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

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

   In dimensions $d = 1, 2, 3$ which are most relevant to us, $L^d = L, L^2, L^3$ are equal to the length, the system area $A = L^2$ (e.g. of a graphene sheet) and the system volume $V = L^3$, respectively (not to be confused with V_d, which is the "volume" of the unit ball).
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.

Cont.

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?

Cont.

Solution to Exercise 1

Question (a). As in the example, we begin by computing the total number of states below the energy ϵ, which will correspond to the number of points within a cutoff radius R on a grid of possible wave vectors $\mathbf{k}$ with a separation of $2\pi/L$ in each direction. Since we are in two dimensions, this is

$$g_{\text{tot}}(R) \approx \frac{\text{Area of Disc}}{\text{Area per rectangle}} = \frac{\pi R^2}{\left(\frac{2\pi}{L}\right)^2} = \frac{L^2}{4\pi} R^2$$

As the next step, we express this radius as a function of the energy. Using the dispersion relation

$$\epsilon = \frac{\hbar^2}{2m} k^2 \Rightarrow |\mathbf{k}| = \sqrt{\frac{2m\epsilon}{\hbar^2}} = R \tag{22}$$

we obtain:

$$g_{\text{tot}}(\epsilon) = \frac{L^2}{4\pi} R^2 = \frac{L^2}{4\pi} \frac{2m\epsilon}{\hbar^2} = \frac{L^2 m}{2\pi\hbar^2} \epsilon \tag{23}$$

To obtain the density of states at energy ϵ, we differentiate with respect to ϵ to obtain

$$g(\epsilon) = \frac{dg_{\text{tot}}}{d\epsilon} = \frac{L^2 m}{2\pi\hbar^2}. \tag{24}$$

As a final adjustment, we recall that electrons have two possible spin states, so the actual number will be twice as large, namely

$$g(\epsilon) = \frac{Am}{\pi\hbar^2}. \tag{25}$$

Using the fact that $L^2 = A$ corresponds to the surface area of the interface, we can also write

$$g(\epsilon) = \frac{Am}{\pi\hbar^2} \tag{26}$$

Question (b). There are N electrons in the system, which at $T = 0K$ will fill up all energy levels up to the Fermi level E_F. The total number of states in the energy interval $[0, E_F]$ therefore has to be equal to the number of electrons. We thus solve the equation

$$N = \int_0^{E_F} g(\epsilon) d\epsilon = \int_0^{E_F} \frac{Am}{\pi\hbar^2} d\epsilon = \frac{Am}{\pi\hbar^2} E_F \tag{27}$$

Thus, solving for E_F, we get

$$E_F = \frac{\pi\hbar^2 N}{Am}. \tag{28}$$

We can see that the Fermi level is proportional to the number density N/A of electrons.

Question (c). We use the general relation

$$N = \int_{\mathbb{R}} f(\epsilon) g(\epsilon) d\epsilon.$$

In our case, we only have states at energies $\epsilon \geqslant 0$ and use the fermionic function for f, leading to

$$N = \int_0^{\infty} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \frac{Am}{\pi\hbar^2} d\epsilon = \frac{Am}{\pi\hbar^2} \int_0^{\infty} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} d\epsilon \tag{29}$$

Cont.

We can bring the integral to the form

$$\int \frac{1}{e^x+1} \tag{30}$$

by first shifting the integration variable by μ, i.e. $y = \epsilon - \mu$ leading to

$$\int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)}+1} d\epsilon = \int_{-\mu}^\infty \frac{1}{e^{\beta y}+1} dy \tag{31}$$

and then by rescaling the variable $x = \beta y$

$$\int_{-\mu}^\infty \frac{1}{e^{\beta y}+1} dy = k_B T \int_{-\beta\mu}^\infty \frac{1}{e^{\beta x}+1} dx = k_B T \left[x - \log\left(e^x+1\right)\right]_{-\beta\mu}^\infty \tag{32}$$

For the upper integral limit, we can see that

$$\log(e^x+1) \to \log(e^x) = x \tag{33}$$

as $x \to \infty$. Thus, the integral vanishes as

$$x - \log\left(e^x+1\right) \to x - x = 0. \tag{34}$$

For the lower limit, we simply plug in $-\beta\mu$ and obtain

$$k_B T \left(\beta\mu + \log\left(e^{-\beta\mu}+1\right)\right) = \mu + k_B T \log\left(e^{-\beta\mu}+1\right). \tag{35}$$

Combining this with all the prefactors, we finally get

$$N = \frac{Am}{\pi\hbar^2} \int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)}+1} d\epsilon = \frac{Am}{\pi\hbar^2} \left(\mu + k_B T \log\left(e^{-\beta\mu}+1\right)\right). \tag{36}$$

To examine this result, we can bring the factors of $Am/\pi\hbar^2$ to the other side:

$$\frac{\pi\hbar^2 N}{Am} \overset{(b)}{=} E_F = \mu + k_B T \log\left(e^{-\beta\mu}+1\right) \tag{37}$$

We can thus interpret the second term as the correction to the chemical potential as we increase the temperature.

