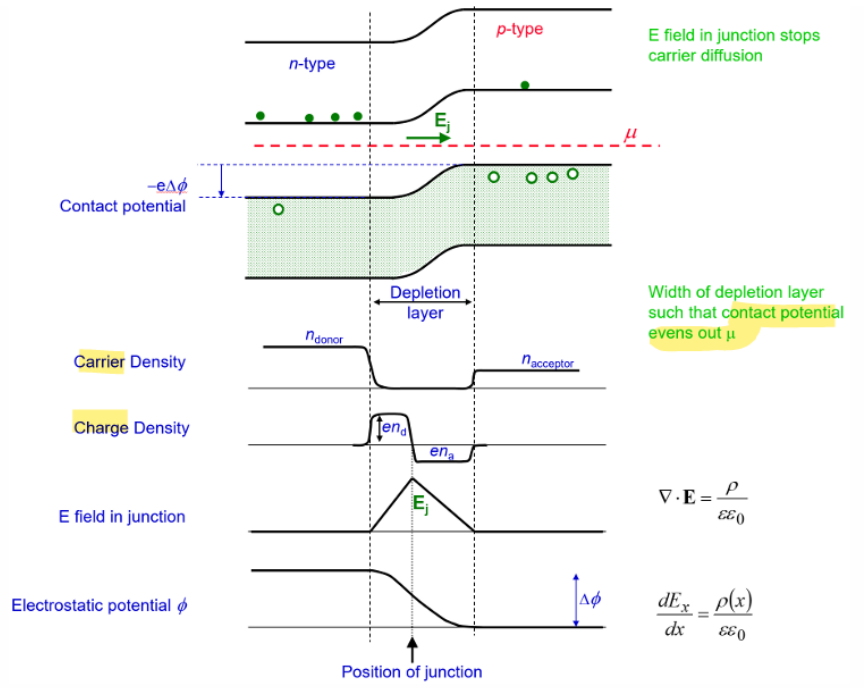
Straight line is energy state for 'bound' state/Hydrogen atom style, $E_n = -\dfrac{m_e^* e^4}{2(4\pi n \epsilon_r \epsilon_0 \hbar)^2}$, $r_n = \dfrac{4\pi\epsilon_r\epsilon_0 n^2\hbar^2}{m_e^* e^2}$ (ϵ_r is the relative permittivity)



Notes:

- μ moves towards the middle of the gap as T increases.
- At higher T the number of thermally excited carriers increases, so donor states become less important.

2.

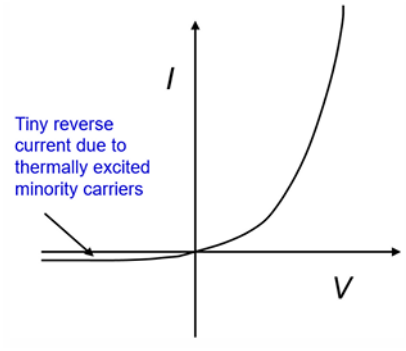


3.

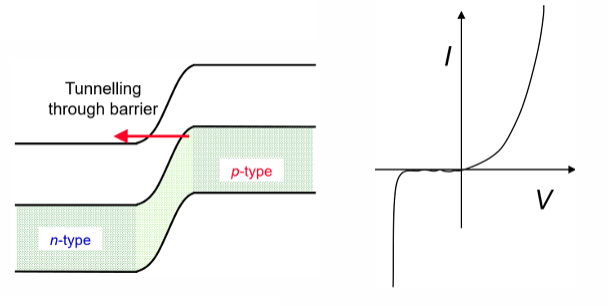
- Majority carrier: e^- in n, holes in p
- Forward bias: force majority carriers towards junction, shrinks depletion zone
- Without electric potential, chemical potential of n-type μ_n is just below conduction band; chemical potential of p-type μ_p is just above valence band
- ★Chemical potential/electrochemical potential/Fermi level of e^-/n-type is $\mu_n - eV$; of hole/p-type is $\mu_p + eV$ (so does energy bands)
- Depletion zone creates a potential difference (contact potential/built-in potential), balancing the μ ($\Delta V = e(\mu_n - \mu_p)$)
- Generation current - e^- moves from valence band to conduction band (thermal excitation or light absorption). Depends on temperature and band gap, independent of voltage applied
- Recombination current - annihilation of holes and electrons, energy emitted as light (LED) or heat.

