PHYS 427 - Discussion 06

March 4th, 2025

For the past few weeks we have been dealing with equilibrium thermodynamics using the canonical ensemble. This formalism treats the system's particle number as fixed; however, there are many cases in which particles can actually flow into and out of a system[1] . If a system is in both **thermal** and **diffusive** contact with a reservoir at temperature T and chemical potential μ (i.e. the system and reservoir can exchange energy and particles), then in thermal equilibrium the probability the system is in microstate "i" is given by

$$p_i = \frac{e^{-\beta(\varepsilon_i - \mu N_i)}}{\mathcal{Z}} \tag{1}$$

where ε_i and N_i are the system's energy and number of particles respectively in state "i", $\beta \equiv 1/k_B T$, and $\mathcal{Z}$ is the **grand partition function**:

$$\mathcal{Z} \equiv \sum_i e^{-\beta(\varepsilon_i - \mu N_i)} \tag{2}$$

When we work with equilibrated systems that are in thermal and diffusive contact with a reservoir, we say we're working in the **grand canonical ensemble**. In this case, all of thermodynamics follows from the grand partition function!

Algorithm: Thermodynamics in the grand canonical ensemble
1. Compute the grand partition function of the system: $\mathcal{Z}$.
2. Compute the thermodynamics of the system using the grand partition function (generally, this means taking an appropriate derivative of $\mathcal{Z}$).

For instance, the average number of particles in a system is defined by $N = \sum_i p_i N_i$ and the average energy is defined by $U = \sum_i p_i \varepsilon_i$. In the grand canonical ensemble, one can insert (1), shuffle things around, and arrive at the convenient expressions

$$N = k_B T \left(\frac{\partial}{\partial \mu} \ln \mathcal{Z} \right)_T \tag{3}$$

$$U - \mu N = - \left(\frac{\partial}{\partial \beta} \ln \mathcal{Z} \right)_\mu . \tag{4}$$

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[1]Side note: even when the system's particle number and energy are actually fixed, in some circumstances it is useful to *imagine* that it's connected to a reservoir. Relationships between macroscopic average quantities (i.e. equations of state) derived with this imaginary reservoir can be shown to be the same as without the reservoir. But the calculation is much easier to do with the imaginary reservoir. For example, consider that we found the same equation of state $pV = N k_B T$ for an ideal gas in the microcanonical ensemble as in the canonical ensemble, but it was easier in the canonical ensemble. When we discuss quantum gases later in the course, we'll find it useful to work in the grand canonical ensemble, even if the gas is well isolated (like a Bose-Einstein condensate in a trap). However, it's important to bear in mind that not all properties are the same in the microcanonical and canonical ensembles, e.g. those related to fluctuations.

1. **What is the chemical potential?** We defined $\mu \equiv (\partial S/\partial N)_{U,V}$, so $dU = TdS - pdV + \mu dN$. To be concrete, we consider a pressure-volume-temperature system here, but our conclusions hold just as well for magnetic systems and other types of systems.

   (a) Suppose you add a small amount ΔU of internal energy to a closed system without changing the volume or number of particles. Express the change in entropy in terms of ΔU and T. Use this expression to the describe the difference between a high-temperature system and a low-temperature one. Use the phrase "accessible microstates" in your answer.

   (b) Suppose instead you add a small number ΔN of particles without changing the volume or internal energy. Express the change in entropy in terms of ΔN, T, and μ. Use this expression to the describe the difference between a high-chemical-potential system and a low-chemical-potential one. Use the phrase "accessible microstates" in your answer.

   (c) Using the second law of thermodynamics, argue that particles spontaneously flow from high to low chemical potential (just like heat spontaneously flows from high to low temperature).

   (d) From the fundamental thermodynamic relation, show that $\mu = (\partial U/\partial N)_{S,V}$. From this expression, argue the following: if we add a single particle to the system at fixed volume, we must also add energy μ or else the entropy will change. That's an equivalent definition of μ.