Question (d). By exponentiating both sides of the equation, we get

$$e^{\beta E_F} = e^{\beta\mu} \cdot \left(e^{-\beta\mu}+1\right) = 1 + e^{\beta\mu} \tag{38}$$

This can easily be solved for μ, namely

$$e^{\beta\mu} = e^{\beta E_F} - 1 \tag{39}$$

$$\mu = k_B T \log\left(e^{\beta E_F} - 1\right), \tag{40}$$

where E_F can be expressed in terms of N using the result from (b).
Question (e). The energy can in principle be obtained from the integral

$$E = \int_0^\infty \epsilon f(\epsilon) g(\epsilon) d\epsilon = \int_0^\infty \epsilon \frac{1}{e^{\beta(\epsilon-\mu)}+1} \frac{Am}{\pi\hbar^2} d\epsilon = \frac{Am}{\pi\hbar^2} \int_0^\infty \frac{\epsilon}{e^{\beta(\epsilon-\mu)}+1} d\epsilon \tag{41}$$

For a given (T, N, A), we can first compute the chemical potential μ using the formula in the previous part and numerically evaluate this integral for these fixed values of T and μ.

Cont.

Solution to Exercise 2

Question (a). The energy levels of a quantum mechanical harmonic oscillator at frequency ω are given by

$$\epsilon_n = n\hbar\omega \tag{42}$$

ignoring the constant term $\frac{1}{2}\hbar\omega$ which is irrelevant to experimental predictions. This leads to the partition function

$$Q = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n} = \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n = \frac{1}{1-e^{-\beta\hbar\omega}} \tag{43}$$

Question (b). The probability of being in the n-th state is given by

$$P(n) = \frac{1}{Q}e^{-\beta\epsilon_n} = \frac{e^{-n\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \tag{44}$$

Question (c). The expected value of the energy can be obtained as

$$E = -\frac{\partial \log Q}{\partial\beta} = +\partial\log(1-e^{-\beta\hbar\omega})/\partial\beta = \frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{\hbar\omega}{e^{+\beta\hbar\omega}-1} \tag{45}$$

Question (d). For the phonon energy, we obtain

$$\epsilon = \hbar\omega = c\hbar|\mathbf{k}|. \tag{46}$$

Using this and the fact that two valid wave vectors are separated by $2\pi/L$ in the three coordinate directions, we obtain the radius in wave vector space

$$|\mathbf{k}| = \frac{\epsilon}{c\hbar} =: R \tag{47}$$

get for the total number of states below and energy ϵ:

$$g_{\text{tot}}(R) \approx \frac{\text{Volume of Ball}}{\text{Volume per box}} = \frac{\frac{4\pi}{3}R^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{L^3R^3}{6\pi^3} = \frac{V}{6\pi^3c^3\hbar^3}\epsilon^3$$

Differentiating with respect to ϵ and taking into account that there are three possible polarizaions of elastic waves (2 transversal + 1 longitudinal), we get the density of states

$$g(\epsilon) = 3\cdot\frac{dg_{\text{tot}}}{d\epsilon} = \frac{3V}{2\pi^3c^3\hbar^3}\epsilon^2. \tag{48}$$

Question (e). We can argue in two ways why there has to be a cutoff. First, we know that each atom contributes 3 vibrational modes, meaning that there should only be 3N modes in total.

Note that the density of states allows us to calculate the total number of vibrational states between energies E_1 and E_2 as $\int_{E_1}^{E_2} g(\epsilon)d\epsilon$. This leads us to the equation

$$3N = \int_0^{E_D} g(\epsilon)d\epsilon \tag{49}$$

for E_D. Which is simply

$$N = gtot(E_D) - gtot(0) = gtot(E_D) = \frac{V}{6\pi^3c^3\hbar^3}E_D^3 \tag{50}$$

Cont.

and thus

$$E_D = \left[\frac{6\pi^3 c^3 \hbar^3 N}{V}\right]^{\frac{1}{3}} = \pi c\hbar \left[\frac{6N}{V}\right]^{\frac{1}{3}} \tag{51}$$

An alternative and more crude way to estimate E_D is to recognize that in a crystal with nearest neighbor distance a, the smallest possible wavelength of any elastic wave is $2a$, and thus the maximal wave vector equal to

$$k_{\text{max}} = \frac{2\pi}{\lambda_{\text{min}}} = \frac{\pi}{a} \tag{52}$$

Such a wave vector leads to an energy

$$E_{\text{max}} = c\hbar k_{\text{max}} = \frac{\pi c\hbar}{a} \tag{53}$$

We can compare this crude estimate to E_D that we obtained using the density of states. Note that V/N is the typical volume per atom, so its cube root will provide us with an average distance d between atoms. Thus,

$$E_D \approx \frac{\pi c\hbar}{d} \tag{54}$$

up to factors on the order of 1 arising from the crude estimate in using the distance d. Thus, we see that both approaches essentially yield the same result.

