

# CMP PS1

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# 1 Einstein Solid

## (a) Classical Einstein Solid (or “Boltzmann” Solid)

Consider a single harmonic oscillator in three dimensions with Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + \frac{k\mathbf{x}^2}{2}.$$

Calculate the classical partition function

$$Z = \int \frac{d\mathbf{p}}{(2\pi\hbar)^3} \int d\mathbf{x} e^{-\beta H(\mathbf{p}, \mathbf{x})}.$$

Note: In this problem  $\mathbf{p}$  and  $\mathbf{x}$  are three-dimensional vectors.

This is a remarkably simple problem in Gaussian integration. We simply split the exponential into six and perform the integration over each separate term,

$$Z = \prod_{i=\{x,y,z\}} \left( \int \frac{dp_i}{2\pi\hbar} e^{-\frac{\beta}{2m} p_i^2} \int dx_i e^{-\frac{\beta k}{2} x_i^2} \right)$$

where these integrals are over the whole of  $\mathbb{R}$ . We can then use the identity,

$$\int dy e^{-\alpha y^2} = \frac{1}{\sqrt{\alpha}} \int dy' e^{-y'^2} = \sqrt{\frac{\pi}{\alpha}}.$$

Thus, we simply have

$$Z = \left( \frac{1}{\beta\hbar} \sqrt{\frac{m}{k}} \right)^3.$$

What if the energy had an  $x^4$  term in it? We can imagine this being important at high temperatures when the oscillations are large. Here,

$$Z = \int \frac{d\mathbf{p}}{(2\pi\hbar)^3} e^{-\frac{\beta}{2m} \mathbf{p}^2} \int d\mathbf{x} e^{-\frac{\beta k}{2} \mathbf{x}^2 - \frac{\beta\lambda}{4!} \mathbf{x}^4}.$$

The first integral remains simple but the second is not so simple. We expand to first order in  $\lambda$  to see the effect.

$$\begin{aligned} Z &= \left( \frac{m}{2\pi\beta\hbar^2} \right)^{\frac{3}{2}} \int d\mathbf{x} e^{-\frac{\beta k}{2} \mathbf{x}^2} \left( 1 - \frac{\beta\lambda}{4!} \mathbf{x}^4 \right) \\ &= \left( \frac{m}{\pi\beta^2 k \hbar^2} \right)^{\frac{3}{2}} \int d\mathbf{x} e^{-\mathbf{x}^2} \left( 1 - \frac{\lambda}{6\beta k^2} \mathbf{x}^4 \right). \end{aligned}$$

To perform these integrals we should go to radial coordinates,

$$\begin{aligned} Z &= 4\pi \left( \frac{m}{\pi\beta^2 k \hbar^2} \right)^{\frac{3}{2}} \int_0^\infty dx e^{-x^2} \left( x^2 - \frac{\lambda}{6\beta k^2} x^6 \right) \\ &= \left( \frac{m}{\beta^2 k \hbar^2} \right)^{\frac{3}{2}} \left( 1 - \frac{5\lambda}{8\beta k^2} \right). \end{aligned}$$

We will use this later.

Using the partition function, calculate the heat capacity  $3k_B$ .

Recall that the heat capacity (at constant volume) is defined as

$$C_V = \left( \frac{\partial Q}{\partial T} \right)_V = \frac{\partial U}{\partial T}$$

where  $U$  is the energy and  $T$  the temperature. To find the energy we must perform the average,

$$U = \frac{1}{Z} \sum_{\text{configurations}} E_i e^{-\beta E_i} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}.$$

Thus, the energy and heat capacity are

$$U = \frac{3}{\beta} \quad \Rightarrow \quad C_V = 3k_B.$$

Now consider instead what the RMS position of the oscillator is. We can calculate this by differentiating,

$$\langle x^2 \rangle = \frac{1}{Z} \int \frac{d\mathbf{p}}{(2\pi\hbar)^3} \int d\mathbf{x} x^2 e^{-\frac{\beta}{2m} \mathbf{p}^2 - \frac{\beta k}{2} x^2} = -\frac{2}{\beta Z} \frac{\partial Z}{\partial k}.$$

So consider our anharmonic partition function and let's calculate this,

$$\begin{aligned} \langle x^2 \rangle &= 2k_B T \frac{\partial}{\partial k} \left( \frac{3}{2} \ln k - \ln \left( 1 - \frac{5\lambda}{8\beta k^2} \right) \right) \\ &= \left( \frac{3k_B T}{k} - \frac{\frac{5\lambda}{4} (k_B T)^2}{k \left( k^2 - \frac{5\lambda}{8} k_B T \right)} \right) \end{aligned}$$

but recall this is only for small  $\lambda$  so

$$\langle x^2 \rangle = \frac{3k_B T}{k} - \frac{5\lambda (k_B T)^2}{4k^3}.$$

Thus, as should be expected, the anharmonic term reduces the RMS deviation from the origin and does so more at high temperatures.

