

PHYS 427 - Discussion 06

1. **What is the chemical potential???** We defined $\mu \equiv -T(\partial S/\partial N)_{U,V}$, 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 describe the difference between a high-temperature system and a low-temperature one. Use the phrase “accessible microstates” in your answer.

Solution. We have $\Delta S = \Delta U/T$. If a system has high, positive temperature, then its entropy doesn’t change much when we increase its internal energy (without changing the volume or particle number). If a system has low, positive temperature, then its entropy changes a lot when we increase its internal energy (without changing the volume or particle number). In summary, if we add a given amount of energy to a system, the number of accessible microstates $\Omega = e^{S/k_B}$ will increase more for a low-temperature system than a high-temperature one. That’s why heat spontaneously flows from high temperature to low temperature. The number of accessible microstates of the high-temperature system decreases a little bit when it gives up energy, but when the low-temperature system receives that energy its number of accessible microstates increases a lot. Therefore the number of accessible microstates of the universe (both systems combined) increases, so this process can happen spontaneously according to the second law of thermodynamics.

- (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 describe the difference between a high-chemical-potential system and a low-chemical-potential one. Use the phrase “accessible microstates” in your answer.

Solution. Follow the template of the solution to part (a). The point of this problem isn’t to gain some great insight, but just to practice thinking about the definition of μ . The reason chemical potential is a useful concept is the same as the reason temperature is useful. Both quantify how the number of accessible microstates changes as we make some kind of change to the system.

- (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).

Solution. Follow the template of the solution to part (a). Here is a way to write it mathematically. Suppose $\mu_1 > \mu_2$ but $T_1 = T_2 \equiv T$. Then, if we exchange particles so that $\Delta N_1 = -\Delta N_2$ but no energy or volume is exchanged, we have

$$\Delta S_{\text{universe}} = \Delta S_1 + \Delta S_2 = \left[\left(\frac{\partial S_1}{\partial N_1} \right)_{U,V} - \left(\frac{\partial S_2}{\partial N_2} \right)_{U,V} \right] \Delta N_1 = \frac{1}{T} [-\mu_1 + \mu_2] \Delta N_1. \quad (1)$$

This is positive if $\Delta N_1 < 0$, so according to the 2nd law of thermodynamics, particles will flow out of system 1 into system 2.

- (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 .

Solution. From $dU = TdS - pdV + \mu dN$, if we set $dS = dV = 0$, then $\mu = dU/dN$. Therefore, by definition of the partial derivative, $\mu = (\partial U / \partial N)_{S,V}$. Hopefully this type of argument is getting boring by now.

In a finite process where U changes by ΔU and N changes by $\Delta N = 1$, but S and V remain constant, we have $\mu \approx \Delta U$. Therefore, we can say that μ is (approximately) the amount of energy that must be added when adding an additional particle in order to keep S and V constant.

- (e) Consider a system of distinguishable, non-interacting particles. The energy eigenstates for a single particle are labelled by one integer $n = 0, 1, 2, \dots$, 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 ?

Solution. When there are two particles (let's call them red and blue), and the total energy is $U = 2\epsilon$, there are three microstates. Red can be in the 0-energy state while blue is in the 2ϵ -energy state. Or red can be in the ϵ -energy state while blue is in the ϵ -energy state. Or red can be in the 2ϵ -energy state while blue is in the 0-energy state.

If we add a third particle (call it green), and the total energy is $U = \epsilon$, then there will be three microstates. One of these states is when red has energy ϵ and blue and green both have energy 0. The other two states are permutations of this one. Hence we had to *decrease* the total energy by ϵ in order to keep S constant when adding a particle. Hence $\mu = -\epsilon$.