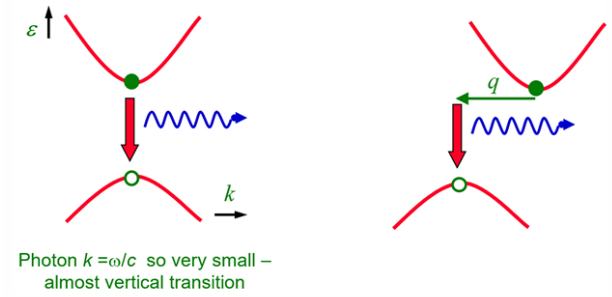
4.

- For $\epsilon \gg \mu$, $p_0(\epsilon) = \dfrac{1}{\exp[(\epsilon-\mu)/k_BT]+1} \approx \exp(-(\epsilon-\mu)/k_BT)$
- Apply voltage V changes μ from μ_n to $\mu_n + eV$, $p_V(\epsilon) \approx \exp[-(\epsilon-(\mu_n+eV))/k_BT] = p_0(\epsilon)\exp(eV/k_BT)$
- Chemical potential difference **maintained**, until battery is drained
- The generation current I_0 balances the recombination current when $V = 0$
- If $V \neq 0$, the generation current is still I_0; recombination current is changed to $I_0 \exp(eV/k_BT)$

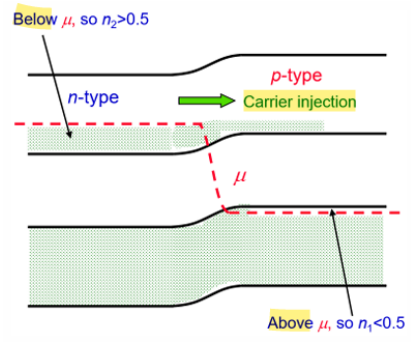
- $\boxed{I = I_0(\exp[eV/k_BT] - 1)}$
- 

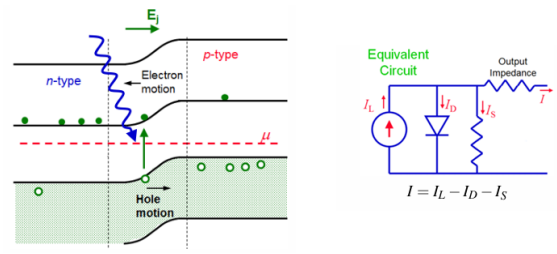
5. Zener breakdown: large **reverse** bias, raises valence band for p-type to above conduction band in n-type, electron can tunnel through to lower its energy



6. Avalanche breakdown:
   - strong reverse bias
   - thermally excited carriers gain energy
   - create more electron-hole pairs (avalanche)
   - form large current
   - release a lot of heat (possiblely break the device)
   - Usage: protection device, single photon detectors (designed to trigger avalanche with a photon)
7. LED
   - Forward bias
   - Energy released when carriers *recombine*
   - In most cases, for a *direct* band gap, energy becomes a photon
   - If band gap indirect, energy becomes heat
   - Photon wavelength controlled by band-gap
   - Energy efficient lighting
   - 

8. Semiconductor laser
   - Coherent LED

- Normal population: Boltzmann distribution, higher energy less populated
- **Population inversion**: Higher energy states more populated, non-equilibrium 'pumped' constantly
- Strong forward bias
- μ **above** band in n-type, **below** band in p-type, caused by very heavy doping
- Electrons **injected** from n-type side to maintain populated inversion
- **Stimulated emission**: one photon knocks off an electron, to produce two photons with the same energy. Fully derivation available if you learn QED.
- 

9. Solar cell
   - Reverse of LED
   - Equivalent to a current source, a diode and a shunt resistor (resistive leakage)
   - 

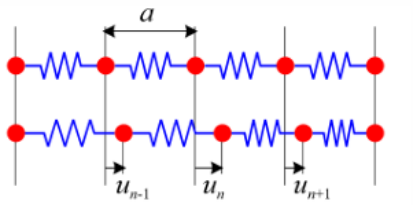
10. npn transistor, op-amps, silicon wafer and lithographics

Proofs

1. ★ $\delta(a) = \dfrac{1}{2\pi}\displaystyle\int_{-\infty}^{\infty} e^{ipa}\mathrm{d}p$