   (e) Consider a system of distinguishable, non-interacting particles. The energy eigenstates for a single particle are labelled by one integer $n = 0, 1, 2, \ldots$, and the energies are ϵn. Suppose there are only two particles in the system, with total energy $U = 2\epsilon$. If we add a third particle, how much energy must be added to keep the entropy the same? That is, what is μ?

   (f) The entropy of a classical, monatomic ideal gas is given by the Sackur-Tetrode equation

$$S = Nk_B \left[\ln \frac{n_Q}{n} + \frac{5}{2} \right], \qquad \text{where} \qquad n_Q = \left(\frac{mk_BT}{2\pi\hbar^2} \right)^{3/2} \qquad \text{and} \qquad n = \frac{N}{V}. \qquad (5)$$

   Let S' denote the entropy after we add one particle and change the energy by ΔU. Equate $S' = S$ and solve for ΔU. Your answer is μ (make sure you understand why). Show that your answer agrees with $\mu = (\partial S/\partial N)_{U,V}$. Is the chemical potential of a classical ideal gas positive or negative? *Hint: what condition must n obey for equation (5) to apply?*

2. **Impurity in a metal**: Consider a metal containing an impurity atom which has a single active orbital. Treat the impurity as the system and the metal as the reservoir. The system and the reservoir can exchange energy and electrons (you can think of the metal as a gas of electrons).

Put the system-plus-reservoir in a strong uniform magnetic field. This ensures that all the electron spins are aligned in the same direction. In this case, we can ignore the electron's spin degree of freedom.

If no electrons are bound to the impurity atom, the system has zero energy; if 1 electron is bound to the atom, the system has energy Δ. When the impurity atom is in thermal and diffusive equilibrium with the metal:

(a) Compute the grand partition function for the system.

(b) Compute the average number of bound electrons.

(c) Sketch the average number of bound electrons as a function of Δ at three different temperatures. Notice how the chemical potential affects the result.

(d) Compute the energy of the system.

Now, turn off the magnetic field. In this case, an electron can be found in either its spin-up or spin-down state. Now we can also find *two* electrons bound to the impurity: one spin-up and the other spin-down.[2] If two electrons are bound to the atom, the system has energy $2\Delta + V$. The parameter $V(> 0)$ is meant to describe the repulsive Coulomb interaction between two the electrons.

When the impurity atom is in thermal and diffusive equilibrium with the metal:

(e) Compute the grand partition function for the system.

(f) Compute the average number of bound electrons.

Your answers to the previous questions are functions of the system's temperature and chemical potential. If we wanted to "plug in" numbers to these equations we would need to set T and μ. The temperature would be that of the lab the metal is sitting in, but how do we set the chemical potential? Because the impurity is in diffusive equilibrium with the metal (which we're treating like an electron gas), we can determine the chemical potential as a function of the density of this gas.

To be able to calculate μ explicitly, we will model the metal as a three-dimensional ideal gas of electrons and assume that the temperature is high enough that we can treat the gas classically.[3]

(g) Treating the gas classically, show that the chemical potential of the system is

$$\mu = \begin{cases} k_B T \ln\left(n_{3\text{DEG}}/n_Q\right) & \text{if the magnetic field is } \textbf{on} \\ k_B T \ln\left(n_{3\text{DEG}}/2n_Q\right) & \text{if the magnetic field is } \textbf{off} \end{cases} \tag{6}$$

where $n_{3\text{DEG}}$ is the density of the three-dimensional electron gas and $n_Q(T) = (mk_B T/2\pi\hbar^2)^{3/2}$ is the quantum density.

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[2] We didn't need to worry about this before, because the electrons were all in the same spin state. Soon we're going to discuss a class of particles known as **fermions** (electrons belong to this class). These particles obey the **Pauli-exclusion principle** which means no two particles can occupy the same state.

[3] This is a very bad approximation. We will do better later in the course when we discuss quantum statistics and the degenerate Fermi gas.