Conclude that if you can consider a solid to consist of  $N$  atoms all in harmonic wells, then the heat capacity should be  $3Nk_B = 3R$ , in agreement with the law of Dulong and Petit.

There are two ways at this. Firstly we can simply say “we calculated this for one well and so, for  $N$  wells we just multiply by  $N$ ”. A nicer answer revolves around degrees of freedom. To solve the  $N$  particle problem we take our 6-dimensional system to a  $6N$ -dimensional system and so

$$Z = \int \prod_{i=1}^{3N} \left( \frac{dp_i dx_i}{2\pi\hbar} \right) e^{-\beta H(\mathbf{p}, \mathbf{x})}.$$

Thus, exactly analogous to the previous calculation,

$$Z = \left( \frac{1}{\beta\hbar} \sqrt{\frac{m}{k}} \right)^{3N}.$$

This power was what gave us the 3 in front of  $k_B$  so now we get  $3N$ .

### (b) Quantum Einstein Solid

Calculate the quantum partition function

$$Z = \sum_j e^{-\beta E_j}$$

where the sum over  $j$  is a sum over all eigenstates.

The energies of a one-dimensional simple harmonic well are simply

$$E_j = \left(j + \frac{1}{2}\right) \hbar\omega$$

where  $\omega = \sqrt{\frac{k}{m}}$  (as a harmonic oscillator Hamiltonian has the form  $H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$ ). The three-dimensional case simply has some  $j_x, j_y$  and  $j_z$  but, given that the sum over  $j$ 's in the partition function can be easily separated, we need only worry about the one-dimensional partition function for now. Thus,

$$Z = e^{-\frac{\beta\hbar\omega}{2}} \sum_{j=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^j.$$

Thus we perform sum, recalling

$$S = 1 + r + r^2 + \dots = \frac{1}{1-r}$$

and so

$$Z = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2 \sinh \frac{\beta\hbar\omega}{2}}.$$

What if the simple harmonic oscillator were a Fermi oscillator, i.e. one with two levels only at energies  $\pm \frac{1}{2}\hbar\omega$ . Then

$$Z = 2 \cosh \frac{\beta\hbar\omega}{2}.$$

Explain the relationship with Bose statistics.

The Bose occupation factor at energy  $E$  is given by

$$n_B(E) = \frac{1}{e^{\beta E} - 1}$$

and we have something similar here. This shouldn't surprise us at all because the simple harmonic oscillator is just a system of bosons as denoted by the ladder operators  $a, a^\dagger$  and with Hamiltonian

$$H = \left(a^\dagger a + \frac{1}{2}\right) \hbar\omega$$

where  $a^\dagger a$  plays the role of a counting operator, counting the number of bosons.

Find an expression for the heat capacity.

We find the energy as before,

$$U = \frac{\partial}{\partial \beta} \ln \sinh \frac{\beta \hbar \omega}{2} = \frac{\hbar \omega}{2} \coth \frac{\beta \hbar \omega}{2}.$$

At this point we can answer the question above in a little more detail, noting that

$$U = \hbar \omega \left( \frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right) = \hbar \omega \left( n_B(\beta \hbar \omega) + \frac{1}{2} \right),$$

thus making the equivalence to bosons again. Getting back on track we calculate the heat capacity as before,

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} = -k_B \beta^2 \frac{\partial U}{\partial \beta} \\ &= -\frac{k_B(\beta \hbar \omega)^2}{2} \frac{\partial}{\partial(\beta \hbar \omega)} \frac{e^{\beta \hbar \omega} + 1}{e^{\beta \hbar \omega} - 1} \\ &= k_B(\beta \hbar \omega)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}. \end{aligned}$$

Now let us think about the heat capacity of a Fermi oscillator. Well,

$$U = -\frac{\hbar \omega}{2} \tanh \frac{\beta \hbar \omega}{2} = \hbar \omega \left( \frac{1}{e^{\beta \hbar \omega} + 1} - \frac{1}{2} \right)$$

and so

$$C_V = \frac{k_B(\beta \hbar \omega)^2}{2} \frac{\partial}{\partial(\beta \hbar \omega)} \frac{e^{\beta \hbar \omega} - 1}{e^{\beta \hbar \omega} + 1} = k_B(\beta \hbar \omega)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} + 1)^2}.$$

So this is exactly the same except we have a Fermi distribution  $\frac{1}{e^{\beta \hbar \omega} + 1}$  instead of the Bose distribution. At low temperature this is no different, which makes sense because the behaviour is driven mainly by the lowest two levels. For high temperature however, the picture is very different and the heat capacity actually decays as  $\frac{1}{T^2}$ .

Show that the high temperature limit agrees with the law of Dulong and Petit.

High temperature is small  $\beta$  so we expand,

$$C_V = k_B(\beta \hbar \omega)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \rightarrow k_B.$$

This was simply for one of the degrees of freedom though, and so we find the law of Dulong and Petit by considering that each of the  $N$  sites have 3 independent harmonic oscillators (one for each dimension) and so

$$C_V^{(\text{total})} = 3Nk_B.$$

Sketch the heat capacity as a function of temperature.

