CH 6: FREE ELECTRON GAS

"In a very pure specimen at low temperatures, the mean free path may be as long as 10^8 interatomic spacings."

Hamiltonian and TISE for free space:
$$H = \frac{p^2}{2m}; \quad H\psi_n = \epsilon_n\psi_n = -\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2}$$

1D wave functions and related energies:
$$\psi_n = A\sin\left(\frac{n\pi}{L}x\right); \quad \epsilon_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$

Fermi Energy with 2 e^- in each orbital:
$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{n_F\pi}{L}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2$$

In three dimensions with $k_i = n_i\pi/L$:
$$\psi_k = \exp(i\boldsymbol{k}\cdot\boldsymbol{r}); \quad \epsilon_k = \hbar^2\boldsymbol{k}^2/2m$$

The Fermi Energy may be solved for:
$$\epsilon_F = \frac{\hbar^2}{2m}\boldsymbol{k}_F^2; \ N = \frac{2\cdot 4\pi k_F^3}{3\cdot(2\pi/L)^3}; \ \epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

At low T use Fermi-Dirac Distribution:
$$f(\epsilon) = (\exp((\epsilon - \mu)/k_B T) + 1)^{-1}$$

Taylor Expansion of the exponential:
$$\exp(x) = \sum_{n=0}^{\infty}\frac{x^n}{n!} = 1+x+\frac{x^2}{2}+\frac{x^3}{6}+\ldots$$

Total number of e^- is found through:
$$N = \int_0^{\infty}d\epsilon\ D(\epsilon)f(\epsilon) = \int_0^{\epsilon_F}d\epsilon\ D(\epsilon)$$

Momentum of a free electron is:
$$\boldsymbol{p} = m\boldsymbol{v} = \hbar\boldsymbol{k}$$

Lorentz Force law for charged particles:
$$\boldsymbol{F} = m\frac{d\boldsymbol{v}}{dt} = -e(\boldsymbol{E} + \boldsymbol{v}\times\boldsymbol{B})$$

Collision time τ; Matthiessen's Rule:
$$\frac{1}{\tau} = \frac{1}{\tau_{\text{phonons}}} + \frac{1}{\tau_{\text{defects}}} + \ldots$$

The velocity in a uniform electric field:
$$\boldsymbol{v} = -e\boldsymbol{E}\tau/m$$

Ohm's Law is then $(I = V/R)$:
$$\boldsymbol{j} = nqv = ne^2\boldsymbol{E}\tau/m = \sigma\boldsymbol{E}$$

With steady state electric field:
$$v_x = -(e\tau/m)E_x - \omega_c\tau v_y$$
$$v_y = -(e\tau/m)E_y + \omega_c\tau v_x$$
$$v_z = -(e\tau/m)E_z$$

Hall experiment, induced field across:
$$E_y = -\omega_c\tau E_x = -\frac{eB}{m}\tau E_x$$

Hall Coefficient for a current and field:
$$R_H = \frac{E_y}{j_x B} = -\frac{1}{ne}$$

CH 1: CRYSTAL STRUCTURE

Primitive basis vectors of a lattice:
$$\boldsymbol{a_1} \qquad \boldsymbol{a_2} \qquad \boldsymbol{a_3}$$

The primitive cell is the smallest cell that tessellates the volume:
$$V_{\text{cell}} = |\boldsymbol{a_1}\cdot\boldsymbol{a_2}\times\boldsymbol{a_3}|$$

The lattice site j is, for integers x, y, z:
$$\boldsymbol{r_j} = x_j\boldsymbol{a_1} + y_j\boldsymbol{a_2} + z_j\boldsymbol{a_3}$$

Translations are, for integers u:
$$\boldsymbol{T} = u_1\boldsymbol{a_1} + u_2\boldsymbol{a_2} + u_3\boldsymbol{a_3}$$
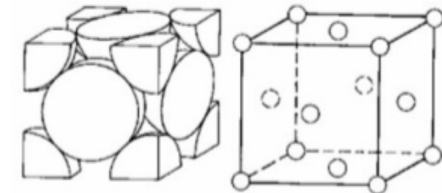
Miller Indices are (hkl), where Z makes h, k, l integers; x, y, z are intercepts:
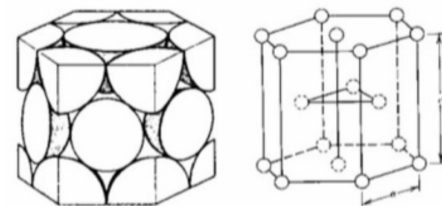$$h = \frac{Z}{x_{\text{int}}} \qquad k = \frac{Z}{y_{\text{int}}} \qquad l = \frac{Z}{z_{\text{int}}}$$

