Exercise 1 Calculating the Density of States

In this exercise, we learn how to calculate the density of states (DOS) for different systems. In general, the DOS can either be written as $g(\epsilon)$ in terms of the energy ϵ or $g(\omega)$ in terms of the frequency ω.

In the following, we assume that the material has size L and is d-dimensional (usually $d = 3$, but modern nanomaterials can also be one- or two-dimensional).

1. Start from the dispersion relation $\epsilon(k)$ or $\omega(k)$
2. Solve the previous equation for k
3. Define the total number of states up to energy ϵ or frequency ω by

$$\Omega = \left(\frac{L}{2\pi}\right)^d V_d k^d \tag{1}$$

4. If needed, multiply by the degeneracy factor due to spin (for electrons), polarization (for phonons) etc.
5. Take the derivative

$$g(\epsilon) = \frac{d\Omega}{d\epsilon}, \quad g(\omega) = \frac{d\Omega}{d\omega} \tag{2}$$

There are two types of important dispersion relations.

- **Free electrons** are electrons for which $E_{\text{pot}} = 0$ and hence $\epsilon = E_{\text{kin}} = \frac{p^2}{2m}$. Using the relation $p = \hbar k$ from quantum mechanics, this becomes $\epsilon(k) = \frac{\hbar^2 k^2}{2m}$. This is an approximation used to describe electrons in metals, which are strongly delocalized as if there was no potential energy due to the ion cores. Especially for Alkali metals, and also the nobel metals (Cu, Ag, Au) to some extent, this provides a reasonably good description.
- **Phonons** are the "quantum particles" associated with lattice vibrations or elastic waves. As a first approximation, elastic waves have a constant speed c of propagation, regardless of frequency (this, strictly speaking, only is true for waves with a wavelength much bigger than the atomic bonding length). Then: $c = \lambda\nu = \frac{\omega}{k}$ and hence $\omega(k) = ck$.

(a) Show that the for free electrons in **3D**, the total number of states up to energy ϵ (taking into account the degeneracy due to spin) is equal to

$$\Omega_{\text{elec,3D}}(\epsilon) = \frac{V}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{\frac{3}{2}}, \tag{3}$$

where $V = L^3$ is the volume is the system, and conclude that

$$g_{\text{elec,3D}}(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\epsilon} \tag{4}$$

(b) Show that for free electrons in **2D**, the total number of states up to energy ϵ (taking into account the degeneracy due to spin) is equal to

$$\Omega_{\text{elec,2D}}(\epsilon) = 2 \cdot \frac{A}{4\pi^2} \cdot \pi \cdot \frac{2m\epsilon}{\hbar^2} = \frac{Am}{\pi\hbar^2}\epsilon \tag{5}$$

where $A = L^2$ is the total area of the system, and conclude that

$$g_{\text{elec,2D}}(\epsilon) = \frac{Am}{\pi\hbar^2} \tag{6}$$

In particular, as opposed to the 3D case, the DOS is just a constant function.

(c) You probably noticed that keeping track of all factors of $\hbar, m, \pi$ etc. is quite annoying. Thankfully, these prefactors do not matter so much if we only care about getting a qualitative understanding. Without doing any complicated extra calculations, and starting from $\Omega = \left(\frac{L}{2\pi}\right)^d V_d k^d$, show that $\Omega \propto \epsilon^{\frac{d}{2}}$ for the free electron gas in d-dimensions, and conclude that the DOS will thus be of the form

$$g_{\text{elec}}(\epsilon) = a \cdot \epsilon^{\frac{d}{2}-1} \tag{7}$$

for some constant a. Verify that the exponent $\frac{d}{2} - 1$ is consistent with your results from parts (a) and (b).

(d) Starting from $\omega = ck$ for phonons, show that for **phonons in 3D**, the total number of states up to frequency ω taking into account the **three-fold degeneracy due to polarization** (transveral and longitudinal modes) is given by

$$\Omega_{\text{phonons,3D}} = \frac{V}{2\pi^2}\left(\frac{\omega}{c}\right)^3 \tag{8}$$

and conclude that

$$g_{\text{phonons,3D}} = \frac{3V}{2\pi^2 c^3}\omega^2 \tag{9}$$

(e) We can again generalize this. Show that in d-dimensions,

$$\Omega_{\text{phonons}}(\omega) \propto \omega^d \tag{10}$$

and hence that the DOS is of the form

$$g_{\text{phonons}}(\omega) = a\omega^{d-1} \tag{11}$$

for some constant a.

(f) The phonon modes in graphene are more complicated, because it is a 2D sheet which lies in a 3D ambient space. We assume that the graphene sheet lies (more or less, if we ignore the curvature) in the $x-y-$ plane. Out of the 3 possible phonon polarization modes, two are described by vibrations of atoms within the graphene sheet, while there is a third set of vibrations in the z-direction (out of the graphene sheet). For the first two modes, the dispersion is given by $\omega(k) \propto k$ as for usual lattice vibrations, while for the mode along the z-axis, $\omega(k) \propto k^2$. Combine what you have calculated so far to show that the DOS for graphene has one part behaving as $g(\omega) \propto \omega$ from the first two (in-plane) modes, while another part behaves as $g(\omega) \propto 1$ (a constant) from the z-direction modes. *Hint*: $\omega(k) \propto k^2$ should behave similarly to free electrons.

