CMP
Lecture 2

School of Physics
The University of Sydney

THE UNIVERSITY OF
SYDNEY

Drude theory

Lorenz number $\qquad L = \dfrac{\kappa}{T\sigma} = \dfrac{3}{2}\left(\dfrac{k_B}{e}\right)^2 \approx 1.11 \times 10^{-8} \text{ WattOhm/K}^2$

Viewed at the time as huge success since almost all metals have roughly the same value of this ratio – known as the Wiedemann-Franz law.
Drude's predicted Lorenz number is close to the measured one
– off by a factor of about 2.

Failures of the Drude model

- Despite this correct prediction, there are some serious problems with the Drude model.

- It is fortuitous – since the measured specific heat is not close to

$$c_v = \frac{3}{2}k_B \quad \text{per electron}$$

Due to two mistakes that roughly cancel:
specific heat far too large, velocity far too small!
(Due to not taking Fermi statistics of the electrons into account)

too small

$$\kappa = \frac{1}{3}nc_v\langle v\rangle\lambda \qquad\qquad L = \frac{\kappa}{T\sigma}$$

too big

It has to have failures since no information about actual material, atomic species, geometry etc

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Failures of the Drude model

Also: the Drude model predicts a roughly 100 times larger value of the **Peltier** coefficient

$$\mathbf{j}^q = \Pi\,\mathbf{j}$$

The Peltier coefficient represents how much heat is carried per unit charge

Peltier effect: running a current through a material also transports heat

heat of an electron

$$\mathbf{j}^q = \frac{1}{3}(c_vT)n\mathbf{v}$$ thermal current density

$$\mathbf{j} = -en\mathbf{v}$$ electrical current density

$$\Pi = \frac{-c_vT}{3e} = \frac{-k_BT}{2e}$$

$n=$ electron density
$c_v = 3k_B/2$
electronic specific heat or "heat capacity" of an electron gas

The ratio known as the thermopower or "Seebeck coefficient":

$$S = \frac{\Pi}{T} = \frac{-k_B}{2e} = -4.3\times10^{-4}$$

For most metals value is 100 times smaller

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A good thermoelectric material should have a high Seebeck coefficient – it is a measure of the magnitude of an induced voltage in response to a temperature difference across a material.
Active area of current research to find materials with high Seebeck coefficients.

## Computational strategies for design and discovery of nanostructured thermoelectrics

Shiqiang Hao[1], Vinayak P. Dravid[1], Mercouri G. Kanatzidis[2] and Christopher Wolverton[1]

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_L}.$$ Figure of merit   (2)

In this expression, S, σ, κ_e, and κ_L are the Seebeck coefficient, electrical conductivity, and electric and lattice thermal conductivities, respectively.[3] Therefore, to obtain a high value of ZT, both σ and S must be maximized, whereas κ_e and κ_l must be minimized.

Based on first-principles quantum mechanical calculations, density functional theory

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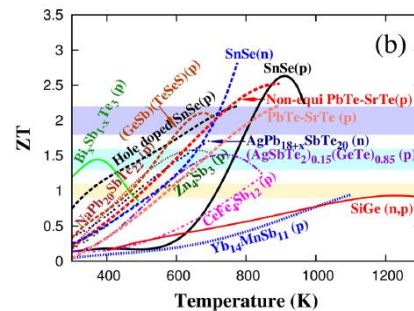
Question

The thermal conductivity of a metal is 123.92 W m^{-1} K^{-1}. Find the electrical conductivity and Lorenz number when the metal possesses a relaxation time of 10^{-14} s at 300 K. (Density of electrons $n = 6 \times 10^{28}$ per m^3)

$\sigma = 1.686 \times 10^7$ Ω^{-1}m^{-1}
$L = 2.45 \times 10^{-8}$ WΩ/K^2

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Summary

- Drude theory is based on the kinetic theory of gases.
- Assumes some scattering time τ, resulting in a conductivity $\sigma = ne^2\tau/m$.
- Hall coefficient measures density of electrons.

- Successes of Drude theory:

– Wiedemann–Franz ratio $\kappa/(\sigma T)$ comes out close to right for most materials.
– Many other transport properties predicted correctly (for example, conductivity at finite frequency).
– Hall coefficient measurement of the density seems reasonable for many metals.

