Thermal conductivity and thermopower: 
Drude model fails  
(see later)

Specific heat  
(Drude model — classical free electrons) — fails

Sommerfeld model:
Free charges are quantum-mechanical
Must take into account Fermi statistics in discussing properties of electron gas.
Electrons are spin-1/2 Fermi particles
(a). Electron gas V(R) Free, non-interacting electron gas at temperature $T = 0$.

Electron wave functions satisfy 3D Schrödinger eq:

$$ H\psi = E\psi $$

$$ H = -\frac{\hbar^2}{2m} \nabla^2 $$

Solution:

$$ H = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) $$

Try plane-wave solution:

$$ \psi \propto e^{i k \cdot \mathbf{r}} $$

$$ \mathbf{r} = (x, y, z) $$
\( \frac{\partial^2}{\partial x^2} \rightarrow -k_x^2 \), so etc. so

\[ -\frac{h^2}{2m} \nabla^2 \psi = +\frac{h^2k^2}{2m} \psi = E\psi \quad \vec{k} = (k_x, k_y, k_z) \]

\[ \Rightarrow E = \frac{\hbar^2k^2}{2m} = E(\vec{k}) \]

Normalization: \( \int |\psi|^2 d^3x = 1 \)

\[ \Rightarrow \psi = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \]

Momentum \( \vec{p} = \int \psi^* (-i\hbar \nabla \psi) d^3x \)

\[ = \hbar \vec{k} \left( \frac{\psi^* \psi d^3r}{V} \right) = \frac{\hbar \vec{k}}{\sqrt{V}} = \frac{\hbar \vec{k}}{m} \]

How many states?

Use box normalization

\[ \psi(x, y, z + L) = \psi(x, y, z) \]

\[ \frac{1}{\sqrt{V}} e^{i[k_x x + k_y y + k_z (z + L)]} = \frac{1}{\sqrt{V}} e^{i[k_x x + k_y y + k_z z]} \]
\[ e^{ik_zL} = 1 \]

\[ k_zL = 2\pi n_z, \quad k_z = \frac{2\pi n_z}{L} \]

So in general

\[ \mathbf{k} = \frac{2\pi}{L} (n_x, n_y, n_z) \]

\[ n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots \]

"\( \mathbf{k} \)-space" = space where states are distributed

\[ \text{Density of points in } \mathbf{k} \text{-space:} \]

\[ \frac{1}{[\frac{4\pi}{L}(2\pi)^3]} = \frac{V}{(2\pi)^3} \]

Density of allowed states = \[ \frac{2V}{(2\pi)^3} = \frac{V}{4\pi^3} \]

(factor of 2 for spin degeneracy)

Fermi sphere. States at \( T = 0 \) filled up till \( k_F \) wave vector defined by

\[ \frac{4\pi}{3} k_F^3 \cdot \frac{V}{4\pi^3} = N \]

or

\[ k_F^3 = \frac{3\pi^2 N}{V} \]

\[ k_F = \left( \frac{3\pi^2 N}{V} \right)^{1/3} \]
Typically, \( k_F = \left( 27 \cdot 5 \times 10^{22} \right)^{1/3} \approx 5 \times 10^7 \text{ cm}^{-1} \)

\( E_F = \text{highest filled energy at } t=0 \)

\[ \frac{\hbar^2}{2m} \]

Typically \( E_F \approx 1 \text{ eV} \) in most solids

Note \( k_B T \approx 0.02 - 0.03 \text{ eV} \) at room temperature

Read \( k_F \) \( \gg k_B T \).

