Electrons & Phonons

- Ohm’s & Fourier’s Laws
- Mobility & Thermal Conductivity
- Heat Capacity
- Wiedemann-Franz Relationship
- Size Effects and Breakdown of Classical Laws

Thermal Resistance, Electrical Resistance

\[ P = I^2 \times R \]
\[ \Delta T = P \times R_{TH} \]
\[ R = f(\Delta T) \]
\[ \Delta V = I \times R \]

Fourier’s Law (1822)
Ohm’s Law (1827)
Poisson and Fourier’s Equations

\[ \nabla \cdot (\epsilon \nabla V) - \rho = 0 \]

\[ J_E = -\sigma \nabla V + qD \nabla n \]

\[ J_T = -k \nabla T \]

Note: check units!

Some other differences:

- Charge can be fixed or mobile; Fermions vs. bosons…

Mosquitoes on a Windy Day

- Some are slow
- Some are fast
- Some go against the wind

Also characterized by some spatial distribution and average \( n(x,y,z) \)

Can be characterized by some velocity histogram (distribution and average)

© 2008 Eric Pop, UIUC
Calculating Mosquito Current Density

- Current = # Mosquitoes through A per second
- \( N_A = n(r,v) \times \text{Vol} = n(r,v) \times A \times dr \)
- Per area per second: \( J_A = \frac{dN_A}{dt} = n \frac{dr}{dt} = nv \)

Charge and Energy Current Density

- What if mosquitoes carry charge (q) or energy (E) each?
- Charge current: \( J = qnv \) → Units?
- Energy current: \( J = Env \) → Units?
**Particles or Waves?**

- Recall, particles are also “matter waves” (de Broglie)
- Momentum can be written in either picture
  \[ p = m^* v = h k = h \frac{2\pi}{\lambda} \]
- So can energy
  \[ E = h \omega \]
  \[ E = \frac{m^* v^2}{2} = \frac{p^2}{2m^*} = \frac{h^2 k^2}{2m^*} \]
- Acknowledging this, we usually write \( n(k) \) or \( n(E) \)

**Charge and Energy Flux (Current)**

- Total number of particles in the distribution:
  \[ N = \sum_k n(k) = \sum_k g(k)f(k) \]
- Charge & energy current density (flux):
  \[ J_q = q \sum_k n(k)v(k) = q \sum_k [g(k)f(k)]v(k) \]
  \[ J_E = \sum_k E(k)n(k)v(k) = \sum_k E(k)[g(k)f(k)]v(k) \]
- Of course, these are usually integrals (Slide 10)
What is the Density of States $g(k)$?

- Number of parking spaces in a parking lot
- $g(k) =$ number of quantum states in device per unit volume
- How “big” is one state and how many particles in it?

$$L = n \lambda = n \frac{2 \pi}{k}$$

$$\text{vol, } d = \frac{1}{s} \left( \frac{2 \pi}{L} \right)^d$$

“d” dimensions

“s” spins or polarizations

$L^d \rightarrow L$, $A$, or $V$

Constant Energy Surface in 1-, 2-, 3-D

- For isotropic $m^*$, the constant energy surface is a sphere in 3-D $k$-space, circle in 2-D $k$-space, etc.
- Ellipsoids for Si conduction band
- Odd shapes for most metals
**Counting States in 1-, 2-, or 3-D**

- System has N particles (n=N/V), total energy U (u=U/V)
- This is obtained by counting states, e.g. in 3-D:
  \[
  N = \int_0^\infty g(k) f(k) dk \\
  u = \frac{U}{V} = \frac{1}{V} \int_0^\infty E(k) g(k) f(k) dk
  \]

**What is the Probability Distribution?**

- Probability (0 ≤ f(k) ≤ 1) that a parking spot is occupied
- Probability must be properly normalized
  \[
  1 = \sum_k f(k)
  \]
- Just like the number of particles must add up
  \[
  N = \sum_k n(k) = \sum_k g(k) f(k)
  \]
- But people generally prefer to work with *energy* distributions, so we convert everything to E instead of k, and work with integrals rather than sums
Fermi-Dirac vs. Bose-Einstein Statistics

\[ f_{FD}(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} \]

\[ f_{BE}(E) = \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1} \]

Fermions = half-integer spin (electrons, protons, neutrons)
Bosons = integer spin (phonons, photons, \(^{12}\)C nuclei)

- In the limit of high energy, both reduce to the classical Boltzmann statistics:

Temperature and (Non-)Equilibrium

- Statistical distributions (FD or BE) establish a link between temperature, quantum state, and energy level
- Particles in thermal equilibrium obey FD or BE statistics
- Hence temperature is a measure of the internal energy of a system in thermal equilibrium