Exercise 2 Electrons in Metals: Free Electron Gas in 2D

Consider a system of N non-interacting electrons (fermions) moving on a surface at finite temperature. The appropriate distribution function is the Fermi-Dirac distribution,

$$f_{FD}(\epsilon, T, \mu) = \frac{1}{e^{\beta(E-\mu)}+1},$$

where ϵ and μ are the energy and the chemical potential, respectively. Physically, it tells us the average number of particles that occupy a state at energy ϵ for a given temperature T and chemical potential μ.

(a) Show that in the limit of low temperatures $T \to 0$, the Fermi-Dirac function converges to a step function

$$\lim_{T\to 0} f_{FD} = \begin{cases} 1 & \epsilon < \mu \\ 0 & \epsilon \geqslant \mu \end{cases} \tag{12}$$

Hint: In statistical mechanics, it is often easier to work with β instead of T. The limit as $T \to 0$ (from above) corresponds to $\beta \to +\infty$.

(b) The total number of particles N and the total energy E of the system can both be calculated by first looking at how many particles have energy ϵ, and then adding this up for ϵ ranging from $-\infty$ to $+\infty$. In our case:

$$N = \int_{-\infty}^{\infty} g(\epsilon) f_{FD}(\epsilon)\, d\epsilon \tag{13}$$

$$E = \int_{-\infty}^{\infty} \epsilon g(\epsilon) f_{FD}(\epsilon)\, d\epsilon \tag{14}$$

For a free electron gas in 2D the density of states (DOS) $g(\epsilon) = \frac{Am}{\pi\hbar^2}$ is just a constant for $\epsilon > 0$, and $g(\epsilon) = 0$ if $\epsilon < 0$ since there are no states of negative energy. For this system, show that in the limit as $T \to 0$, the integrals above can be evaluated to give

$$N = \frac{Am}{\pi\hbar^2}\mu \tag{15}$$

$$E = \frac{Am}{2\pi\hbar^2}\mu^2 \tag{16}$$

(c) In reality, if we have a material (imagine: a chunk of metal for instance), we know the number N of free electrons (= number of valence electrons), but not the chemical potential μ. From the equations above, write the chemical potential as a function of the particle number N, and show that the chemical potential only depends on the particle density $\rho = N/A$. This chemical potential (namely the one in the limit as $T \to 0$) is called **Fermi energy** (or Fermi level), and is usually written as ϵ_F or E_F.

(d) The Fermi energy has the interpretation as the energy ϵ of the highest occupied state as $T \to 0$. In a free electron gas, the energy of a state is given by $\epsilon = \frac{\hbar^2 k^2}{2m}$. Find the corresponding Fermi wave vector k_F, which satisfies $\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$, which corresponds to the largest occupied wave vector.

(e) Use the relation between μ (or the Fermi energy ϵ_F) and the density ρ that you found above to show that

$$E_0(N, A) = E(N, A, T \to 0) = \frac{\pi\hbar^2}{2m} A\rho^2 \propto A\rho^2 \tag{17}$$

In particular, the energy per area E/A grows quadratically with the density.

Cont.

(f) So far, we have managed to calculate the energy as a function of the particle number N and surface area A, but only in the limit of low temperatures as $T \to 0$. For larger temperatures, there will be quadratic corrections to the energy of the form

$$E(N, A, T) = E_0(N, A) + \alpha T^2, \tag{18}$$

where α is some constant that depends on the density of states. Calculate the heat capacity of this system, and show that it scales linearly with temperature.

(g) We have previously calculated the integrals for N and E, but only in the limit of $T \to 0$. But in reality, we can also calculate the N-integral for any temperature. This gives us the full behavior of the chemical potential $\mu(T)$ for any temperature! Show that the number of electrons N can be expressed using the chemical potential as

$$N = \frac{Am}{\pi\hbar^2}\left(\mu + k_B T \log\left(e^{-\beta\mu} + 1\right)\right). \tag{19}$$

Using the Fermi level from part (b), how can we interpret the second term? *Hint: You can use* $\int \frac{1}{e^x+1} dx = x - \log(e^x + 1)$.

(h) Express μ as a function of N. *Hint: Exponentiate both sides of eq. (1). It might be helpful to first bring the equation to the form*

$$\beta\epsilon_F = \beta\mu + \log\left(e^{-\beta\mu} + 1\right) \tag{20}$$

by multiplying by $\frac{\pi\hbar}{Am}$ *to save the amount of calculation steps.*

Exercise 3 Phonon Gas

In this exercise, we will deepen our understanding of the thermal vibrations in a solid. We start by repeating some simple calculations from exercise sheet 1 which are very important to understand this topic.

(a) Consider a single (quantum) harmonic oscillator with frequency ω. Compute the (single particle) canonical partition function of this system.

(b) What is the probability that the oscillator is the n-th energy state? What is the probability for this system to have n phonons? How can we interpret this in the grand canonical ensemble?

(c) What is the average number of phonons and the expected energy of this system? How are the two related?

(d) We now combine these insights with the Debye model of solids, in which the dispersion is given by

$$\omega = c|\mathbf{k}|. \tag{21}$$

Compute the density of states for this system assuming no cutoff in the frequency.

(e) In reality, we need to introduce a cutoff energy E_D. Derive / estimate this cutoff using two different approaches:

1. by combining the total number N of particles with the density of states
2. by assuming that the atoms in the crystal have a lattice parameter of a: what is the largest possible wave vector (smallest possible wavelength) in this case?

(f) Ignoring the cutoff E_D, show that the energy E is proportional to T^4 and deduce that the heat capacity C_V is proportional to T^3 **at all temperatures**.

(g) What is the effect of adding a cutoff on the energy and heat capacity?

The End.