Fermi sphere

Fermi velocity \( V_F = \frac{\hbar k_F}{m} \approx 10^8 \text{ cm/sec.} \) Still \( \ll c \) so NR

Note: if electron gas were classical, we would have \( \frac{3}{2} m v_F^2 \approx \frac{3}{2} k_B T \)

So \( v_F \approx \sqrt{\frac{3k_B T}{m \sqrt{3 \times 1.4 \times 10^{-14} \times 3 \times 10^7}}} \approx 10 \text{ cm/sec.} \)
Total energy of Fermi gas at \( T = 0 \):

\[
E = 2 \sum_{k < k_F} \frac{k^2}{2m}
\]

\[
= 2 \cdot \frac{V}{(2\pi)^3} \int \frac{d^3k}{k < k_F} \frac{k^2}{2m}
\]

\[
= \frac{V}{4\pi^3} \cdot 4\pi \cdot \frac{\hbar^2}{2m} \int_{0}^{k_F} k^4 \, dk
\]

\[
= \frac{V}{\pi^2} \cdot \frac{\hbar^2}{2m} \frac{k_F^5}{5}
\]

\[
= \frac{V}{\pi^2} E_F \frac{k_F^3}{5} = \frac{V}{\pi^2} E_F \frac{3\pi^2 N}{5V}
\]

\[
= \sqrt[5]{\frac{3N}{5} E_F} \quad (>> Nk_B T)
\]

Recall for classical ideal gas

\[
E = \frac{3}{2} N k_B T \quad \text{(internal energy)}
\]

\[
E_F = k_B T_F, \quad T_F = \text{Fermi temperature} \quad \sim 20,000 \text{K}.
\]
Compressibility (or bulk modulus)

\[ P = -\left(\frac{\partial E}{\partial V}\right)_N \]

\[ = -\frac{\partial}{\partial V}\left\{ \frac{3}{5} N \times \frac{t^2}{2m} (3\pi^2)^{2/3} N^{2/3} \right\} \]

\[ = \frac{2}{3} \left\{ \frac{3}{5} N \times \frac{t^2}{2m} (3\pi^2)^{2/3} N^{2/3} \right\} \]

\[ = \frac{2}{3} \frac{E}{V} \]

Bulk modulus

\[ B = \frac{1}{K} = \frac{1}{\kappa} \left\{ \frac{\partial}{\partial V} \right\}_N \]

\[ = -V \left( \frac{\partial P}{\partial V} \right)_N = \frac{5}{3} p \]

since \( P \propto \sqrt[3]{\frac{N}{V}} \)

\[ -\frac{\partial P}{\partial V} = \frac{5}{3} \frac{C}{\sqrt[3]{V}} = \frac{5}{3} \frac{P}{V} \]

Can write this as

\[ B = \frac{10}{9} \frac{E}{V} = \frac{10}{9} \left( \frac{3N}{5V} \right) E \]

\[ = \frac{2}{3} N E_p \quad \text{(same order of magn. as many metals!)} \]
See table in Ashcroft and Mermin:

**Thermal properties of free electron gas:**

(i). **Fermi-Dirac distribution**

What is probability that state \( k \) is occupied at temperature \( T \)?

The occupation probability is given by the Fermi distribution function

\[
f(E_k) = \frac{1}{1 + e^{(E_k - \mu)/k_B T}}
\]

where \( T \) is the temperature

\( \mu \) is chemical potential

(at \( T = 0 \), \( \mu = E_F \))

\( k_B = \) Boltzmann's constant.

At low temp, \( f(e) \) looks as below:

![Graph of Fermi-Dirac distribution](image-url)
Quick derivation (not needed if you accept the result)

Say \( n_i \) fermions in state \( i \)

Probability of having the state \( \{ n_i \} \) is (at Temp \( T \))

\[
P(\{ n_i \}, T) = \frac{K}{\mathcal{Z}} \exp \left[ -\beta (E - \mu N) \right] \quad K = \text{norm. const.}
\]

where \( \beta = \frac{1}{k_B T} \) \quad \( E = \sum_i n_i \epsilon_i \)

\( N = \sum_i n_i \)