where h represents h planes per $Z\boldsymbol{a_1}$
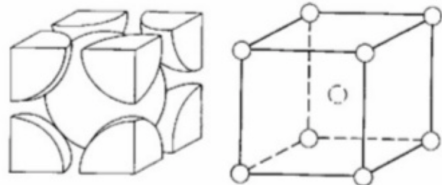
$a(\hat{\boldsymbol{x}}+\hat{\boldsymbol{y}}-\hat{\boldsymbol{z}})/2; \quad a(-\hat{\boldsymbol{x}}+\hat{\boldsymbol{y}}+\hat{\boldsymbol{z}})/2; \quad a(\hat{\boldsymbol{x}}-\hat{\boldsymbol{y}}+\hat{\boldsymbol{z}})/2$

$a(\hat{\boldsymbol{x}}+\hat{\boldsymbol{y}})/2; \qquad a(\hat{\boldsymbol{y}}+\hat{\boldsymbol{z}})/2; \qquad a(\hat{\boldsymbol{x}}+\hat{\boldsymbol{z}})/2$

$a(\sqrt{3}\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}})/2; \qquad a(-\sqrt{3}\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}})/2; \qquad c\hat{\boldsymbol{z}}$

Parameter	SC	BCC	FCC
Conventional vol.	a^3	a^3	a^3
Points per cell	1	2	4
Near neighbors	6	8	12
Neighbor distance	a	$\sqrt{3}a/2$	$\sqrt{2}a/2$
Packing fraction	$\pi/6$	$\pi\sqrt{3}/8$	$\pi\sqrt{2}/6$

Structure	Positions of A	Positions of B
NaCl	$000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}; 00\frac{1}{2}; 0\frac{1}{2}0; \frac{1}{2}00$
CsCl	$000; 001; 010\ldots 111$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$ (BCC)
HCP	$000; \ldots\frac{2}{3}\frac{1}{3}\frac{1}{2}; \ldots$	N/A
Diamond	$000; \ldots\frac{1}{4}\frac{1}{4}\frac{1}{4}; \ldots$	N/A (FCC)
ZnS	$000; 0\frac{1}{2}\frac{1}{2}; \frac{1}{2}0\frac{1}{2}; \frac{1}{2}\frac{1}{2}0$	$\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}$

CH 2: RECIPROCAL LATTICE

Transform from a point on or a vector to a reciprocal lattice point or vector.

Fourier Expansion periodic functions:
$$n(x) = \sum_p n_p\exp(i\cdot 2\pi p/a\cdot x) = n(x+a)$$

The Fourier Coefficients are given by:
$$n_p = \frac{1}{a}\int_0^a dx\ n(x)\exp(-i2\pi p/a\cdot x)$$

In three dimensions, this is equivalent:
$$n(\boldsymbol{r}) = \sum_{\boldsymbol{G}} n_{\boldsymbol{G}}\exp(i\boldsymbol{G}\cdot\boldsymbol{r}) = n(\boldsymbol{r} + \boldsymbol{T})$$

With the Fourier Coefficients given by:
$$n_{\boldsymbol{G}} = \frac{1}{V_{\text{cell}}}\int_{\text{cell}} dV\ n(\boldsymbol{r})\exp(-i\boldsymbol{G}\cdot\boldsymbol{r})$$

The reciprocal lattice vectors fulfill:
$$\boldsymbol{b_i}\cdot\boldsymbol{a_j} = 2\pi\delta_{i,j}; \quad \boldsymbol{G} = v_1\boldsymbol{b_1}+v_2\boldsymbol{b_2}+v_3\boldsymbol{b_3}$$

Reciprocal lattice vectors are found by:
$$\boldsymbol{b_1} = \frac{2\pi}{V_c}(\boldsymbol{a_2}\times\boldsymbol{a_3}); \ \boldsymbol{b_2} = \frac{2\pi}{V_c}(\boldsymbol{a_3}\times\boldsymbol{a_1}); \ \boldsymbol{b_3} = \frac{2\pi}{V_c}(\boldsymbol{a_1}\times\boldsymbol{a_2})$$