- Failures of Drude theory:

– Hall coefficient frequently is measured to have the wrong sign, indicating a charge carrier with charge opposite to that of the electron.
– There is no $3k_B/2$ heat capacity per particle measured for electrons in metals. This then makes the Peltier and Seebeck coefficients come out wrong by a factor of 100.

Despite the shortcomings of Drude theory, it nonetheless was the only theory of metallic conductivity for a quarter of a century (until the Sommerfeld theory improved it), and it remains quite useful today—particularly for semiconductors and other systems with low densities of electrons.

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Electrons in metals:
Sommerfeld (free electron) theory: 1927

Take into account electrons are fermions – can't all be in same state

(Nominated 81 times for Nobel Prize, more than any other physicist)

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Basic Fermi-Dirac statistics

In 1925 Pauli discovered the exclusion principle, that no two electrons may be in the exact same state. In 1926, Fermi and Dirac separately derived what we now call Fermi–Dirac statistics. Upon learning about these developments, Sommerfeld realized that Drude's theory of metals could easily be generalized to incorporate Fermi statistics.

Given a system of free electrons with chemical potential μ the probability of an eigenstate of energy E being occupied is given by the Fermi factor,

$$n_F(\beta(E - \mu)) = \frac{1}{e^{\beta(E-\mu)} + 1}$$

At low temperature the Fermi function becomes a step function (states below the chemical potential are filled, those above it are empty). At higher temperatures the step function becomes smeared out, where the number of states removed from below the chemical potential equals the number of states that are added above the chemical potential.

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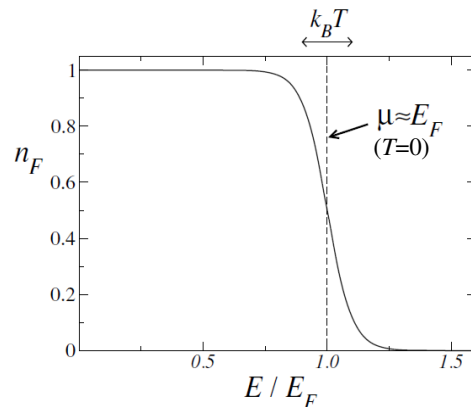
Question

Evaluate the Fermi function for energy k_BT above the Fermi energy.

$n_F = 0.2689$

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Basic Fermi-Dirac statistics

Consider electrons in a box of size $V = L^3$ with periodic boundary conditions. The plane waves are of the form $e^{i\mathbf{k}\cdot\mathbf{r}}$ and due to the boundary conditions, $\mathbf{k}$ has the value $(2\pi/L)(n_1, n_2, n_3)$ with n_i integers. These plane waves have energies,

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 |\mathbf{k}|^2}{2m}$$

The total number of electrons is given by,

$$N = 2 \sum_{\mathbf{k}} n_F(\beta(\epsilon(\mathbf{k}) - \mu)) = 2\frac{V}{(2\pi)^3} \int \mathbf{dk}\, n_F(\beta(\epsilon(\mathbf{k}) - \mu))$$

volume per k is $\left(\frac{2\pi}{L}\right)^3$ so need to divide by this to get number of states

with the prefactor 2 accounting for the two possible spin states.

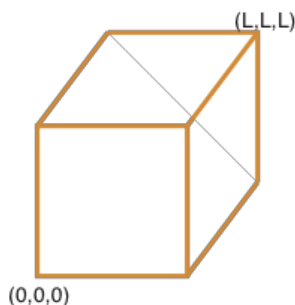<u>Definition:</u> *the Fermi energy, E_F is the chemical potential at temperature T=0.*