Since \( \sum_{\{ n_i \}} P(\{ n_i \}, T) = 1 \), we must have

\[
k \cdot \sum_{\{ n_i \}} \prod_i \exp \left[ -\beta (\sum_j n_j (\epsilon_j - \mu)) \right] = 1
\]

\[
= k \prod_i \left[ \sum_{n_i = 0}^{\infty} \exp \left( -\beta n_i (\epsilon_i - \mu) \right) \right]
\]

\[
= k \prod_i \left( 1 + e^{-\beta(\epsilon_i - \mu)} \right)
\]

So \( K = \frac{1}{\mathcal{Z}} = \left[ \prod_i (1 + e^{-\beta(\epsilon_i - \mu)}) \right]^{-1} \)
The probability of having exactly $n_i$ particles in state $i$ irrespective of $n_j$ in other states is

$$p(n_i) = \frac{1}{Z} e^{-\beta n_i (\varepsilon_i - \mu)} \prod_{j \neq i} (1 + e^{-\beta n_j (\varepsilon_j - \mu)})$$

$$= \frac{e^{-\beta n_i (\varepsilon_i - \mu)}}{1 + e^{-\beta n_i (\varepsilon_i - \mu)}} = \frac{1}{1 + e^{\beta (\varepsilon_i - \mu)}}$$

$$f(\varepsilon_i) = \frac{1}{1 + e^{\beta (\varepsilon_i - \mu)}}$$

is the probability that the $i$th state is occupied.

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How to determine $\mu$? If there are a total of $N$ electrons, then

$$\sum_i f(\varepsilon_i) = N = 2 \sum_{i} \frac{1}{e^{\beta (\varepsilon_i - \mu)} + 1}$$

for free electrons.

At $T = 0$, $f(\varepsilon_i) = 1$ if $\varepsilon_i < \mu(0)$, $\varepsilon_i > \mu(0)$, and $f(\varepsilon_i) = 0$ otherwise, and

$$N = 2 \sum_{k < k_F} (1)$$

which we already worked out.
Total energy is

$$U = \sum_k \frac{e_k}{e^{\beta(e_k - \mu)} + 1}$$

Specific heat is (at const. vol.)

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{N, V} = T \left( \frac{\partial S}{\partial T} \right)_{N, V} = N_0 V$$

Rewrite in terms of density of states:

Note: Typically in metal $E_F \gg k_B T$

So region where $f(x)$ is changing from 1 to 0 is a small part of Fermi energy.

For free electrons

$$N = \frac{2}{(2\pi)^3} \int_{k\text{-space}} d^3k \frac{1}{e^{\beta(e_k - \mu)} + 1}$$

$$U = \frac{V}{4\pi^3} \int d^3k \frac{e_k}{e^{\beta(e_k - \mu)} + 1}$$
Now write \[ \epsilon_k = \frac{\hbar^2 k^2}{2m} \equiv \epsilon \]

\[ k = \left( \frac{2m \epsilon}{\hbar^2} \right)^{1/2} \]

\[ dk = \sqrt{\frac{2m}{\hbar^2}} \frac{1}{2} \epsilon^{-1/2} \, d\epsilon \]

\[ d^3k = 4\pi k^2 \, dk \] since integrand is spherically symmetric (independent of angle)

So we have

\[ N = \frac{2}{(2\pi)^3} \int_0^\infty 4\pi k^2 \, dk \frac{1}{e^{\beta (\epsilon - \mu)} + 1} \]

\[ = \frac{V}{4\pi^2} \int_0^\infty \left( \frac{2m \epsilon}{\hbar^2} \right) \left( \frac{2m}{\hbar^2} \right)^{1/2} \frac{1}{2} \epsilon^{-1/2} \, d\epsilon \frac{1}{e^{\beta (\epsilon - \mu)} + 1} \]

\[ = \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{V}{2\pi^2} \int_0^\infty \epsilon^{1/2} \frac{1}{e^{\beta (\epsilon - \mu)} + 1} \, d\epsilon \]

or \[ N = V \left[ g(\epsilon) f(\epsilon) \right]_{\epsilon^2}^{1/2} \]

\[ g(\epsilon) = \left( \frac{2m}{\hbar^2} \right)^{3/2} \frac{1}{2\pi^2} \nu \nu \epsilon^{1/2} \] = density of states

\[ g(\epsilon) \, d\epsilon = \# \text{ of states between } \epsilon \text{ and } \epsilon + d\epsilon \]

\[ f(\epsilon) = \frac{1}{2} \frac{e^{\beta (\epsilon - \mu)} + 1}{\epsilon} \] per unit volume
Similarly
\[ U = -\int_{-\infty}^{\infty} \varepsilon g(\varepsilon) f(\varepsilon) \, d\varepsilon \]