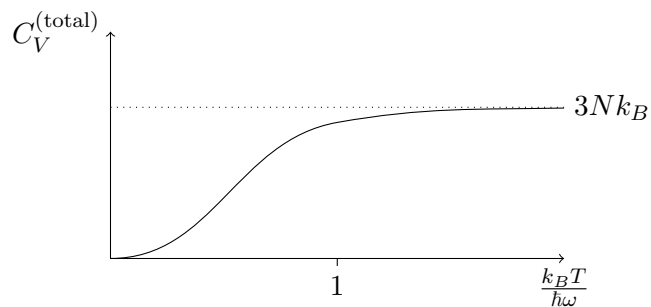
At low temperatures  $\beta$  is large. Thus we can approximate the behaviour of  $C_V$  there too,

$$C_V \rightarrow k_B(\beta\hbar\omega)^2 e^{-\beta\hbar\omega}.$$

Because exponential always wins,  $C_V \rightarrow 0$  as  $T \rightarrow 0$  (or as  $\beta \rightarrow \infty$ ) in an exponential fashion. For large  $T$  we have just calculated that the heat capacity tends to some constant. Finally, we may also wish to consider the intermediate region, where  $\beta\hbar\omega \simeq 1$ . Here we find

$$C_V \simeq 0.92k_B.$$

Thus we can make the sketch.



## 2 Debye Theory

(a) State the assumptions of the Debye model of heat capacity of a solid.

In the Debye model we assume that all phonons have the same velocity  $v$  for small wavenumbers and that the dispersion is linear,  $\omega = vk$  and that these phonons are bosonic, following a simple harmonic oscillator spectrum. We assume this to be true up to some cutoff  $\omega_D$  which is defined such that the number of modes in the system is equal to the total number of degrees of freedom ( $3N$  for an  $N$ -site system).

Derive the Debye heat capacity as a function of temperature (you will have to leave the final result in terms of an integral that cannot be done analytically).

In Debye theory we use the fact that phonons are bosonic and therefore distributed as

$$n_B(\beta\hbar\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}.$$

Therefore, if we want to find the total energy we sum over all possible states, taking the energy as  $\hbar\omega \left(n + \frac{1}{2}\right)$  and we take  $n = n_B$ . Thus,

$$U = \sum_{\mathbf{k}, p} \hbar\omega_p(\mathbf{k}) \left( n_B(\beta\hbar\omega_p(\mathbf{k})) + \frac{1}{2} \right)$$

where  $p$  denotes the polarisation. Given that we assume both transverse and the longitudinal polarisations have the same dispersion then

$$U = 3 \sum_{\mathbf{k}} \hbar vk \left( n_B(\beta\hbar vk) + \frac{1}{2} \right)$$

where  $k = |\mathbf{k}|$ . We sum only up to  $k_D = \frac{\omega_D}{v}$ . Now, taking  $N$ , the system size, to be large we can convert the sum to an integral and find

$$U = 3 \int \frac{dk_x}{2\pi/L_x} \frac{dk_y}{2\pi/L_y} \frac{dk_z}{2\pi/L_z} \hbar vk \left( n_B(\beta\hbar vk) + \frac{1}{2} \right)$$

where  $L_x$ ,  $L_y$  and  $L_z$  are the length of the system in each direction and  $V = L_x L_y L_z$  is the volume of the system (recall that these factors come from wavenumber quantisation,  $k = n \frac{2\pi}{L}$  due to periodic boundary conditions). Thus, given that the dispersion is spherically symmetric and assuming the sample can also be taken as such,

$$U = \frac{3\hbar v V}{2\pi^2} \int_0^{k_D} k^3 dk \left( n_B(\beta\hbar vk) + \frac{1}{2} \right).$$

The heat capacity is found by differentiating with respect to temperature,

$$C_V = \frac{3k_B(\beta\hbar v)^2 V}{2\pi^2} \int_0^{k_D} dk \frac{k^4 e^{\beta\hbar vk}}{(e^{\beta\hbar vk} - 1)^2}.$$

Finally we leave the integral as some dimensionless number with the change of variables  $x = \beta\hbar vk$ ,

$$C_V = \frac{3k_B V}{2\pi^2(\beta\hbar v)^3} \int_0^{\beta\hbar vk_D} dx \frac{x^4 e^x}{(e^x - 1)^2}.$$

From the final result, obtain the high and low temperature limits of the heat capacity analytically.

First we consider the high temperature limit, where  $\beta \rightarrow 0$ . Thus,  $x$  in our integral will always be small and so we expand

$$C_V \rightarrow \frac{3k_B V}{2\pi^2(\beta\hbar v)^3} \int_0^{\beta\hbar v k_D} dx x^2 = \frac{k_B V}{2\pi^2 v^3} \omega_D^3.$$

At this point we would like to know what  $\omega_D$  is and we do so with the assumption that we have  $3N$  modes in the system (3 per site from the three simple harmonic oscillators per site), so

$$3V \int_0^{k_D} \frac{4\pi k^2 dk}{(2\pi)^3} = 3N \quad \implies \quad \omega_D^3 = 6\pi^2 n v^3.$$

Therefore,

$$C_V \rightarrow 3Nk_B$$

as expected by Dulong and Petit.