   $F = \displaystyle\sum_G \int n_G e^{i(\mathbf{G}-\Delta\mathbf{k})\cdot\mathbf{r}}\mathrm{d}V = 2\pi\sum_G n_G\delta(\mathbf{G}-\Delta\mathbf{k})$

2. ★

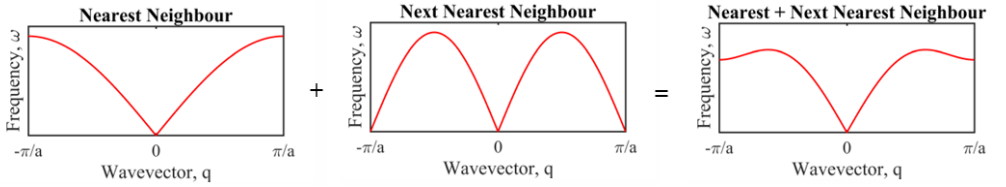


   Assume
   - monoatomic
   - cyclic structure $u_{N+1} = u_1$
   - simple spring between **adjacent** atoms $m\ddot{u}_n = k(u_{n+1} - u_n) - k(u_n - u_{n-1}) = k(u_{n+1} + u_{n-1} - 2u_n)$

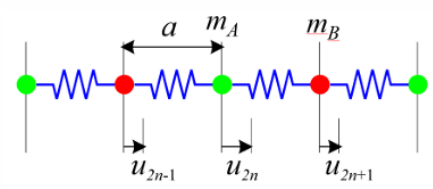
- symmetry thus constant phase differece $u_{n+1} = u_n e^{i\delta}$, $\delta = qa$
- Trial solution $u_n = ue^{-i\omega t}$

$$-m\omega^2 u e^{-i\omega t} = k(e^{i\delta} + e^{-i\delta} - 2)ue^{-i\omega t}$$
$$m\omega^2 = 2k(1 - \cos\delta)$$
$$\omega^2 = \frac{4k}{m}\sin^2\left(\frac{\delta}{2}\right)$$

Consider next neighbour: $\omega^2 = \frac{4}{m}\left(k_1 \sin^2\left(\frac{qa}{2}\right) + k_2 \sin^2(qa)\right)$ (linear, add solutions)

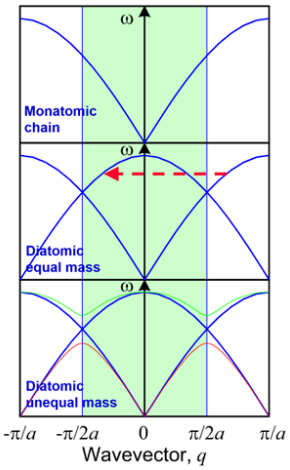


3. ★ Diatomic lattice:



- $$m_A\ddot{u}_{2n} = k(u_{2n+1} + u_{2n-1} - 2u_{2n})$$
$$m_B\ddot{u}_{2n+1} = k(u_{2n+2} + u_{2n} - 2u_{2n+1})$$

Some intuition with backfolding



- Trial solutions

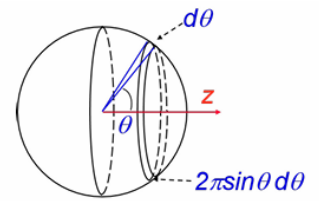
$$u_{2n} = U_1 e^{i(2nqa - \omega t)}$$
$$u_{2n+1} = U_2 e^{i((2n+1)qa - \omega t)}$$

- $$\begin{cases} (m_A\omega^2 - 2k)U_1 + 2k\cos(qa)U_2 &= 0 \\ 2k\cos(qa)U_1 + (m_B\omega^2 - 2k)U_2 &= 0 \end{cases}$$
has zero determinant (to be consistent)
- $\omega^2 = \frac{k}{m_A m_B}\left[(m_A + m_B) \pm \sqrt{(m_A + m_B)^2 - 4m_A m_B \sin^2(qa)}\right]$

4. ★
- Net phonon flow in x direction $\frac{1}{2}n\langle|v|\rangle$, n is phonon density
- c_{ph} heat capacity of a phonon; heat flux from T to $T+\Delta T$ is $j_{T\to T+\Delta T} = -\frac{1}{2}n\langle|v_x|\rangle c_{ph}\Delta T$ ($-$ve sign because heat flow from high to low T)
- Similarly heat flux from $T + \Delta T$ to T is $j_{T+DeltaT\to T} = -\frac{1}{2}n\langle|v_x|\rangle c_{ph}\Delta T$ (phonons travelling in both directions move heat in the same direction)
- Mean free path - distance between two collisions (in which phonons change its temperature); Between two collisions, $\Delta T = l\frac{\partial T}{\partial x} = \frac{\partial T}{\partial x}|v_x|\tau$, where $\tau = l/|v_x|$