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

An alternate way to estimate the specific heat:

**Important consequence:**

\[ C_V \propto T \text{ at low temperature} \]

\[ (k_B T << E_F) \]

**Simple argument**

At finite \( T \), Fermi \( f \) is broadened by about \( k_B T \)

Thus about \( g(E_F) k_B T \) electrons are excited across Fermi energy per unit volume.

Each gains energy \( \sim k_B T \)

Increase in energy is \[ g(E_F)(k_B T)^2 \]
So \( c_v \sim \left( \frac{2U}{N} \right) \sim \frac{2}{k_B T^2} \frac{2 k_B T^2}{g(\varepsilon_F)} \) per unit volume

Exact: \( c_v = \frac{\pi^2}{3} k_B T g(\varepsilon_F) \)

Can also be written

\( c_v = \frac{\pi^2}{3} n k_B \left( \frac{k_B T}{\varepsilon_F} \right) \)

where \( \varepsilon_F = (\frac{3}{2} \pi^2 n)^{\frac{2}{3}} \cdot \frac{h^2}{2m} \)

and \( g(\varepsilon_F) = \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \varepsilon_F^{1/2} \)

Compare to \( \frac{3}{2} n k_B \) for classical gas

Only a fraction \( \sim \frac{k_B T}{\varepsilon_F} \) participate in thermal excitation
More accurate calculation of specific heat:

Consider integral of form

\[ I = \int_0^\infty H(e) f(e) \, de \]

Let \( K(e) = \int_0^e H(e') \, de' \)

\[ \therefore H(e) = \frac{dK}{de} \]

\[ I = \int_0^\infty \frac{dK}{de} f(e) \, de \]

\[ = \left[ K(e) f(e) \right]_0^\infty - \int_0^\infty K(e) \frac{df}{de} \, de \]

\[ \sim - \int_{-\infty}^\infty K(e) \frac{df}{de} \, de \quad \text{since} \quad \frac{df}{de} \sim 0 \quad \text{at} \quad e = 0. \]

\[ \frac{df}{de} \text{ has this shape: } \mu \]
Specifically, \[ \frac{df}{d\varepsilon} = \frac{d}{d\varepsilon} \frac{1}{1 + e^{\beta(\varepsilon - \mu)}} = -\beta e^{\beta(\varepsilon - \mu)} \frac{\beta}{[1 + e^{\beta(\varepsilon - \mu)}]^2} \]

RHS \sim \int_{-\infty}^{\infty} \left( -\frac{df}{d\varepsilon} \right) \left[ K(\mu) + (\varepsilon - \mu) K'(\mu) + \frac{1}{2}(\varepsilon - \mu)^2 K''(\mu) + \ldots \right]

First term is
\[ K(\mu) \int_{-\infty}^{\infty} \left(-\frac{df}{d\varepsilon}\right) d\varepsilon = \left[ f(-\infty) - f(+\infty) \right] K(\mu) = K(\mu) \]

Second term is zero since \((\varepsilon - \mu)\) is odd around \(\varepsilon = \mu\) while \(-\frac{df}{d\varepsilon}\) is even,

i.e. \(-\frac{df}{d\varepsilon}(\mu + \mu) = -\frac{df}{d\varepsilon}(\mu - \mu)\)