For the low-temperature case  $\beta \rightarrow \infty$  which means that our integration limit tends to  $\infty$  as well. Thus,

$$C_V \rightarrow \frac{3k_B V}{2\pi^2(\beta\hbar v)^3} \int_0^\infty dx \frac{x^4 e^x}{(e^x - 1)^2} = \frac{2k_B^4 \pi^2 V}{5(\hbar v)^3} T^3.$$

We generally then define a Debye temperature

$$k_B T_D = \hbar \omega_D$$

so

$$C_V \rightarrow \frac{12k_B \pi^4 N}{5} \left( \frac{T}{T_D} \right)^3$$

(b) The following table gives the heat capacity  $C$  for potassium iodide (KI) as a function of temperature.

Discuss, with reference to the Debye theory, and make an estimate of the Debye temperature.

$T(\text{K})$	0.1	1.0	5	8	10	15	20
$C(\text{JK}^{-1}\text{mol}^{-1})$	$8.5 \times 10^{-7}$	$8.6 \times 10^{-4}$	$1.2 \times 10^{-1}$	$5.9 \times 10^{-1}$	1.1	2.8	6.3

The  $T^3$  scaling works very well at the lowest temperatures and even maintains a reasonable agreement for the higher temperatures given. Discrepancies are expected to increase as  $T$  increases due both to the assumption that only linear modes contribute and the low- $T$  approximations we made.

As for the Debye temperature, we note that for one mole  $Nk_B = R$ , the gas constant. Thus, taking the lowest temperature reading we solve for

$$T_D^3 = \frac{12\pi^4 R}{5} \frac{T^3}{C} \quad \implies \quad T_D \simeq 130\text{K}.$$



## 3

## Drude Theory of Transport in Metals

(a) Assume a scattering time  $\tau$  and use Drude theory to derive an expression for the conductivity of a metal.

Consider that the probability for an electron in the metal scatter in a time period  $\delta t$  goes as

$$P_{\text{scatter}}([t, t + \delta t]) = \frac{\delta t}{\tau}.$$

We then assume that scattering processes are a white noise process such that the velocity after scattering is, on average, zero. We can formulate this into an equation for the momentum,  $\mathbf{p}$ ,

$$\begin{aligned} \langle \mathbf{p}(t + \delta t) \rangle &= P_{\text{no scattering}} \langle \mathbf{p}(t + \delta t) \rangle_{\text{no scattering}} + P_{\text{scatter}} \langle \mathbf{p}(t + \delta t) \rangle_{\text{scatter}} \\ &= \left(1 - \frac{\delta t}{\tau}\right) (\langle \mathbf{p}(t) \rangle + \langle \mathbf{F}(t) \rangle \delta t) + \frac{\delta t}{\tau} \mathbf{0}. \end{aligned}$$

Thus, taking all variables now to be macroscopic averages (so we get rid of  $\langle \cdot \rangle$  notation) and expanding both sides to order  $\delta t$  we find

$$\frac{\partial \mathbf{p}(t)}{\partial t} = \mathbf{F}(t) - \frac{\mathbf{p}(t)}{\tau}.$$

Knowing this we can try to find the conductivity of a metal with scattering time  $\tau$ . In the steady state we can simply solve the Drude equation to find  $\mathbf{F} = \frac{\mathbf{p}}{\tau}$ . Conductivity  $\sigma$  is then defined by the equation

$$\mathbf{J} = \sigma \mathbf{E}$$

where  $\mathbf{J}$  is the current and  $\mathbf{E}$  the electric field. We can approximate  $\mathbf{J} = n(-e)\mathbf{v}$  where  $n$  is the density of electrons,  $-e$  the electronic charge and  $\mathbf{v} = \frac{\mathbf{p}}{m}$  the velocity (where  $m$  is the electron mass here). Thus,

$$-\frac{ne}{m} \mathbf{p} = \sigma \mathbf{E}.$$

Using the solution to the Drude equation then

$$-\frac{ne\tau}{m} \mathbf{F} = \sigma \mathbf{E}.$$

It is then implicit in the question that the only force applied is some electric field, so  $\mathbf{F} = (-e)\mathbf{E}$  and so

$$\sigma = \frac{ne^2\tau}{m} \mathbb{1}$$

where  $\mathbb{1}$  is the identity matrix.

(b) Define the resistivity matrix  $\rho$  as  $\mathbf{E} = \rho \mathbf{J}$ .

Use Drude theory to derive an expression for the matrix  $\rho$  for a metal in a magnetic field.

(You might find it convenient to assume  $\mathbf{B}$  parallel to the  $\hat{z}$  axis.)