Also the *Fermi temperature* $T_F = E_F/k_B$

    Fermi wavevector k_F defined via $E_F = \dfrac{\hbar^2 k_F^2}{2m}$

    Fermi momentum $p_F = \hbar k_F$ *Fermi velocity* $v_F = \hbar k_F/m$

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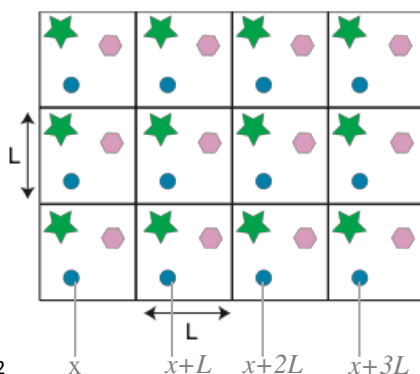

Periodic boundary conditions

(L,L,L)
(0,0,0)

cube of side length L, periodic boundary conditions

electron density *n* and total number of electrons *N*

$$n = \frac{N}{V}$$

$$\psi(\mathbf{r}) = \psi(x, y, z) = \psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L)$$

$$-\frac{\hbar^2 \nabla^2}{2m_e}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Solutions: $\psi(\mathbf{r}) = \dfrac{1}{\sqrt{V}}e^{i\mathbf{k}\mathbf{r}}$

$\mathbf{k}=(k_x, k_y, k_z)$ wavevector

12   x   x+L   x+2L   x+3L

Working

The free electron model

Schrödinger equation

$$-\frac{\hbar^2\nabla^2}{2m_e}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Solutions

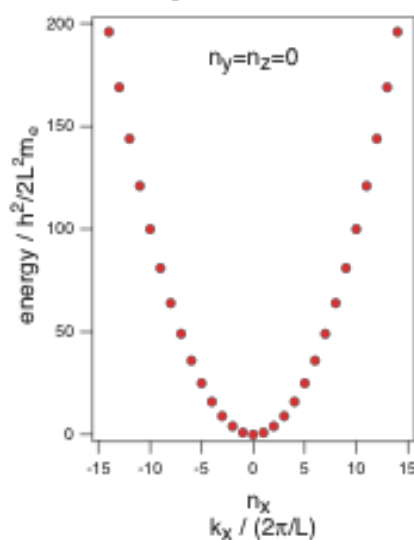$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{kr}}$$

Energy levels

$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2}{2m_e}(k_x^2 + k_y^2 + k_z^2)$$

Boundary conditions give

$$\mathbf{k} = (k_x, k_y, k_z) = (\frac{n_x 2\pi}{L}, \frac{n_y 2\pi}{L} \frac{n_z 2\pi}{L})$$

n_x, n_y, n_z integers

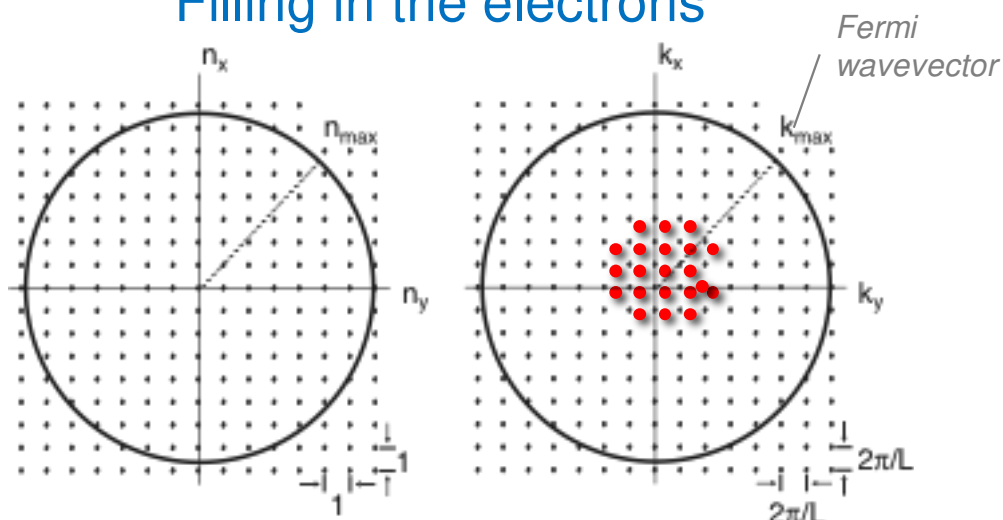$$\mathrm{E}(\mathbf{k}_x) = \frac{\hbar^2}{2m_e}\left(\frac{2\pi}{L}\right)^2 n_x^2$$

plot in 1D (x-direction)