- What if (through an external process) I greatly boost occupation of electrons at E=0.1 eV?
- Result: “hot electrons” with effective temperature, e.g., at T=1000
- Non-equilibrium distribution
Counting Free Electrons in a 3-D Metal

\[ n = \frac{N}{V} = \frac{1}{V} \int_{0}^{\infty} g(k) f(k) dk = \frac{1}{L^3} \int_{0}^{\infty} \frac{4\pi k^2 dk}{(2\pi / L)^3} f(k) \]

- Convert integral over \( k \) to integral over \( E \) since we know energy distribution (for electrons, Fermi-Dirac)

\[ \int_{0}^{\infty} g(E) dE \propto E^{3/2} \]

\[
E_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 n}{2} \right)^{(3/2)} \approx \frac{\hbar^2}{8m} \left( \frac{3\pi}{2} \right)^{(3/2)}
\]

\[
E_F = \left( \frac{6.6 \times 10^{-34} \text{ J}}{8.9 \times 10^{-31} \text{ J}} \right)^{1/3} \approx 6 \text{ eV}
\]

\[ T_F = E_F / k_B \approx \text{few} \times 10^4 \text{ K} \]

So \( E_F \gg k_B T \) for most temperatures

---

Counting Free Electrons Over \( E \)

- At \( T = 0 \), all states up to \( E_F \) are filled, and above are empty
- This also serves as a definition of \( E_F \)

\[ f(\varepsilon) = \begin{cases} 1, & \varepsilon \leq E_F \\ 0, & \varepsilon > E_F \end{cases} \]

\[ g(\varepsilon) = \frac{1}{\varepsilon^{1/2}} \left( \frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{3/2} \]

\[ n = \int_{0}^{\infty} g(\varepsilon) f(\varepsilon) d\varepsilon = \int_{0}^{E_F} g(\varepsilon) d\varepsilon = \frac{1}{3\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} (E_F)^{3/2} \]
Density of States in 1-, 2-, 3-D
(with the nearly-free electron model and quadratic energy bands!)

\[
g^{3D}(E) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2}
\]

\[
g^{2D}(E) = \frac{m^*}{\pi\hbar^2}
\]

\[
g^{1D}(E) = \frac{m^{3/2}2^{1/2}}{\pi\hbar} E^{-1/2}
\]

Electronic Properties of Real Metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>n ((10^{28} \text{ m}^{-3}))</th>
<th>(m^*/m_0)</th>
<th>(v_F \times 10^6 \text{ m/s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8.45</td>
<td>1.38</td>
<td>1.57</td>
</tr>
<tr>
<td>Ag</td>
<td>5.85</td>
<td>1.00</td>
<td>1.39</td>
</tr>
<tr>
<td>Au</td>
<td>5.90</td>
<td>1.14</td>
<td>1.39</td>
</tr>
<tr>
<td>Al</td>
<td>18.06</td>
<td>1.48</td>
<td>2.02</td>
</tr>
<tr>
<td>Pb</td>
<td>13.20</td>
<td>1.97</td>
<td>1.82</td>
</tr>
</tbody>
</table>

source: C. Kittel (1996)

- In practice, \(E_F\) and \(m^*\) must be determined experimentally
- \(m^* \neq m_0\) due to electron-electron and electron-ion interactions (electrons are not entirely “free”)
- Fermi energy: \(E_F = m^* v_F^2/2\)
Energy Density and Heat Capacity

\[ u = \frac{U}{V} = \frac{1}{V} \int_{k_0}^{\infty} E(k) g(k) f(k) dk = \frac{1}{L^3} \int_{k_0}^{\infty} 2E(k) \frac{4\pi k^2 dk}{(2\pi / L)^3} f(k) \]

similar to before, but don’t forget \( E(k) \)

\[ C_V = \frac{\partial u}{\partial T} = \int_{0}^{\infty} E \frac{\partial f(E)}{\partial T} g(E) dE \]

\[ C_V = \frac{\pi^2}{2} \frac{n k_B T}{E_F} \]

• For nearly-free electron gas, heat capacity is linear in \( T \) and \( << 3/2nk_B \) we’d get from equipartition
• Why so small? And what are the units for \( C_V \)?

Heat Capacity of Non-Interacting Gas

• Simplest example, e.g. low-pressure monatomic gas
• Back to the mosquito cloud
• From classical equipartition each molecule has energy \( 1/2k_B T \) per degree of motion (here, translational)
• Hence the heat capacity is simply \( C_V = \frac{3}{2} nk_B \)

• Why is \( C_V \) of electrons in metal so much lower if they are nearly free?
Current Density and Energy Flux

- Current density:
  \[ J_q = q \sum_k n(k) v(k) = q \int g(k) f(k) v(k) \, dk \]

  \[ v = \frac{1}{\hbar} \frac{\partial E}{\partial k} \]

- What if \( f(k) \) is a symmetric distribution?