The force is now

$$\mathbf{F} = (-e)(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

and so Drude tells us that

$$-e\tau\mathbf{E} = \mathbf{p} + \frac{e\tau}{m}\mathbf{p} \times \mathbf{B}.$$

Then, given that  $\mathbf{p} = -\frac{m}{ne}\mathbf{J}$  this reads

$$\mathbf{E} = \frac{m}{ne^2\tau} \left( \mathbf{J} + \frac{e\tau}{m}\mathbf{J} \times \mathbf{B} \right).$$

Now, as suggested in the question, let us, without loss of generality (we could just rotate back), take  $\mathbf{B}$  along the  $z$  direction. Therefore,

$$\mathbf{E} = \frac{m}{ne^2\tau} \begin{pmatrix} J_x + J_y \frac{eB\tau}{m} \\ J_y - J_x \frac{eB\tau}{m} \\ J_z \end{pmatrix} = \begin{pmatrix} \frac{m}{ne^2\tau} & \frac{B}{ne} & 0 \\ -\frac{B}{ne} & \frac{m}{ne^2\tau} & 0 \\ 0 & 0 & \frac{m}{ne^2\tau} \end{pmatrix} \mathbf{J}.$$

Thus, one can simply read off the matrix.

Invert this matrix to obtain an expression for the conductivity matrix  $\sigma$ .

The inversion is only needed for the nontrivial  $2 \times 2$  part as the  $z$  coordinate separates out and the conductivity is just  $\sigma_{zz} = \frac{ne^2\tau}{m}$ . For this  $2 \times 2$  section,

$$\det(\rho) = \left( \frac{m}{ne^2\tau} \right)^2 \left( 1 + \left( \frac{eB\tau}{m} \right)^2 \right)$$

so

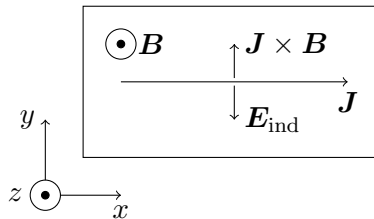
$$\sigma = \frac{\left( \frac{ne^2\tau}{m} \right)^2}{1 + \left( \frac{eB\tau}{m} \right)^2} \begin{pmatrix} \frac{m}{ne^2\tau} & -\frac{B}{ne} \\ \frac{B}{ne} & \frac{m}{ne^2\tau} \end{pmatrix}.$$

(c) Define the Hall coefficient.

The Hall coefficient is the off-diagonal resistance per unit magnetic field found when applying a current through a sample in the presence of a perpendicular magnetic field. More specifically,

$$R_H = \frac{\rho_{yx}}{B} = -\frac{1}{ne}.$$

So we constrain the current to flow in the  $x$ -direction and the electrons want to move in the positive  $y$ -direction (where  $\mathbf{B}$  is aligned in the positive  $z$ -direction). This force is counter-balanced with an induced field,  $\mathbf{E}_{\text{ind}}$ , across the sample in the negative  $y$ -direction.



Estimate the magnitude of the Hall voltage for a specimen of sodium in the form of a rod of rectangular cross section 5mm by 5mm carrying a current of 1A in a magnetic field of 1T orthogonal to the direction of the current. The density of sodium is roughly  $1\text{g/cm}^3$ , and sodium has atomic mass of roughly 23u. You may assume that there is one free electron per sodium atom (sodium has valence one).

First we need the size of the electric field induced. This is

$$E_{\text{ind}} = \frac{B}{ne}J$$

so we need to estimate  $n$ . We are told that sodium has mass density  $10^3\text{kg/m}^3$  so the number density is this divided by the per-atom mass, 23u,

$$n_{\text{sodium}} = 2.6 \times 10^{28}\text{m}^{-3}.$$

Given that the valence is one, this also happens to be the density of free electrons. We then find  $J$  given that  $J = \frac{I}{A}$  where  $A$  is the cross-section of the sample and so

$$E_{\text{ind}} = 9.6 \times 10^{-6}\text{V/m}.$$

To find the voltage we integrate the field over the sample and so

$$V_H = 4.8 \times 10^{-8}\text{V}.$$

What practical difficulties would there be in measuring the Hall voltage and resistivity of such a specimen (and how might these difficulties be addressed).

This voltage is very small so we either need a very sensitive piece of equipment or we could increase some of the magnetic field or current through the sample. It may even be the case that this voltage is smaller than the contact resistance so one needs to worry about this also. Furthermore, we need to ensure a good alignment of the contacts so they measure voltage exactly perpendicular to the input current. Realistically this can't be done perfectly but we can remove the non-perpendicular part by reversing the field or current and comparing the two results (i.e, we assume that, due to poor contact placement, we have

$$V_{\text{measured}} = V_H + V_{\text{normal}}.$$

By reversing the current we would find

$$V_{\text{measured}} = V_H - V_{\text{normal}}.$$

Then we add the measurements and divide by 2.)

d) What properties of metals does Drude theory not explain well?