Filling in the electrons

$$\mathbf{k} = (k_x, k_y, k_z) = (\frac{n_x 2\pi}{L}, \frac{n_y 2\pi}{L}, \frac{n_z 2\pi}{L}) \qquad E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m_e} = \frac{\hbar^2}{2m_e}(k_x^2 + k_y^2 + k_z^2)$$

2 electrons per k-point. If the electron density is N/V,
we have to distribute N electrons on N/2 k-points.

fill in start at 0,0,0 ....
and we should choose those states which have the lowest energy (in the centre)
- we will occupy up to a sphere of filled electrons, can work out the radius of this sphere

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Basic Fermi-Dirac statistics

Consider a 3D metal with N electrons in it. At $T=0$ the Fermi function becomes
a step function, i.e. $\Theta(x) = 1$ for $x \geqslant 0$ and $\Theta(x) = 0$ for $x < 0$
Then,

$$N = 2\frac{V}{(2\pi)^3} \int \mathbf{dk} \, \Theta(E_F - \epsilon(\mathbf{k})) = 2\frac{V}{(2\pi)^3} \int^{|k| < k_F} \mathbf{dk}$$

Where the last integral is over a sphere of radius k_F so that the integral gives
the volume of the sphere ($4\pi/3$ times the cube of the radius) giving,

$$N = 2\frac{V}{(2\pi)^3} \left(\frac{4}{3}\pi k_F^3 \right)$$

So at $T=0$, the electrons fill a sphere in $\mathbf{k}$-space of radius k_F.
The surface of this sphere is called the *Fermi surface* – the surface dividing
filled from unfilled states at zero temperature.
Rearranging the above equation, and using $n = N/V$ we obtain,

$$k_F = (3\pi^2 n)^{1/3}$$

$$E_F = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m}$$

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Basic Fermi-Dirac statistics: the free electron model

$$E_F = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m}$$

We can estimate the Fermi energy since we roughly know how many free electrons there are in a metal, e.g. one per atom for monovalent metals like sodium or copper (so we can get the electron density, *n*).

Find values as high as 7 eV, with corresponding Fermi temperature of 80,000K. This is a result of Fermi statistics and the high density of electrons in metals. For all metals $T_F \gg T$ for any temperature near room temperature. The Fermi velocity is also extremely large.

Given the large Fermi energy and a deep Fermi sea, any temperature can only make excitation of electrons that are already very close to the Fermi level – they can jump from just below the Fermi surface to just above it with only a small energy increase.

Electrons deep within the Fermi sea, near k=0 cannot be moved by any low-energy perturbation because there are no available unfilled states for them to move into.

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The Fermi-Dirac distribution

Some states below Fermi level become empty, and some states above become occupied.
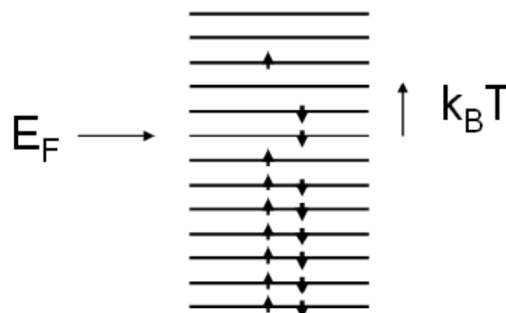
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The Fermi velocity

$$\frac{1}{2}m_e v_F^2 = E_F$$

$$v_F^2 = \frac{2E_F}{m_e}$$

element	E_F(eV)	v_F(ms^{-1})
Na	3.22	1.07x10^6
Al	11.63	2.02x10^6
Cu	7.00	1.57x10^6

Recall Drude velocity where we had an order of magnitude less (at RT)

Question

The free electron density of aluminum is 18.1×10^{28} m^{-3}. Calculate its Fermi energy at 0 K.