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

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

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 $\mu = -T(\partial S / \partial N)_{U,V}$. Is the chemical potential of a classical ideal gas positive or negative? *Hint: what condition must n obey for equation (2) to apply?*

Solution. For convenience, let's define the constant $C = \left(\frac{mk_B}{3k_B\pi\hbar^2} \right)^{3/2} V$. It's constant because we're not changing the volume. The reason this is convenient is because, when we insert the equipartition theorem result $T = \frac{2}{3} \frac{U}{Nk_B}$ into S and simplify the result, we get

$$S = Nk_B \left[\frac{3}{2} \ln U - \frac{5}{2} \ln N + \frac{5}{2} + \ln C \right] \quad (3)$$

We then have

$$S' = (N+1)k_B \left[\frac{3}{2} \ln(U + \Delta U) - \frac{5}{2} \ln(N+1) + \frac{5}{2} + \ln C \right] \quad (4)$$

Since $N \gg 1$, we have $\ln(N+1) = \ln N + \ln(1+1/N) \approx \ln N + 1/N$ from the first-order Taylor expansion $\ln(1+\epsilon) \approx \epsilon$. Similarly, since $\Delta U \ll U$, we have $\ln(U + \Delta U) \approx \ln U + \Delta U/U$. Inserting these gives

$$S' - S \approx k_B \left[\frac{3}{2} \ln U - \frac{5}{2} \ln N + \frac{5}{2} + \ln C \right] + (N+1)k_B \left[\frac{3}{2} \frac{\Delta U}{U} - \frac{5}{2} \frac{1}{N} \right] \quad (5)$$

$$\approx \frac{S}{N} + Nk_B \left[\frac{3}{2} \frac{\Delta U}{U} - \frac{5}{2} \frac{1}{N} \right], \quad (6)$$

Where in the last step I noticed the first term is just S/N and I approximated $N + 1 \approx N$ (you can leave it as $N + 1$ until the very end to convince yourself it has a small effect on the final answer). Setting $S - S' = 0$ and solving for ΔU , using equipartition $U = \frac{3}{2}Nk_bT$ and reinserting S from equation (2), gives

$$\Delta U = \mu = k_B T \ln \frac{n}{n_Q}, \quad (7)$$

which was found in lecture more directly by evaluating $\mu = (\partial F / \partial N)_{T,V}$. Note that equation (2), and indeed our entire treatment of the ideal gas so far in this class, is only valid when $n \ll n_Q$. Just notice that (2) would be negative if $n \gtrsim n_Q$, and it doesn't make sense for the number of accessible microstates $\Omega = e^{S/k_B}$ to be less than one! The reason is that some of the approximations made in deriving (2) make it inapplicable at high densities. We'll do better soon when we discuss Bose and Fermi gases. For now, just note that whenever $n \ll n_Q$, the expression for the chemical potential (7) is negative. Therefore, from part (b), when we add a particle without changing the total energy or volume, the entropy will increase. Not an obvious result, as far as I can tell¹.

¹There's a story about a math professor who, during a lecture, said that some result was "obvious". A student stopped the professor to ask why it was obvious. The professor paused, paced back and forth a bit, scribbled some things on the board, but had trouble answering the student's question. After a few minutes of this, the professor finally shouted "ah, of course, it *is* obvious!"

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.³ 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.⁴

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

$$\mu = \begin{cases} k_B T \ln(n_{3\text{DEG}}/n_Q) & \text{if the magnetic field is **on**} \\ k_B T \ln(n_{3\text{DEG}}/2n_Q) & \text{if the magnetic field is **off**} \end{cases} \quad (28)$$

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.

³We 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.

⁴This is a very bad approximation. We will do better later in the course when we discuss quantum statistics and the degenerate Fermi gas.

- (a) There are two states in this case: 1) zero electrons bound to the atom with energy 0; 2) one electron bound to the atom with energy Δ . Thus

$$\mathcal{Z} = e^{-\beta(0-\mu 0)} + e^{-\beta(\Delta-\mu 1)} \quad (29)$$

$$= 1 + e^{-\beta(\Delta-\mu)} \quad (30)$$

- (b) The thermal average number of electrons bound to the atom is given by:

$$N = \sum_i N_i \frac{e^{-\beta(\varepsilon_i - \mu N_i)}}{\mathcal{Z}} \quad (31)$$

$$= \frac{0e^{-\beta(0-\mu 0)} + 1e^{-\beta(\Delta-\mu 1)}}{1 + e^{-\beta(\Delta-\mu)}} \quad (32)$$

