Exercise 1 Designing energy levels

Start by opening "levels-discrete.cdf", which allows you to design a hierarchy of energy levels and to observe how the thermo-physical properties of this system are determined by canonical (i.e., constant-temperature) occupations of these levels. For instance, you can observe the temperature variation of the mean energy $\langle E \rangle (T)$ and the heat capacity $c_V(T)$, and understand how the distribution of energy levels determines these properties.

The main goal of this exercise is to understand the most central concept in thermodynamics: under constant temperature conditions, nature tries to minimize the free energy $A = E - TS$.

(a) Create a system with two levels E_1 and $E_2 > E_1$ in the notebook. Without doing any complicated calculations, and only using the intuition about minimization of the free energy A, describe to which value the following quantities will converge to in the limit as $T \to 0$ and $T \to \infty$:

- the probabilities $P(1)$ and $P(2)$ of being in the two microstates
- the internal energy $\langle E \rangle (T)$
- the entropy $S(T)$ *Hint*: what is the number of "possible states" Ω in the two limits?

Make sure to explain your results using the free energy.

(b) Go to the notebook, and for different values of E_1 and E_2, verify the predictions you made above for the probabilities and $\langle E \rangle$ are correct. Furthermore, comment on the behavior of the heat capacity $c_V(T)$. What does it converge to zero for $T \to 0$ and $T \to \infty$? Provide an explanation using the results from the previous exercise.

(c) So far, we focused on the limits as $T \to 0$ and $T \to \infty$, which correspond to the limits of "low temperature" and "high temperature". But where does the transition between low and high temperatures happen?

To get a feeling for this question, examine what happens to the heat capacity curves and the location of the peak in particular, if you change the spacing between E_1 and E_2 (for example, you can use $\Delta E = 0.5, 5, 50$). How (very roughly, just in terms of order of magnitude) is the location of the peak in the heat capacity related to ΔE? Why could the location of the peak be a good measure for the transition between low and high temperatures?

(d) In both classical and quantum mechanics, the energy of a system is only defined up to a constant. For example, the gravitational potential energy is $E_{\text{pot}} = mgh$, where m is the mass, $g \approx 9.81 \text{m/s}^2$ and h is the height of the particle. This energy clearly depends on where we start measuring the height from. If we shift the reference height by Δh, all heights become $h' = h + \Delta h$ and the potential energy shifts becomes $E' = mgh' = mgh + mg\Delta h = E + \text{Const.}$. But this freedom does not affect any experimental predictions, since we never directly measure the energy itself. What matters are only energy differences: if an object falls from height h_1 and lands at h_2, the energy difference $mg(h_1 - h_2)$ gets converted to kinetic energy. And height differences such as $h_1 - h_2$ do not depend on where we start measuring the height from. This is why we always predict the same final speed for the object.

How does such a constant shift in energy influence results in statistical mechanics? For this, change the energy levels E_1 and E_2 while keeping their difference ΔE constant. Comment on how this affects both the mean energy and heat capacity. Your results from part (a) might also help you figuring out the correct behavior for the energy.

In principle, the 2-level systems studied so far are simple enough that we could have performed all calculations just using pen and paper. But the power of simulations is that we can also extend this to much more complicated systems!

(e) Now include multiple levels and keep the spacing constant (you could try something that looks like $E_n = n$, for example). Comment again the behavior of $\langle E \rangle$, C_V as well as the probabilities $P(n)$ that you observe in the two limits as $T \to 0$ and $T \to \infty$. Make a prediction about which value the entropy S would converge to in the two limits (although you won't be able to verify this in the notebook), and provide a simple explanation for why we obtain all these values using the free energy similarly to part (a).

(f) Keeping the energy spacing ΔE fixed, which system does the behavior converge to in the limit in which the number of energy levels $n \to \infty$? *Hint*: You will need to have a look at problem sheet 2 for this.

In real materials, energy levels can look much more complicated.

(g) Design a sequence of levels of your choosing, and explain a possible application of a material exhibiting that series of energy levels. *Hint: for example, what conditions will lead to a double peak in the heat capacity? What kind of use might a material with this property have?*

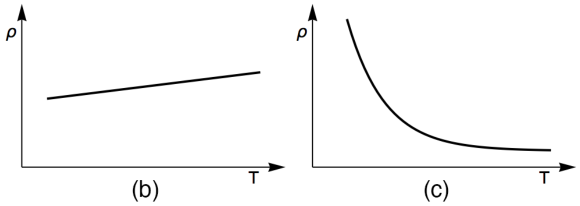
(h) In parts (b) and (d), you developed some tricks to estimate various thermodynamic quantities for the limits as $T \to 0$ and $T \to \infty$. Would these tricks also work for systems with infinitely many energy levels? You should see that this will be possible for one of the two limits, but not the other. For the limit where the same trick doesn't work, what alternative approach could we use to "guess" the correct behavior? *Hint*: Problem sheet 2 might be helpful.