Next term is
\[ \frac{1}{2} K''(\mu) \int_{-\infty}^{\infty} (\varepsilon - \mu)^2 \left(-\frac{df}{d\varepsilon}\right) d\varepsilon \]

\[ = \frac{1}{2} K''(\mu) \int_{-\infty}^{\infty} (\varepsilon - \mu)^2 \frac{\beta e^{\beta(\varepsilon - \mu)}}{(1 + e^{\beta(\varepsilon - \mu)})^2} d\varepsilon \]

Change variables: \( x = \beta(\varepsilon - \mu) \) \( dx = \beta d\varepsilon \)
\( d\varepsilon = dx / \beta \)
\[ I = \frac{1}{2} K''(\mu)(k_B T)^2 \int_{-\infty}^{\infty} \frac{x^2 e^x}{(1 + e^x)^2} \, dx \]

\[ = \frac{\pi^2}{3} \]

So \[ I \sim K(\mu) + \frac{\pi^2}{6} K''(\mu)(k_B T)^2 + O((k_B T)^4) \]

Now apply to specific heat problem:

\[ N = V \int_{0}^{\infty} g(e) f(e) \, de \]

\[ \sim V \left[ K(\mu) + \frac{\pi^2}{6} (k_B T)^2 K''(\mu) \right] \]

where \[ K(\mu) = \int_{0}^{\mu} g(e') \, de' \]

\[ K''(\mu) = g''(\mu) \]

So \[ N \sim V \int_{0}^{\mu} g(e') \, de' + \frac{\pi^2}{6} (k_B T)^2 \left[ \frac{d}{de} g(e) \right]_{e = \mu} \]

Also, \[ U \sim V \int_{0}^{\mu} e' g(e') \, de' + \frac{\pi^2}{6} (k_B T)^2 \left[ \frac{d}{de} (e' g(e)) \right]_{e = \mu} \]
The first term can be written
\[ N \sim V \int_0^{E_F} g(e')de' + V \int_{E_F}^{\mu} g(e')de' + \frac{\pi^2}{6} (k_BT)^2 g'(E_F) 
\]
\[ \sim N + V(\mu - E_F) g(E_F) + \frac{\pi^2}{6} (k_BT)^2 g'(E_F) V 
\]
So \( \mu - E_F \sim -\frac{\pi^2}{6} (k_BT)^2 \frac{g'(E_F)}{g(E_F)} \)

Also
\[ U(T) \sim V \int_0^{E_F} e'g(e')de' + V \int_{E_F}^{\mu} e'g(e')de' 
\]
\[ + \frac{\pi^2}{6} (k_BT)^2 \left( g(\mu) + e g'(\mu) \right) V 
\]
\[ \sim U(0) + V(\mu - E_F) E_F g(E_F) 
\]
\[ + \frac{\pi^2}{6} (k_BT)^2 g(E_F + E_F g'(E_F)) V 
\]
\[ \sim U(0) + \frac{\pi^2}{6} (k_BT)^2 g(E_F) V 
\]
So
\[ CV = \frac{1}{V} \left( \frac{\partial U}{\partial T} \right)_{V,N} = \frac{\pi^2}{3} k_b T g(E_F) \]
which can be written

\[ C_V = \frac{1}{2} \frac{N}{k_B} T \]  
where

\[ \chi^d = \frac{2}{3} \frac{N}{k_B} T g(E_F) \]

Sommerfeld theory of transport in metals

(i) Electrical transport:

\[ \sigma = \frac{N e^2 \nu}{m} \]

\[ F = \frac{\hbar}{e} v - e \vec{E} - m \vec{v} \]

but now \( \nu \) is interpreted as

\[ \text{drift velocity} = -\frac{e \vec{E}}{m} \]

and

\[ \vec{\jmath} = -n e \vec{v}_g = \sigma \vec{E} \]

\( \vec{v}_g \) is an. drift velocity per electron.

(ii) Thermal conductivity

\[ \vec{\jmath}_{\theta\theta} = -k \vec{\nabla} T \]

\[ \vec{\jmath}_{\theta} = \frac{1}{2} n v \left[ E(x-v t) - E(x+v t) \right] \]