$$N = \frac{1}{e^{\beta(\Delta-\mu)} + 1} \quad (33)$$

Alternatively, using derivatives of the partition function:

$$N = k_B T \left(\frac{\partial}{\partial \mu} \ln \mathcal{Z} \right)_T \quad (34)$$

$$= k_B T \frac{1}{\mathcal{Z}} \partial_\mu \mathcal{Z} \quad (35)$$

$$= k_B T \frac{1}{\mathcal{Z}} (0 + e^{-\beta(\Delta-\mu)} \beta) \quad (36)$$

$$= \frac{e^{-\beta(\Delta-\mu)}}{1 + e^{-\beta(\Delta-\mu)}} \quad (37)$$

$$N = \frac{1}{e^{\beta(\Delta-\mu)} + 1} \quad (38)$$

- (c) The function,

$$f(\varepsilon) \equiv \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} \quad (39)$$

appears so frequently in statistical mechanics that we give it a name. It is called the **Fermi-Dirac distribution function**. It appears naturally in systems of fermions as we'll see in the upcoming weeks.

Figure 1 shows a plot of the function at various temperatures. Notice that the function is bounded between 0 and 1 — this makes sense since there can only be 0 or 1 electrons bound to the impurity (in the case of a large magnetic field), so the average should be between 0 and 1. Furthermore, as the temperature of the system is lowered, the function begins to resemble a **step function**. For $\Delta < \mu$, it is energetically **favourable** for an electron to bind to the atom — hence it makes sense that $N > 1/2$ in this region. For $\Delta > \mu$, it is energetically **costly** for an electron to bind to the atom — hence it makes sense that $N < 1/2$ in this region.

- (d) The energy of the system is given by

$$U = \sum_i \varepsilon_i \frac{e^{-\beta(\varepsilon_i - \mu N_i)}}{\mathcal{Z}} \quad (40)$$

$$= \frac{0e^{-\beta(0-\mu 0)} + \Delta e^{-\beta(\Delta-\mu 1)}}{1 + e^{-\beta(\Delta-\mu)}} \quad (41)$$

$$U = \frac{\Delta}{e^{\beta(\Delta-\mu)} + 1} = N\Delta \quad (42)$$

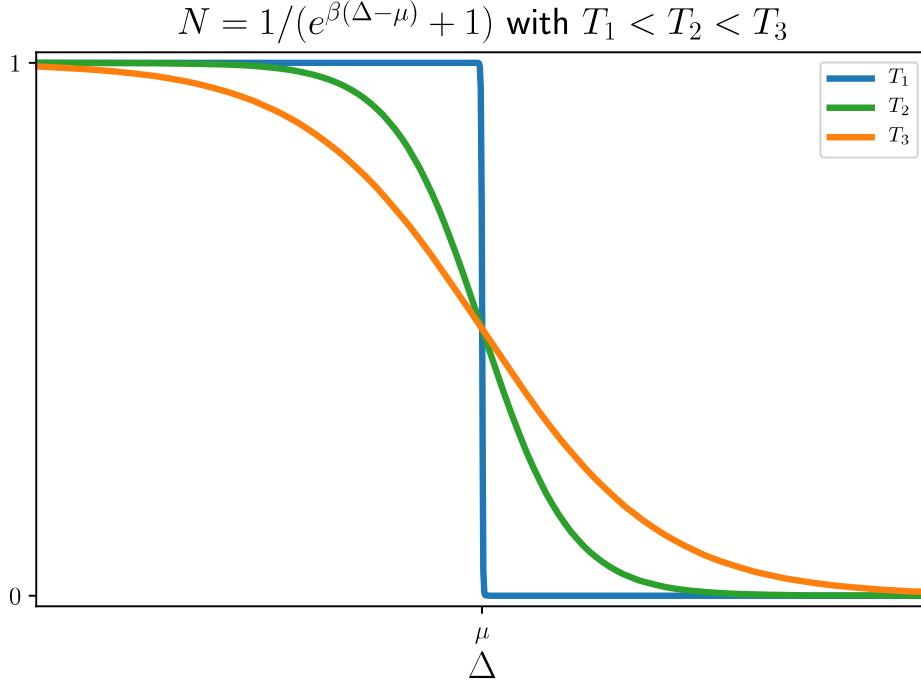


Figure 1

Alternatively, using derivatives of the partition function:

$$U - \mu N = - \left(\frac{\partial}{\partial \beta} \ln \mathcal{Z} \right)_{\mu} \quad (43)$$

$$= - \frac{1}{\mathcal{Z}} \partial_{\beta} \mathcal{Z} \quad (44)$$

$$= - \frac{1}{1 + e^{-\beta(\Delta-\mu)}} (0 - e^{-\beta(\Delta-\mu)} (\Delta - \mu)) \quad (45)$$

$$= N(\Delta - \mu) \quad (46)$$

$$U = N\Delta \quad (47)$$

(e) When we turn off the magnetic field, there are four states: 1) zero electrons bound to the atom with energy 0; 2) a spin-up electron bound to the atom with energy Δ ; 3) a spin-down electron bound to the atom with energy Δ ; 4) both a spin-up and spin-down electron bound to the atom with energy $2\Delta + V$. Thus

$$\mathcal{Z} = e^{-\beta(0-\mu 0)} + e^{-\beta(\Delta-\mu 1)} + e^{-\beta(\Delta-\mu 1)} + e^{-\beta(2\Delta+V-\mu 2)} \quad (48)$$

$$= 1 + 2e^{-\beta(\Delta-\mu)} + e^{-\beta(2(\Delta-\mu)+V)} \quad (49)$$

(f) The average number of electrons bound to the atom is given by:

$$N = k_B T \left(\frac{\partial}{\partial \mu} \ln \mathcal{Z} \right)_T \quad (50)$$

$$= k_B T \frac{1}{\mathcal{Z}} \partial_{\mu} \mathcal{Z} \quad (51)$$

$$= k_B T \frac{1}{\mathcal{Z}} (0 + 2e^{-\beta(\Delta-\mu)} \beta + e^{-\beta(2(\Delta-\mu)+V)} 2\beta) \quad (52)$$

$$N = 2 \frac{e^{-\beta(\Delta-\mu)} + e^{-\beta(2(\Delta-\mu)+V)}}{1 + 2e^{-\beta(\Delta-\mu)} + e^{-\beta(2(\Delta-\mu)+V)}} \quad (53)$$

(g) Recall, we've seen before that the chemical potential of a monatomic ideal gas is

$$\mu_{\text{ideal gas}} = k_B T \ln \left(\frac{n_{\text{ideal gas}}}{n_Q} \right) \quad (54)$$

In the first case, the magnetic field is **on** and all the spins are aligned in the same direction. Treating the metal as an ideal gas means the chemical potential of the metal is given by Eq. 54. In diffusive equilibrium the chemical potential of the system (electrons on the impurity atom) is equal to that of the reservoir (the electron gas), hence:

$$\mu = k_B T \ln \left(\frac{n_{3\text{DEG}}}{n_Q} \right) \quad (55)$$

In the second case, the magnetic field is **off** and the spins can be aligned in either spin state. We can treat the electron gas as a gas composed of 2 species of particles: a gas of spin-up particles and a gas of spin-down particles. Both gases obey Eq. 54:

$$\mu_{\uparrow} = k_B T \ln \left(\frac{n_{\uparrow}}{n_Q} \right) \quad (56)$$

$$\mu_{\downarrow} = k_B T \ln \left(\frac{n_{\downarrow}}{n_Q} \right) \quad (57)$$

where n_{\uparrow} (n_{\downarrow}) is the density of spin-up (down) electrons. In diffusive equilibrium: $\mu_{\uparrow} = \mu_{\downarrow}$ and hence $n_{\uparrow} = n_{\downarrow}$. Since the total density of the electron gas is $n_{3\text{DEG}} = n_{\uparrow} + n_{\downarrow}$ that means $n_{\uparrow} = n_{\downarrow} = n_{3\text{DEG}}/2$. The impurity is in diffusive equilibrium with the electron gas, hence the chemical potential of the system is

$$\mu = k_B T \ln \left(\frac{n_{3\text{DEG}}}{2n_Q} \right) \quad (58)$$