Primitive reciprocal lattice vectors are:
BCC: $(2\pi/a)(\hat{\boldsymbol{y}}+\hat{\boldsymbol{z}}); \quad (2\pi/a)(\hat{\boldsymbol{x}}+\hat{\boldsymbol{z}}); \quad (2\pi/a)(\hat{\boldsymbol{x}}+\hat{\boldsymbol{y}})$
FCC: $(2\pi/a)\{(-\hat{\boldsymbol{x}}+\hat{\boldsymbol{y}}+\hat{\boldsymbol{z}}); \ (\hat{\boldsymbol{x}}-\hat{\boldsymbol{y}}+\hat{\boldsymbol{z}}); \ (\hat{\boldsymbol{x}}+\hat{\boldsymbol{y}}-\hat{\boldsymbol{z}})\}$
HCP: $(2\pi/a)(\hat{\boldsymbol{x}}/\sqrt{3}+\hat{\boldsymbol{y}}); (2\pi/a)(-\hat{\boldsymbol{x}}/\sqrt{3}+\hat{\boldsymbol{y}}); (2\pi/c)\hat{\boldsymbol{z}}$

Bragg diffraction from parallel planes:
$$2d\sin(\theta) = n\lambda$$

To exceptionally good agreement:
$$\Delta\boldsymbol{k} = \boldsymbol{k}' - \boldsymbol{k} \approx \boldsymbol{G}$$

In scattering E and λ are conserved:
$$\boldsymbol{k}^2 = \boldsymbol{k}'^{\,2} \Longrightarrow (\boldsymbol{k} + \boldsymbol{G})^2 = \boldsymbol{k}^2$$

symmetry $\Longrightarrow \boldsymbol{k}\cdot(\boldsymbol{G}/2) = (\|\boldsymbol{G}\|/2)^2$

The Laue equations equivalently relate:
$$\boldsymbol{a_i}\cdot\boldsymbol{\Delta k} = 2\pi v_i, \quad \text{for } i = 1, 2, 3$$

"The first Brillouin Zone is the smallest volume entirely enclosed by planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from the origin ... exhibits all wavevectors which can be Bragg-reflected ..."

Scattering intensity is related to scattering amplitude and structure factor:
$$I \propto (F_{\boldsymbol{G}})^2 = (NS_{\boldsymbol{G}})^2$$

Structure factor; sum over the unit cell:
$$S_{\boldsymbol{G}} = \sum_j f_j\exp(-i2\pi(v_1 x_j + v_2 y_j + v_3 z_j))$$

Atomic form factor is the integral:
$$f_j = 4\pi\int_0^{\infty} dr\ r^2 n_j(r)\frac{\sin(Gr)}{Gr}$$

Ch 6: (Continued)

Electronic heat capacity at $T \ll T_\mathrm{F}$:
$$C = \frac{\pi^2 N k_\mathrm{B} T}{2 T_\mathrm{F}}$$

The mean free path is $l = v_\mathrm{F} \tau$, and the thermal conductivity of e^- is given by:
$$K = \frac{C v l}{3} = \frac{\pi^2 n k_\mathrm{B}^2 T \tau}{3m}$$

Lorenz Number ≈ constant for metals:
$$L = \frac{K}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_\mathrm{B}}{e}\right)^2$$

Ch 3: Crystal Bonding

"The cohesive energy of a crystal is defined as the energy that must be added to the crystal to separate its components into neutral free atoms at rest."

Total energy, equilibrium separation:
$$U_\mathrm{tot} = \frac{NU}{2}; \quad F = -\frac{dU}{dr}; \quad \frac{dU(R_0)}{dr} = 0$$
"Charge distribution around an atom is not limited by a spherical boundary." Yet, typical radii are from $0.5 \, \text{Å} - 5 \, \text{Å}$.

The inert gasses $\mathrm{He, Ne, Ar, Kr, Xe}$ are weakly bound $0.1 \, \mathrm{eV/atom}$, relative to the ionization energies $10 \, \mathrm{eV/atom}$, and form the closely packed structures.

Lennard-Jones potential with Pauli Exclusion, and Van der Waals energies:
$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6\right]$$
$$U_\mathrm{tot} = \frac{N4\epsilon}{2}\left(\frac{\sigma^{12}}{R^{12}}\sum_j p_{ij}^{-12} + \frac{\sigma^6}{R^6}\sum_j p_{ij}^{-6}\right)$$

Ionic bonds are electrostatic attractions, and form moderately packed structures.