- $j_v = -n\langle|v_x|\rangle c|v_x|\tau\dfrac{\partial T}{\partial x} = -n\langle v_x^2\rangle c\tau\dfrac{\partial T}{\partial x} = -\dfrac{1}{3}C\langle v^2\rangle\tau\dfrac{\partial T}{\partial x} = -\dfrac{1}{3}C\langle v\rangle l\dfrac{\partial T}{\partial x} = -\kappa\dfrac{\partial T}{\partial x}$, where $\langle v\rangle$ is the average speed.

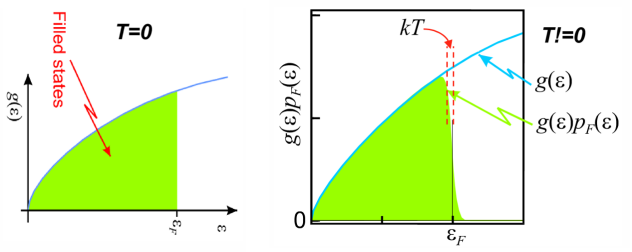
The above is coincidental (or 1D), real 3D proof here (without the weird $\langle v\rangle l = \langle v^2\rangle\tau$)
Use z-axis instead of x



- sphere of radius v
- $\langle c\rangle = \displaystyle\int_0^\infty vf(v)\mathrm{d}v$, where $f(v)$ is the velocity distribution
- v_z for phonons on the ring is $v\cos\theta$
- num of phonons with this v_z is $nf(v)\mathrm{d}v\cdot\dfrac{2\pi\sin\theta\mathrm{d}\theta}{4\pi}$
- heat tranferred by a phonon $-c_{ph}\dfrac{\partial T}{\partial z}l\cos\theta$
-
$$\begin{aligned} j &= -\frac{1}{2}c_{ph}nl\frac{\partial T}{\partial z}\int_0^\pi \sin\theta\cos^2\theta\mathrm{d}\theta\int_0^\infty vf(v)\mathrm{d}v \\ &= -\frac{1}{3}c_{ph}nl\langle c\rangle\frac{\partial T}{\partial z}\end{aligned}$$

5. ★
   - Entropy is $S_0 = k_B\ln\Omega_0$ in ground state (no electron), Ω_0 is the number of reservoir configurations
   - Transfer 1 electron of energy ϵ to this state, $\mathrm{d}U = T\mathrm{d}S + \mu\mathrm{d}N$, no $-p\mathrm{d}V$ work is done, $\mathrm{d}N = 1, \mathrm{d}U = \epsilon$, $\mathrm{d}S = \dfrac{\epsilon}{T} - \dfrac{\mu}{T}$
   - $S_0 + \mathrm{d}S = k_B\ln\Omega$, $\ln\Omega - \ln\Omega_0 = -\dfrac{\epsilon-\mu}{k_BT} = \ln(\Omega/\Omega_0)$
   - Average number of electrons in a state $p_F(\epsilon) = \dfrac{0\cdot\Omega_0 + 1\cdot\Omega}{\Omega+\Omega_0} = \dfrac{1}{1+\Omega_0/\Omega} = \dfrac{1}{1+\exp((\epsilon-\mu)/k_BT)}$

6. ★



- $U(T) = \displaystyle\int_0^\infty \epsilon g(\epsilon)p_F(\epsilon,T,\mu)\mathrm{d}\epsilon$
- $\dfrac{\partial U}{\partial T} = \displaystyle\int_0^\infty \epsilon g(\epsilon)\frac{\partial p_F}{\partial T}\mathrm{d}\epsilon$
- $N = \displaystyle\int_0^{\epsilon_F} g(\epsilon)\mathrm{d}\epsilon = \int_0^\infty g(\epsilon)p_F\mathrm{d}\epsilon$, $\dfrac{\partial N}{\partial T} = 0 = \displaystyle\int_0^\infty g(\epsilon)\frac{\partial p_F}{\partial T}\mathrm{d}\epsilon$
- $\dfrac{\partial U}{\partial T} = \dfrac{\partial U}{\partial T} - \epsilon_F\cdot 0 = \displaystyle\int_0^\infty (\epsilon-\epsilon_F)g(\epsilon)\frac{\partial p_F}{\partial T}\mathrm{d}\epsilon$
- recall that $g(\epsilon) = \dfrac{3N}{2\epsilon}$
- For small T, $\dfrac{\partial U}{\partial T} \approx g(\epsilon_F)\displaystyle\int_0^\infty (\epsilon-\epsilon_F)\frac{\partial p_F}{\partial T}\mathrm{d}\epsilon$ because $\dfrac{\partial p_F}{\partial T}$ looks like a delta function at ϵ_F