1.869x10^{-18} J
or 11.67 eV

Electronic heat capacity (and density of states)

Let's examine the heat capacity of electrons in metals. As we did for the total number of electrons N above, we can write the total energy of our system of electrons as,

$$
\begin{aligned}
E_{total} &= \frac{2V}{(2\pi)^3} \int d\mathbf{k}\, \epsilon(\mathbf{k})\, n_F(\beta(\epsilon(\mathbf{k}) - \mu)) \\
&= \frac{2V}{(2\pi)^3} \int_0^\infty 4\pi k^2 dk\, \epsilon(\mathbf{k})\, n_F(\beta(\epsilon(\mathbf{k}) - \mu))
\end{aligned}
$$

also,

$$
N = \frac{2V}{(2\pi)^3} \int d\mathbf{k}\, n_F(\beta(\epsilon(\mathbf{k}) - \mu)) = \frac{2V}{(2\pi)^3} \int_0^\infty 4\pi k^2 dk\, n_F(\beta(\epsilon(\mathbf{k}) - \mu)).
$$

($4\pi k^2$ arises from changing to spherical coordinates and the integral is now 1-dim.)

Substituting

$$
k = \sqrt{\frac{2\epsilon m}{\hbar^2}}
$$

$$
dk = \sqrt{\frac{m}{2\epsilon\hbar^2}}\, d\epsilon
$$

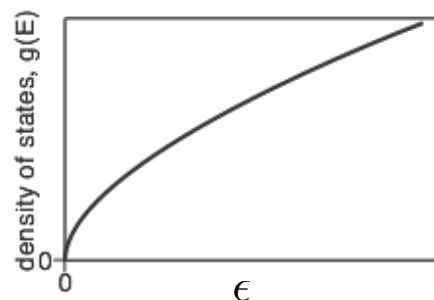into the above equations, we get the following two expressions:

Electronic heat capacity (and density of states)

$$
\begin{aligned}
E_{total} &= V \int_0^\infty d\epsilon\, \epsilon\, g(\epsilon)\, n_F(\beta(\epsilon - \mu)) \\
N &= V \int_0^\infty d\epsilon\, g(\epsilon)\, n_F(\beta(\epsilon - \mu))
\end{aligned}
$$

where,

$$
\begin{aligned}
g(\epsilon)d\epsilon &= \frac{2}{(2\pi)^3} 4\pi k^2 dk = \frac{2}{(2\pi)^3} 4\pi \left(\frac{2\epsilon m}{\hbar^2}\right) \sqrt{\frac{m}{2\epsilon\hbar^2}}\, d\epsilon \\
&= \frac{(2m)^{3/2}}{2\pi^2\hbar^3} \epsilon^{1/2} d\epsilon
\end{aligned}
$$

is the *density of states per unit volume.* That is, $g(\epsilon)d\epsilon$ is the total number of eigenstates (including both spin states) with energies between ϵ and $\epsilon + d\epsilon$.

Electronic heat capacity (and density of states)

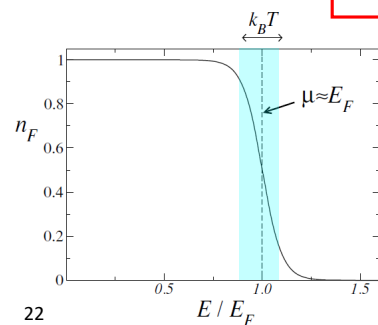From the expression for the Fermi energy obtained above, which is:

$$E_F = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m}$$

we can rearrange it to obtain,

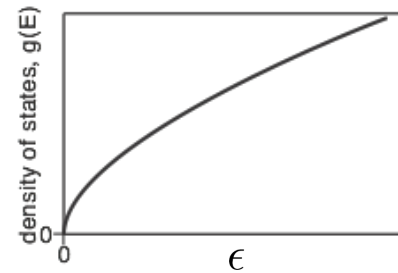$$(2m)^{3/2}/\hbar^3 = 3\pi^2 n/E_F^{3/2}$$