From repulsion, attraction of $2N$ ions, for Madelung constant α, neighbors z, experimental strength λ, and range ρ:
$$U_\mathrm{tot} = NU_i = N\left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{4\pi\epsilon_0 R}\right)$$
$$U_\mathrm{tot}(R_0) = -(N\alpha q^2)/(4\pi\epsilon_0 R_0)\cdot(1-\rho/R_0)$$

"There is a continuous range of crystals between the ionic and covalent limits."

Covalent crystals form strong bonds by "exchange interactions" of: $\uparrow e^- + \downarrow e^-$, and loosely packed structures, ex. $\mathrm{C(s)}$.

Metals have valence and conduction e^-, and somewhat close packed structures.

Hydrogen bonds are ionic with $\sim 0.1 \, \mathrm{eV}$.

Defects, Amorphous Solids

Solids are not always perfect crystals, and may be amorphous, or may have thermally generated defects such as: vacancies, substitutional impurities, or interstitial atoms and impurities.

Vacancies are in the minimization of the free energy $F = E - TS$, with S, the Stirling Approximation, $\partial F/\partial N_\mathrm{v} = 0$, and $N \gg N_\mathrm{v}$: $N_\mathrm{v} = N\exp(-E_\mathrm{v}/k_B T)$.

No long range order in amorphous solids, so to describe atomic positions:
$$\rho(r) = 4\pi r^2 \langle n(r)\rangle$$

Ch 7: Energy Bands

Begin with traveling wave momentum:
$\boldsymbol{p} = \hbar\boldsymbol{k} \Rightarrow \boldsymbol{H} = \boldsymbol{p}^2/2m \Rightarrow \psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$
Electrons reflect at the boundary of the Brillouin Zone, making standing waves.
$$e^{\pm i\pi x/a} \Rightarrow \begin{cases} \psi_+: e^{i\pi x/a} + e^{-i\pi x/a} = 2\cos(\pi x/a) \\ \psi_-: e^{i\pi x/a} - e^{-i\pi x/a} = 2i\sin(\pi x/a) \end{cases}$$
Where cos concentrates e^- at ion cores, and sin concentrates e^- between cores.
$$\rho_+ = \|\psi_+\|^2 \propto \cos^2(\pi x/a); \ \rho_- \propto \sin^2(\pi x/a)$$
Energy gap with the potential $U(x)$ is:
$$\langle E_\mathrm{g}\rangle_\ell = \frac{1}{\|\ell\|}\left|\int_\ell dx \, U(x)(\|\psi_+\|^2 - \|\psi_-\|^2)\right|$$
Bloch's Theorem: "ψ for the periodic potential, U, are the product of a plane wave, $\exp(i\boldsymbol{k}\cdot\boldsymbol{r})$, times a function, u, with the periodicity of the potential."
$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = u_{\boldsymbol{k}}(\boldsymbol{r})\exp(i\boldsymbol{k}\cdot\boldsymbol{r})$$

Kronig Penney Model: periodic $\delta(x)$ potential, spacing a and magnitude P
$$\cos(Ka) + P\sin(Ka)/Ka = \cos(ka)$$

Wave equation for a general potential:
$$U(x) = \sum_G U_G e^{iGx} = 2\sum_{G>0} U_G\cos(Gx)$$
Over an interval, the wave function is:
$$\psi(x) = \sum_k C(k)e^{ikx}$$
With $\lambda_k = \hbar^2 k^2/2m$, central equation is equivalent to Schrödinger Equation:
$$(\lambda_k - \epsilon)C(k) + \sum_G U_G C(k-G) = 0$$
Writing as a matrix, $\boldsymbol{MC} = \boldsymbol{0}$, solving $|\boldsymbol{M}| = 0$ yields the energy spectrum ϵ_k.

"Crystal momentum" is $\boldsymbol{p}_\mathbf{crystal} \equiv \hbar\boldsymbol{k}$

The empty lattice approximation takes all $\boldsymbol{G}$ for a given $\boldsymbol{k}$ direction $[hkl]$:
$$\epsilon(k_x, k_y, k_z) = (\hbar^2/2m)(\boldsymbol{k}+\boldsymbol{G})\cdot(\boldsymbol{k}+\boldsymbol{G})$$
$$= (\hbar^2/2m)((k_x + G_x)^2 + (k_y + G_y)^2 + (k_z + G_z)^2)$$
N cells $\Rightarrow 2N$ orbitals $+ \epsilon_F \to$ conductivity

Ch 4: Crystal Vibrations

Newton's Second Law insists $\boldsymbol{F} = m\boldsymbol{a}$.