Drude theory fails to predict the heat capacity of the electron gas and makes incorrect predictions of other bulk properties, such as the thermoelectric coefficient (heat transfer due to current transfer). It also struggles to explain, by itself, the apparent sign difference

of the Hall coefficient in certain samples (though this is fixed easily enough by considering an effective charge  $e^*$  of each carrier). It also fails to really discuss which electrons are conduction electrons and just assumes that we take only the valence electrons.

(e)\* Consider now an applied AC field  $\mathbf{E} \sim e^{i\omega t}$  which induces an AC current  $\mathbf{J} \sim e^{i\omega t}$ . Modify the above calculation (in the presence of a magnetic field) to obtain an expression for the complex AC conductivity matrix  $\sigma(\omega)$ . For simplicity in this case you may assume that the metal is very clean, meaning that  $\tau \rightarrow \infty$ , and you may assume that  $\mathbf{E} \perp \mathbf{B}$ . You might again find it convenient to assume  $\mathbf{B}$  parallel to the  $\hat{z}$  axis. (This problem might look hard, but if you think about it for a bit, it isn't really much harder than what you did above!) At what frequency is there a divergence in the conductivity?

This problem is exactly what we did above. Consider once again the Drude equation

$$\frac{d\mathbf{p}}{dt} = \mathbf{F} - \frac{\mathbf{p}}{\tau}.$$

We can no longer consider  $\mathbf{p}$  in the steady state as we are told specifically that the current is time dependent. Within Drude theory  $\mathbf{p} = m\mathbf{v} = -\frac{m}{ne}\mathbf{J}$  and so

$$\frac{m}{ne^2} \frac{d\mathbf{J}}{dt} = \mathbf{E} - \frac{1}{ne}\mathbf{J} \times \mathbf{B} - \frac{m}{ne^2\tau}\mathbf{J}.$$

Given that we are told  $\mathbf{J} \sim e^{i\omega t}$  the  $\frac{d}{dt}$  is simply  $i\omega$  and so

$$\left( \frac{im\omega}{ne^2} + \frac{m}{ne^2\tau} \right) \mathbf{J} + \frac{1}{ne}\mathbf{J} \times \mathbf{B} = \mathbf{E}.$$

Therefore, if we are to introduce this time-dependence in a perfectly clean system we can simply replace  $\frac{1}{\tau}$  by  $i\omega$  in our previous considerations. Thus, recalling those results we note that  $\sigma$  diverges when

$$\omega = \pm \frac{eB}{m}.$$

Though in practice, what does this divergence look like? We can look at the previous calculations and note that, with the new time variation,  $\frac{1}{\tau} \rightarrow \frac{1}{\tau} + i\omega$ . So the diagonal elements of the conductivity are

$$\sigma = \frac{ne^2}{m} \frac{\tau^{-1} + i\omega}{(\tau^{-1} + i\omega)^2 + \left(\frac{eB}{m}\right)^2}.$$

What does this divergence mean? (When  $\tau$  is finite, the divergence is cut off).

This is unsurprising as this is the frequency of the orbits of the electrons so we are driving the system resonantly at this frequency. Obviously once there is damping in the system this resonance becomes somewhat broadened.

Explain how one could use this divergence (known as the cyclotron resonance) to measure the mass of the electron. (In fact, in real metals, the measured mass of the electron is generally

not equal to the well known value  $m_e = 9.1095 \times 10^{-31} \text{kg}$ . This is a result of band structure in metals, which we will explain later in the course.)

A resonance peak is rather easy to measure. Thus, we simply measure the peak and invert our relation  $\omega = \frac{eB}{m}$  to find  $m$ .

## 4

## Free Electron Theory of Metals

(a) Explain what is meant by the Fermi energy, Fermi temperature and the Fermi surface of a metal.

The Fermi energy,  $E_F$ , is the chemical potential of the free electron system at zero temperature. The Fermi temperature,  $T_F = \frac{E_F}{k_B}$  can be thought of as the temperature beyond which the low-temperature Fermi distribution becomes significantly smeared out. The Fermi surface is the manifold in momentum space which separates filled and unfilled states at zero temperature (thus tracing out  $E_F$ ).

(b) Obtain an expression for the Fermi wavevector and the Fermi energy for a gas of electrons (in 3D).

Consider that there are  $N$  electrons. Thus,

$$N = \sum_{\mathbf{k}} g_{\mathbf{k}} n_{\mathbf{k}}$$

where  $n_{\mathbf{k}} = 1$  if the energy  $E(\mathbf{k}) < E_F$  and 0 otherwise and  $g_{\mathbf{k}}$  is the degeneracy (2 for electrons with spin- $\frac{1}{2}$ ). Thus,

$$N = \int 2V \frac{d^3\mathbf{k}}{(2\pi)^3} n_{\mathbf{k}}.$$

Now, assuming that  $E(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m}$  we have spherical symmetry in  $n_{\mathbf{k}}$  and quite simply

$$\frac{N}{V} = \int_0^{k_F} \frac{k^2 dk}{\pi^2} = \frac{k_F^3}{3\pi^2}$$

where  $k_F$  is the Fermi wavevector. Thus,

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

where  $n$  is the electron density and

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

Show that the density of states at the Fermi surface,  $\frac{dN}{dE_F}$ , can be written as  $\frac{3N}{2E_F}$ .