And substitute into the expression for the density of states to get,

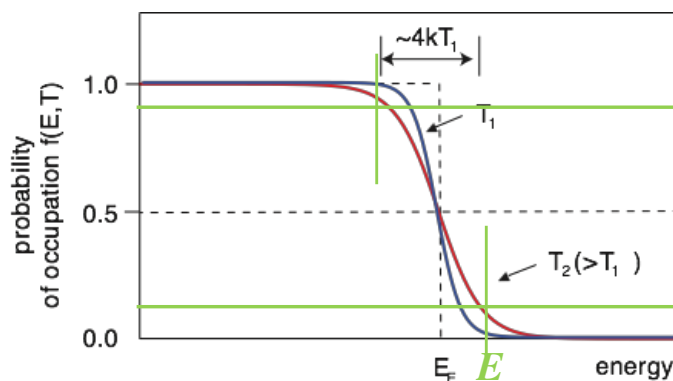$$g(\epsilon) = \frac{3n}{2E_F} \left(\frac{\epsilon}{E_F} \right)^{1/2}$$

At the Fermi energy the density of states is then:

$$g(\epsilon) = \frac{3n}{2E_F}$$

Tells how many states fall in a certain energy interval

The Fermi-Dirac distribution

$$f(E,T) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$$

$$k_B T \ln[\frac{1}{f(E,T)} - 1] = E - E_F$$

If $f(E,T) = 0.1$
then $E - E_F = 2.2 k_B T$

If $f(E,T) = 0.9$
then $E - E_F = -2.2 k_B T$

$$k_B T \ln[\frac{1}{0.1} - 1] = 2.2 k_B T$$

$$k_B T \ln[\frac{1}{0.9} - 1] = -2.2 k_B T$$

The curved zone in the Fermi Dirac distribution increases with temperature.
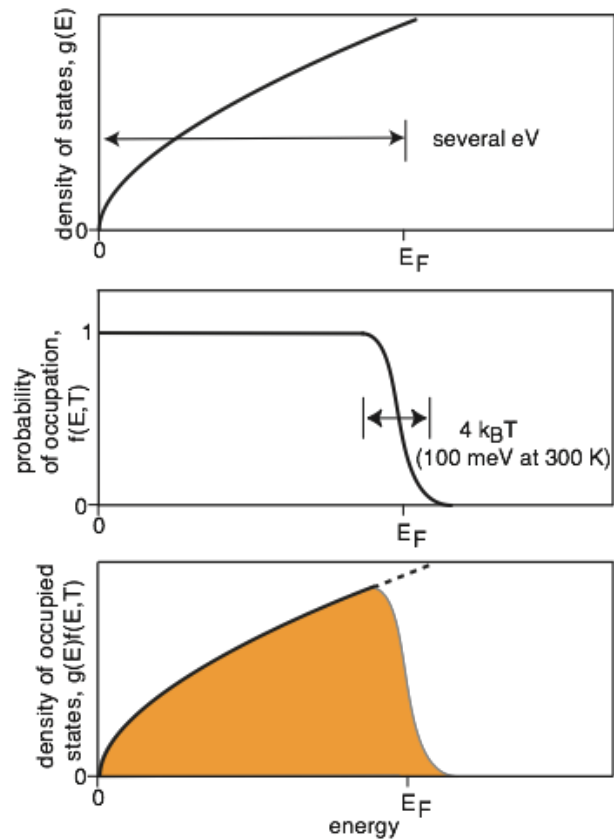
Electrons above E_F behave like ideal gas and approximately obey the Maxwell-Boltzmann distribution

Occupation of the states at finite *T*

$g(E)$

$$f(E,T) = \frac{1}{e^{(E-\mu)/k_BT} + 1}$$

$g(E)f(E,T)$

Electronic heat capacity

Simplified approach to calculate the integral for the energy:

Let's define the kinetic energy at *T*=0 as $E(T=0)$.
At finite *T,* there is a smearing of the step function at the Fermi energy.
Only electrons within k_BT are excited above the Fermi surface.
They are excited above the Fermi surface by about k_BT , thus,

$$E(T) = E(T=0) + (\tilde{\gamma}/2)[Vg(E_F)(k_BT)](k_BT) + \dots .$$

where $Vg(E_F)$ is the density of states (DOS) near the Fermi surface
so the number of particles close enough to the Fermi surface to be
excited is $Vg(E_F)(k_BT)$, and the last factor of (k_BT) is roughly the
amount of energy that each one gets excited by. Full calculation gives
$\tilde{\gamma} = \pi^2/3$ (see A&M).