Exercise 2 Properties of semiconductors

Materials can be classified into three categories, depending on the behavior of their resistivity (ρ) with temperature: insulators, semiconductors and metals.

Category	$\rho(\Omega\text{cm})$
Insulators	10^{12}
Semiconductors	10^{6}–10^{-3}
Metals	10^{-6}

(a)



(b) (c)

Figure 1: (a) Room temperature resistivities for the categories of materials. (b) Resistivity versus temperature for a metal. (c) Resistivity versus temperature for a semiconductor.

From your class on solid-state physics, you should know that the various electrical properties observed in materials can be explained using band structures. The band structure of a solid describes the range of energies that an electron within the solid may have (*allowed bands*, or simply *bands*), and ranges of energy that it may not have (*energy gaps*). A material with a large band gap $E_g > 3$ eV between the top of the highest filled (*valence*) band and the bottom of the lowest empty (*conduction*) band is an insulator. A semiconductor is a material with a small energy gap (E_g between $0.5 - 3$ eV). Pure semiconductors behave as insulators at absolute zero, but have thermal excitation of electrons into the conduction band at higher temperatures. Keep in mind that when an electron is excited from the valence to the conduction band, a hole is left in the valence band. In metals there is no gap.

Another important concept is the fact that quantum states for electrons can be identified by the crystal momentum k, so that in the parabolic band approximation the energies of different levels can be written as,

$$E(k) = \frac{\hbar^2 k^2}{2m^\star}.$$

This is important, since the density of states accessible for a given energy will then depend on the curvature of the bands, which is given by the effective mass $m^\star$.

This lab is intended to help you understand the basic concepts of the physics of semiconductors. Open the "semiconductor.cdf" Mathematica notebook provided.

The most important property of any semiconductor at temperature T is the number of electrons per unit volume (n) in the conduction band and the number of holes per unit volume (p) in the valence band. The simplest possible scenario you can assume is that of a pure crystal with no impurities or dopants, described as an *intrinsic semiconductor*. Note that for intrinsic semiconductors the number of conduction band electrons must be equal to the number of valence band holes:

$$n(T) = p(T) = n_i(T)$$

(a) In semiconductors, resistivity can be defined as

$$\rho(T) = \frac{1}{q(\tau_e n(T) + \tau_h p(T))} = \frac{1}{q(\tau_e + \tau_h) n_i(T)},$$

where q is the electronic charge, whileτ_e and τ_h are the electron and hole mobilities. Given that for silicon $E_g = 1.12$ eV, $\tau_e = 1300\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$, $\tau_h = 500\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$, use the notebook to determine the behavior of $\rho(T)$, and make a plot. Use a value close to unity for the effective mass of both electrons and holes. (*Hint: the units of conductivity and resistivity are respectively* $\text{S}\,\text{m}^{-1}$ *and* $\Omega\,\text{m}$, *and you may want to make your plot using a log scale.*)

Cont.

(b) At which temperature will you notice a "reasonable" conductivity in silicon? *Hint: the conductivity of copper is* $58.3 * 10^6$ S m^{-1}. You may need to experiment with many orders of magnitude.

(c) At $T = 300$ K, what value of E_g gives rise to a reasonable conductivity? You can either directly experiment in the notebook, or try to use your answer from part (b) to directly guess the correct answer.

Because an intrinsic semiconductor is a poor conductor at room temperature, its conductivity is usually increased by adding certain impurities in controlled quantities. Such semiconductors are called *extrinsic semiconductors*.

(d) Emulate the effect of the doping by tuning the number of impurity donors (N_d) and acceptors (N_a). Does the relation $n(T) = p(T) = n_i(T)$ hold in the extrinsic case?

(e) For silicon at room temperature, what is the order of magnitude of *dopant carriers* that you should introduce to increase the conductivity to a reasonable value? Provide a simple (qualitative) explanation for the change in conductivity by adding dopants.

Bonus points: This will be the most challenging, but also most interesting part. You can get bonus points for doing this, but it is not necessary to get a full score on this lab. Our goal is to understand what role the chemical potential μ plays in semiconductors.

(f) Going back to intrinsic (undoped) semiconductors and holding E_g and T constant, change the effective masses of the valence and the conduction band. What happens to the chemical potential μ when the effective masses are not the same? How are effective mass, temperature and chemical potential interrelated?

(g) What happens to μ when you vary N_a and N_d? Can you explain why?

The End.