From the above calculation we can instantly see that, given  $k = \frac{\sqrt{2m}}{\hbar} E^{\frac{1}{2}}$ ,

$$dN = V \frac{k^2 dk}{\pi^2} = V \frac{E^{\frac{1}{2}} dE}{2\pi^2 \hbar^3} (2m)^{\frac{3}{2}}.$$

Thus,

$$\frac{dN}{dE_F} = V \frac{E_F^{\frac{1}{2}}}{2\pi^2 \hbar^3} (2m)^{\frac{3}{2}} = \frac{3N}{2E_F}.$$

(c) Estimate the value of  $E_F$  for sodium [As above, the density of sodium atoms is roughly  $1\text{g/cm}^3$ , and sodium has atomic mass of roughly  $23\text{u}$ . You may assume that there is one free electron per sodium atom (Sodium has valence one)]

We just put numbers in.

$$k_F = 9.21 \times 10^9 \text{m}^{-1}.$$

$$E_F = 5.11 \times 10^{-19} \text{J} = 3.2 \text{eV}.$$

This makes the Fermi temperature about  $37000\text{K}$ , way above even the melting temperature of any metal.

(d) Now consider a two-dimensional Fermi gas. Obtain an expression for the density of states at the Fermi surface.

Here the only difference is in the integral over  $\mathbf{k}$ , so

$$n = 2 \int_0^{k_F} \frac{2\pi k dk}{(2\pi)^2} = \frac{k_F^2}{2\pi}.$$

Then consider that

$$dN = \frac{A}{\pi} k dk = \frac{A}{2\pi} \frac{2m}{\hbar^2} dE$$

and so the density of states is simply

$$\frac{dN}{dE_F} = \frac{A}{2\pi} \frac{2m}{\hbar^2} = \frac{N}{E_F}.$$

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## Velocities in the Free Electron Theory

(a) Assuming that the free electron theory is applicable: show that the speed  $v_F$  of an electron at the Fermi surface of a metal is  $v_F = \frac{\hbar}{m}(3\pi^2n)^{\frac{1}{3}}$  where  $n$  is the density of electron.

We know the Fermi wavevector from the previous question is

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

The Fermi momentum is therefore,  $\hbar k_F$  which we convert to a speed by dividing by  $m$ . This produces the given result.

(b) Show that the mean drift speed  $v_d$  of an electron in an applied electric field  $E$  is  $v_d = \left| \frac{\sigma E}{ne} \right|$ , where  $\sigma$  is the electrical conductivity, and show that  $\sigma$  is given in terms of the mean free path  $\lambda$  of the electrons by  $\sigma = \frac{ne^2\lambda}{mv_F}$ .

For the first part of this question we must consider that

$$J = \sigma E$$

where  $J = nev_d$  (the signs are unimportant here because we just want magnitudes) and so

$$v_d = \left| \frac{\sigma E}{ne} \right|.$$

We then use the steady state Drude equation. We must be careful here as we're considering averages and so, even though the individual electrons travel at  $v_F$ , the average motion is still at  $v_d$ .

$$\frac{mv_d}{\tau} = eE \quad \implies \quad \sigma = \frac{ne^2\tau}{m}$$

which we find by using our previous result. We now think about the mean-free path, nothing that this is dictated by individual electron speeds. Those which can scatter are those at the Fermi surface and thus,

$$\lambda = v_F\tau$$

is the mean free path. So,

$$\sigma = \frac{ne^2\lambda}{mv_F}.$$

(c) Assuming that the free electron theory is applicable to copper:

(i) Calculate the values of both  $v_d$  and  $v_F$  for copper at 300K in an electric field of  $1\text{Vm}^{-1}$  and comment on their relative magnitudes.

(ii) Estimate  $\lambda$  for copper at 300K and comment upon its value compared to the mean spacing between the copper atoms.

Copper is monovalent, meaning there is one free electron per atom. The density of atoms in copper is  $n = 8.45 \times 10^{28}\text{m}^{-3}$ . The conductivity of copper is  $\sigma = 5.9 \times 10^7\Omega^{-1}\text{m}^{-1}$  at 300K.



The temperature is irrelevant here, only that it is so small compared to  $T_F$  that it is basically zero. So

$$v_d = \frac{\sigma E}{ne} = 4.7 \text{mms}^{-1}$$

(which didn't even care about a Fermi distribution) and

$$v_F = \frac{\hbar}{m}(3\pi^2 n)^{\frac{1}{3}} = 0.52c$$

where  $c$  is the speed of light. These speeds are pretty different... (which is not a problem! It just highlights the difference between bulk and individual motion).

We then find  $\lambda$ .

$$\lambda = \frac{mv_F \sigma}{ne^2} = 39 \text{nm}.$$

This is about 170 lattice spacings for the copper atoms (which we find by consider  $d = n^{-\frac{1}{3}}$ ) so it might be realistic but it does feel a little large (but the electrons may have a hard time scattering because they can't find a nearby state to scatter to).