So evaluating the heat capacity, $C = \partial E/\partial T = \tilde{\gamma}k_Bg(E_F)k_BTV$
and by using

$n = N/V$
$E_F = k_BT_F$ and $g(\epsilon) = \frac{3n}{2E_F}\left(\frac{\epsilon}{E_F}\right)^{1/2}$: $\boxed{C = \tilde{\gamma}\left(\frac{3Nk_B}{2}\right)\left(\frac{T}{T_F}\right)}$

Electronic heat capacity

$$C = \tilde{\gamma} \left(\frac{3Nk_B}{2} \right) \left(\frac{T}{T_F} \right)$$

The first term in brackets is the classical result for the heat capacity of a gas, but the factor T/T_F is 0.01 or smaller. This heat capacity of electrons is far smaller than for a classical gas.

$$C = \gamma T + \alpha T^3$$

This Sommerfeld prediction for the electronic (linear T) contribution to the heat capacity of a metal is typically close to experiment (see Table). A few metals, however, have specific heats that deviate from this prediction by a factor of 10 or more.

(γ_{th} calculated as the prefactor above multiplying T)

Material	γ_{exp}	γ_{th}
10^{-4} J/(mol-K)		
Lithium (Li)	18	7.4
Sodium (Na)	15	11
Potassium (K)	20	17
Copper (Cu)	7	5.0
Silver (Ag)	7	6.4
Beryllium (Be)	2	2.5
Bismuth (Bi)	1	5.0
Manganese (Mn)	170	5.2

Heat capacity of a metal: lattice + electrons
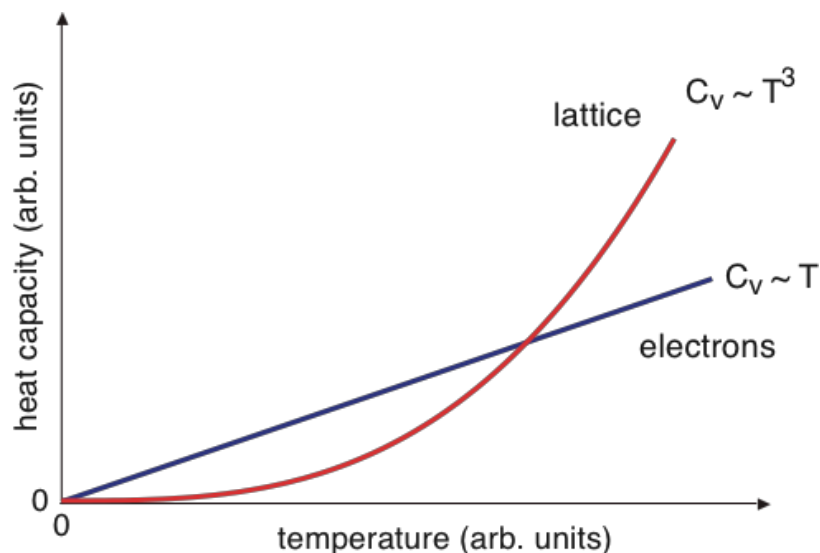
- Two contributions: lattice and electrons

- Electrons unimportant at high T but dominating at sufficiently low T

Electronic heat capacity

Recall, Drude theory predicts a thermopower $S = \Pi/T = -c_v/(3e)$ that is too large by a factor of 100.
The reason for this error is that a value was used for the heat capacity per electron that was for a classical gas, which is too large by roughly a factor $T_F/T \approx 100$.

The heat capacity per particle was also used in the Drude calculation of the thermal conductivity $\kappa = \frac{1}{3}nc_v\langle v\rangle\lambda$
and value of $\langle v\rangle^2$ that Drude used was too small by roughly the same factor so the errors cancelled out.
(Classically, one uses $mv^2/2 \sim k_BT$, whereas for the Sommerfeld model, one should use the Fermi velocity $mv_F^2/2 \sim k_BT_F$)

Thus, Drude's prediction for thermal conductivity came out roughly correct and also the Wiedemann–Franz law correctly holds.

End