- Let $x = \dfrac{\epsilon - \epsilon_F}{k_B T}$, $\dfrac{\partial U}{\partial T} = g(\epsilon_F) \displaystyle\int_{-\epsilon_F/k_B T}^{\infty} (\epsilon - \epsilon_F) \frac{\epsilon - \epsilon_F}{k_B T^2} \frac{e^x}{(e^x+1)^2} (k_B T \mathrm{d}x) \approx k_B^2 T g(\epsilon_F) \displaystyle\int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} \mathrm{d}x = \frac{1}{3}\pi^2 k_B^2 T g(\epsilon_F) = \frac{1}{2\epsilon_F}\pi^2 N k_B^2 T$ (at small T, $\dfrac{-\epsilon_F}{k_B T} \approx -\infty$)
- Define Fermi temperature $T_F = \epsilon_F / k_B$

7. ★
   - $g(\epsilon) \propto \epsilon^{1/2}$
   - $\epsilon_F \propto \left(\dfrac{N}{V}\right)^{2/3}$
   - For each electron $\langle U \rangle = \dfrac{\int_0^{\epsilon_F} \epsilon g(\epsilon) \mathrm{d}\epsilon}{\int_0^{\epsilon_F} g(\epsilon) \mathrm{d}\epsilon} = \dfrac{3}{5}\epsilon_F$
   - For N electrons $\Delta U = -P\Delta V$, $P = \dfrac{\partial U}{\partial V} = -\dfrac{\partial N \langle U \rangle}{\partial \epsilon_F}\dfrac{\partial \epsilon_F}{\partial V} = -\dfrac{3}{5}N\left(-\dfrac{2}{3}\dfrac{\epsilon_F}{V}\right) = \dfrac{2}{5}n\epsilon_F$

Examples

1. Dispersion relations in 3D

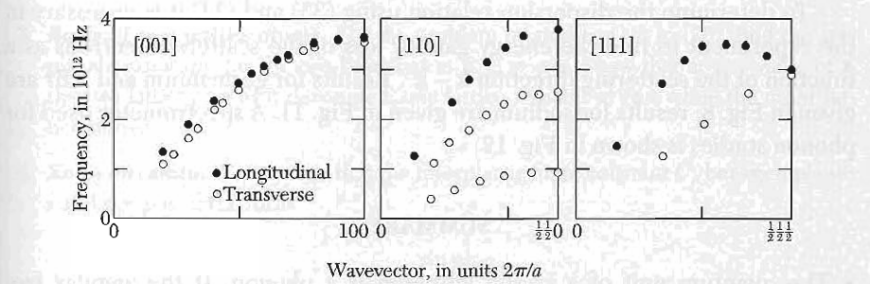
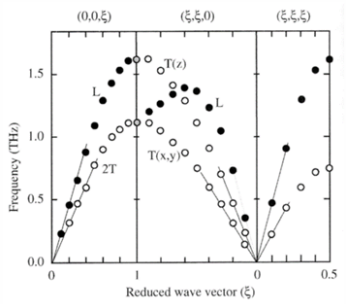
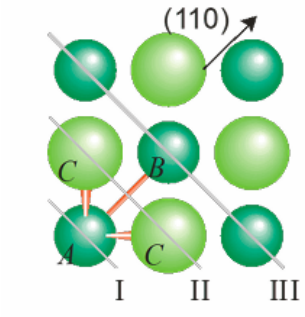


Figure 11 The dispersion curves of sodium for phonons propagating in the [001], [110], and [111] directions at 90 K, as determined by inelastic scattering of neutrons, by Woods, Brockhouse, March and Bowers.

Or joined together, with the 2nd one flipped





Neon's (it's FCC) longitudinal mode in (110) not sinusoidal not because of 2nd nearest neighbours, but neighbours a and $\sqrt{2}a$ away in this direction

2.