- Energy flux:
  \[ J_E = \sum_k n(k) v(k) E(k) = \int g(k) f(k) v(k) E(k) \, dk \]

- Check units?

Conduction in Metals

- Balance equation for forces on electrons (\( q < 0 \))
  \[ m \frac{d\mathbf{v}}{dt} = -m \frac{\mathbf{v}}{\tau} + q(\mathbf{e} + \mathbf{v} \times \mathbf{B}) \]

- Balance equation for energy of electrons
  \[ \frac{dE}{dt} = -\frac{\Delta E}{\tau} + IV \]

- Current (only electrons near \( E_F \) contribute!)
  \[ J \approx q(\delta n)v_F \]
Boltzmann Transport Equation (BTE)

- The particle distribution (mosquitoes or electrons) evolves in a seven-dimensional phase space $f(x,y,z,k_x,k_y,k_z,t)$
- The BTE is just a way of “bookkeeping” particles which:
  - move in geometric space ($dx = v dt$)
  - accelerate in momentum space ($dv = a dt$)
  - scatter
- Consider a small control volume $d\mathbf{r}d\mathbf{k}$

$$
\frac{\partial f}{\partial t} = -\mathbf{v} \nabla f - \frac{\mathbf{F}}{\hbar} \nabla_k f + \left| \frac{\partial f}{\partial t} \right|_{\text{scat}}
$$

Relaxation Time Approximation (RTA)

- Where recall $\mathbf{v} =$ and $\mathbf{F} =$
- In the “relaxation time approximation” (RTA) the system is not driven too far from equilibrium

$$
\left| \frac{\partial f}{\partial t} \right|_{\text{scat}} = -\frac{f(k) - f^0(E)}{\tau_{\text{scat}}} = -\frac{f'(E)}{\tau_{\text{scat}}}
$$

- Where $f^0(E)$ is the equilibrium distribution (e.g. Fermi-Dirac)
- And $f'(E)$ is the distribution departure from equilibrium
BTE in Steady-State ($\partial f/\partial t = 0$)

$$v \nabla_r f + \frac{F}{h} \nabla_k f = -\frac{f'}{\tau}$$

- Still in RTA, approximate $f$ on left-side by $f^0$
- Furthermore by chain rule: $$\frac{F}{h} \nabla_k f^0 = \frac{F}{h} \nabla_k E \frac{\partial f^0}{\partial E} =$$
- So we can obtain the non-equilibrium distribution

$$f' = -\tau v \nabla_r f^0 - \tau F \cdot v \frac{\partial f^0}{\partial E}$$

- And now we can directly calculate the current & flux

Current Density and Mobility

$$J_q = q \int_k g(k) f'(k)v(k) dk = -q \int_k g(k)\tau v \nabla_r f^0 + F \cdot v \frac{\partial f^0}{\partial E} v dk$$

- This may be converted to an integral over energy
- Assume $F$ is along $z$: $\langle v_z^2 \rangle = \langle v^2 \rangle / d$ (dimension d=1,2,3)

$$J_{q,z} = n \left( \frac{q \langle \tau \rangle}{m} \right) F_z + \frac{\partial}{\partial z} \left[ k_B T \left( \frac{q \langle \tau \rangle}{m} \right) n \right]$$

- Assumption: position-independent relaxation time ($\tau$)
Energy Bands & Fermi Surface of Cu

- Fermi surface of Cu is just a slightly distorted sphere \(\rightarrow\) nearly-free electron model is a good approximation

Why the Energy Banding in Solids?

- Key result of wave mechanics (Felix Bloch, 1928)
  - Plane wave in a periodic potential
  - Wave momentum only unique up to \(2\pi/a\)
  - Electron waves with allowed \((k,E)\) can propagate (theoretically) unimpeded in perfectly periodic lattice

\[
\Gamma(x) = u_k(x)e^{ikx}
\]

\[
u_k(x) = u_k(x + a)
\]
What Do Bloch Waves Look Like?

- Periodic potential has a very small effect on the plane-wave character of a free electron wavefunction
- Explains why the free electron model works well in most simple metals

Semiconductors Are Not Metals

- Filled bands cannot conduct current
- What about at $T > 0 \text{ K}$?
- Where is the $E_F$ of a semiconductor?
Semiconductor Energy Bands

- Silicon: six equivalent ellipsoidal pockets ($m_l^*$, $m_t^*$)
- GaAs: spherical conduction band minimum ($m^*$)