To find $\omega(K)$, write equations of motion, ansatz $u(t) = U\exp(-i\omega t)\exp(isKa)$, write in matrix form, and solve the characteristic equation for dispersion.

The first Brillouin Zone contains all possible relative positions of the planes. So, "by subtraction of an appropriate reciprocal lattice vector from K, we always obtain an equivalent wave vector in the first zone," or $-\pi/a < K < \pi/a$.

Phonons do not have linear momentum, only relative momentum determined with a reciprocal vector. In collisions, phonons may be emitted or absorbed:
$$\boldsymbol{k} + \boldsymbol{G} = \boldsymbol{k}' \pm \boldsymbol{K}$$
Phonon scattering may be either normal, $\boldsymbol{k}_1 + \boldsymbol{k}_2 = \boldsymbol{k}_3$, or flipped, $\boldsymbol{k}_1 + \boldsymbol{k}_2 = \boldsymbol{k}_3 + \boldsymbol{G}$. Phonon energy is $E = (n + \frac{1}{2})\hbar\omega$.

Ch 5: Thermal Properties

Bose-Einstein dist. and heat capacity:
$$\langle n\rangle = \frac{1}{\exp(\hbar\omega/k_\mathrm{B}T) - 1}; \ C_\mathrm{v} = \left(\frac{\partial U}{\partial T}\right)_\mathrm{v}$$
The heat capacity is found using non-dimensionalization and differentiation. Note that with density of states $D(\omega)$:
$$U = \sum_s E_s \langle n(E_s)\rangle \Longleftrightarrow U = \int_\omega d\omega \, D(\omega)\langle n(\omega)\rangle E(\omega)$$
For $D = dN/d\omega$, in $1-3$ dimensions, where $N = K_\mathrm{volume}/K_\mathrm{unit}$ for radius K:
$$N_1 = 2K\left(\frac{L}{2\pi}\right)^1; \ N_2 = \pi K^2\left(\frac{L}{2\pi}\right)^2; \ N_3 = \frac{4\pi K^3}{3}\left(\frac{L}{2\pi}\right)^3$$

The Einstein Model is $D = N\delta(\omega - \omega_\mathrm{E})$, and works best when $T \sim T_\mathrm{E} = \hbar\omega_\mathrm{E}/k_\mathrm{B}$:
$$C_\mathrm{v} = 3Nk_\mathrm{B}\left(\frac{\hbar\omega_\mathrm{E}}{k_\mathrm{B}T}\right)^2 \frac{\exp(\hbar\omega_\mathrm{E}/k_\mathrm{B}T)}{(\exp(\hbar\omega_\mathrm{E}/k_\mathrm{B}T) - 1)^2}$$

The Debye Model assumes $\omega = vK$, with a cutoff frequency ω_D, from which the density of states may be calculated. In the low temperature limit, $T \ll T_\mathrm{D}$:
$$T_\mathrm{D} = \frac{\hbar v}{k_\mathrm{B}}\left(\frac{6\pi^2 N}{V}\right)^{1/3}; \ C_\mathrm{v} = \frac{12\pi^4}{5}Nk_\mathrm{B}\left(\frac{T}{T_\mathrm{D}}\right)^3$$

Using $U = cx^2 - gx^3$, displacement is:
$$\langle x\rangle = \int_x dx \, x\langle n\rangle \Big/ \int_x dx \, \langle n\rangle \approx \frac{3g k_\mathrm{B}}{4c^2}\cdot T$$

Thermal and electrical conductivity: (thermal $j = -k\nabla T$, where $k = C_\mathrm{v}vl/3$)

Thermal $T \ll T_\mathrm{D}$	$k \propto C_\mathrm{v} \propto T^{+3}$	
Thermal $T \gg T_\mathrm{D}$	$k \propto 1/\langle n\rangle \propto T^{-1}$	
Electrical $T \ll T_\mathrm{D}$	$\sigma \propto \ldots \propto T^{-5}$	
Electrical $T \gg T_\mathrm{D}$	$\sigma \propto 1/\langle n\rangle \propto T^{-1}$	

$\ldots = 1/\langle n\rangle \cdot 1/\mathrm{coupling} \, (1) \cdot 1/\mathrm{cross \, section} \, (2)$