Question (f). Setting $\epsilon = \hbar\omega$, the energy is given by

$$E = \int_0^\infty \epsilon f(\epsilon) g(\epsilon) d\epsilon = \int_0^\infty \frac{\epsilon}{e^{\beta\epsilon} - 1} \frac{3V}{2\pi^3 c^3 \hbar^3} \epsilon^2 d\epsilon \propto \int_0^\infty \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon, \tag{55}$$

where we ignored prefactors since only care about the behavior of E as a function of the temperature. We now perform a change of variables $\beta\epsilon = \epsilon/k_B T =: x$, which leads to

$$E \propto \int_0^\infty \frac{\epsilon^3}{e^{\beta\epsilon} - 1} d\epsilon = T^4 \int_0^\infty \frac{x^3}{e^x - 1} = T^4 \cdot \text{some number} \tag{56}$$

Thus, $E \propto T^4$ as desired, and thus $C_V = \partial E/\partial T \propto T^3$.

Question (g). By introducing a cutoff, our calculations only become asymptotically correct for $T \to 0$, where the integral is dominated by the region around $\epsilon \approx 0$.

In the limit of high temperatures, $E \to 3Nk_B T$ and $C_V \to 3Nk_B$, which is the classical Dulong-Petit law. We thus see that having a finite number of oscillation modes leads to a saturation of the heat capacity.

This can be understood in the following way: if the thermal energy is still small compared to the cutoff, $k_B T < E_D$, then increasing the temperature has two effects: exciting oscillation modes that are already active to even higher energy states + starting to excite energy levels that are even higher up. It is the combination of both that leads to the T^3 behavior that grows rapidly.

As the thermal energy exceed the largest possible Debye energy, $k_B T > E_D$, all the modes are already active. Increasing the temperature further only brings preexisting modes to higher states, but doesn't activate new modes. Thus, the energy only grows linearly leading to a constant heat capacity as predicted from classical mechanics (because the thermal smearing is larger than the largest possible energy separation in the system).

Cont.

Solution to Exercise 3

Question (a).
The average number of electrons in each single-particle state follow the Fermi distribution, i.e.

$$n(\epsilon_i) = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}.$$

The electrons follow Fermi statistics because they are fermions obeying the Pauli exclusion principle.

Question (b). Because at each single particle state, the number of electron and the number of hole must sum up to 1, so the distribution function for holes is

$$p(\epsilon_i) = 1 - n(\epsilon_i) = 1 - \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}.$$

Question (c). The average number of electrons with energy ϵ_i can be found by multiplying the Fermi distribution $n(\epsilon_i)$ by the degeneracy g_i, i.e.

$$n(\epsilon_i, g_i) = \frac{g_i}{e^{(\epsilon_i - \mu)/k_B T} + 1}.$$

Question (d).
The Fermi level lies half way between E_c and E_v. It is the same thing as the chemical potential of electrons.

Question (e).
As in semiconductors $(E_c - \mu)/k_B T \gg 0$, we can use Boltzmann statistics to describe the distribution of electrons in the conduction band. Taking into account of the degeneracy, the average number of electrons with energy ϵ_k is

$$n_k = \frac{\sqrt{2} m_c^{*2/3}}{\pi^2 \hbar^3} (\epsilon_k - E_c)^{1/2} e^{-(\epsilon_k - \mu)/k_B T}.$$

The total concentration of electrons in the conduction band is therefore

$$n^e = \int_{E_c}^{\infty} n_k d\epsilon_k = \frac{1}{\sqrt{2}} \left(\frac{m_c^* k_B T}{\pi \hbar^2} \right)^{3/2} e^{(\mu - E_c)/k_B T}.$$

Question (f). We do the same procedure as dealing with the electrons. The degeneracy number is

$$g_k^h = \frac{\sqrt{2} m_v^{*2/3}}{\pi^2 \hbar^3} (E_v - \epsilon_k)^{1/2}.$$

The average number of holes with energy ϵ_k is

$$p_k = \frac{\sqrt{2} m_v^{*2/3}}{\pi^2 \hbar^3} (E_v - \epsilon_k)^{1/2} (1 - \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}),$$

which can be simplified into

$$p_k = \frac{\sqrt{2} m_v^{*2/3}}{\pi^2 \hbar^3} (E_v - \epsilon_k)^{1/2} e^{(\epsilon_k - \mu)/k_B T}.$$

The total concentration of holes in the valence band is therefore

$$p = \int_{-\infty}^{E_v} p_k d\epsilon_k = \frac{1}{\sqrt{2}} \left(\frac{m_v^* k_B T}{\pi \hbar^2} \right)^{3/2} e^{(E_v - \mu)/k_B T}$$

Question (g).

$$n^e n^h = \frac{1}{2} \left(\frac{k_B T}{\pi \hbar^2} \right)^3 (m_c^* m_v^*)^{3/2} e^{-E_g/k_B T}.$$

Cont.

The smaller E_g, the higher the carrier concentration, which gives the semiconductor higher conductivity.

Question (h). We can tune the chemical potential through doping,

$$\mu = \mu_i + \frac{k_B T}{2} \ln\left(\frac{n}{p}\right) = \mu_i + \frac{k_B T}{2} \ln\left(\frac{n_i + N_d}{p_i + N_a}\right),$$

where μ_i is chemical potential and n_i and p_i are concentration of electron and holes in the intrinsic case.

The End.