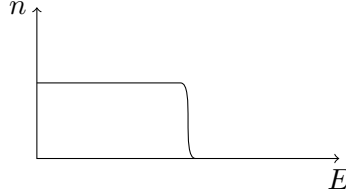
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## Physical Properties of the Free Electron Gas

In both (a) and (b) you may always assume that the temperature is much less than the Fermi temperature.

(a) Give a simple but approximate derivation of the Fermi gas prediction for heat capacity of the conduction electrons in metals.

Consider a graph of the occupations as a function of energy,



The number of electron we can excite over the boundary with only thermal fluctuations is about  $\frac{dN}{dE_F} k_B T$ . The amount of energy we can add to any one is  $k_B T$ . Therefore, we might expect

$$U \sim \frac{dN}{dE_F} (k_B T)^2 \quad \Rightarrow \quad C \sim \frac{dN}{dE_F} k_B^2 T.$$

(b) Give a simple (not approximate) derivation of the Fermi gas prediction for magnetic susceptibility of the conduction electrons in metals. Here susceptibility is  $\chi = \frac{dM}{dH} = \mu_0 \frac{dM}{dB}$  at small  $H$  and is meant to consider the magnetisation of the electron spins only.

The magnetic field creates a term in our energy of the form

$$\Delta H = g\mu_B \mathbf{B} \cdot \mathbf{S}$$

where  $\mathbf{S}$  is the spin of the electron. Thus, up-spins are raised in energy by  $\frac{1}{2}g\mu_B B$  and down-spins are lowered in energy by that same figure. As  $g = 2$  then

$$E_{\uparrow/\downarrow} = \frac{\hbar^2 k^2}{2m} \pm \mu_B B.$$

The magnetisation of our sample is then

$$M = \frac{1}{V} \sum_{\mathbf{k}} (n_{\mathbf{k},\uparrow} - n_{\mathbf{k},\downarrow}) \mu_B.$$

Converting to an integral then

$$M = \mu_B \int \frac{k^2 dk}{2\pi^2} (n_{\mathbf{k},\uparrow} - n_{\mathbf{k},\downarrow}).$$

Now we assume that we are at zero temperature and linearise, assuming that  $B$  is small. Thus, where  $E_F$  is the  $B = 0$  Fermi energy, we must now integrate a step function from 0

to  $E_F \pm \mu_B B$  and take the difference. This is equivalent to integrating from  $E_F - \mu_B B$  to  $E_F + \mu_B B$ . So,

$$M = \frac{\mu_B}{2\pi^2} \int_{E_F - \mu_B B}^{E_F + \mu_B B} \frac{(2m)^{\frac{3}{2}}}{2\hbar^3} E^{\frac{1}{2}} dE.$$

We expand this for small  $B$  to find

$$M = \frac{(2m)^{\frac{3}{2}}}{2\pi^2 \hbar^3} E_F^{\frac{1}{2}} \mu_B^2 B = \frac{3n\mu_B^2 B}{2E_F}.$$

Hence,

$$\chi = \frac{3n}{2E_F} \mu_0 \mu_B^2.$$

(c) How are the results of (a) and (b) different from those for a classical gas of electrons? What other properties of metals may be different from the classical prediction?

For classical electrons the distribution function  $n_{\mathbf{k},\sigma}$  (where  $\sigma$  is the spin) is no longer this step function but obeys a Boltzmann distribution. Thus, for the heat capacity calculation we find the  $C = \frac{3}{2} N k_B$  result. Our prediction is linear in temperature. For the classical paramagnetism calculation, the result is also easily calculable with simple statistical mechanics and we find

$$\mathcal{Z} = e^{\beta\mu_B B} + e^{-\beta\mu_B B} \implies M = \mu_B \tanh \beta\mu_B B.$$

This gives a  $\frac{1}{T}$  dependence for the susceptibility instead of this constant value.

Other properties which deviate include anything requiring the electrons to change their state to do something. For example, thermoelectric coefficients, average electron speeds and compressibility.

(d) The experimental heat capacity of potassium metal at low temperatures has the form:

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

where  $\gamma = 2.08 \text{ mJ mol}^{-1} \text{ K}^{-2}$  and  $\alpha = 2.6 \text{ mJ mol}^{-1} \text{ K}^{-4}$ .

Explain the origin of each of the two terms in this expression.

Make an estimate of the Fermi energy for potassium metal.

The linear term is the heat capacity due to the conduction electrons and the cubic term is the phonon contribution.

To estimate the fermi energy we need to know the constant contribution in front of our previous argument. It happens to be  $\frac{\pi^2}{3}$  so

$$C_{e^-} = \frac{\pi^2}{2} \frac{N}{E_F} k_B^2 T \implies E_F = \frac{\pi^2}{2} \frac{N_A}{\gamma} k_B^2$$

(as the heat capacity we are given is per mole so  $N = N_A$ , Avagadro's number). So

$$E_F = 1.7 \text{ eV}.$$