

Problem 1

The energy of a two-state paramagnet with N spins $\sigma_i = \pm 1$ is

$$U = -\mu B \sum_{i=1}^N \sigma_i$$

Consider two such paramagnets with $N_A = 200$ and $N_B = 100$.

- a) The two paramagnets are initially at temperatures $T_A = \mu B/k_B$ and $T_B = -\mu B/k_B$ respectively. Note the latter is at negative temperature! Using the formulas derived in class and lecture, what are U_A and U_B ?

Solution: From equation 3.31 in the book, we have

$$U = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

so for the given values of T_A and T_B , we have:

$$U_A = -N_A\mu B \tanh\left(\frac{\mu B}{k(\mu B/k)}\right) = -N_A\mu B \tanh(1)$$

$$U_B = -N_B\mu B \tanh\left(\frac{\mu B}{k(-\mu B/k)}\right) = -N_B\mu B \tanh(-1)$$

□

- b) The two paramagnets are brought into contact, and energy flows between them until they reach equilibrium. They are isolated from the environment. Once in equilibrium, what are U_A , U_B , T_A and T_B ? Use Mathematica to obtain a numerical answer for T .

Solution: We're given the formula for T^{-1} :

$$\frac{1}{T} = \frac{k}{2\mu B} \ln\left(\frac{N - U/\mu B}{N + U/\mu B}\right)$$

At thermal equilibrium, we have $T_A = T_B$, so

$$\ln\left(\frac{N_A - U_A/\mu B}{N_A + U_A/\mu B}\right) = \ln\left(\frac{N_B - U_B/\mu B}{N_B + U_B/\mu B}\right)$$

$$\frac{\mu B N_A - U_A}{\mu B N_A + U_A} = \frac{\mu B N_B - U_B}{\mu B N_B + U_B}$$

Simplifying this expression all the way down gets us

$$U_B N_A - U_A N_B = 0 \implies \frac{U_B}{U_A} = \frac{N_B}{N_A} = \frac{1}{2}$$

Therefore, $U_B = 2U_A$. To numerically calculate T , we'll need to calculate U_B and U_A first, which we can do using conservation of energy. We know the initial energy is:

$$U_i = -N_A\mu B \tanh(1) - N_B\mu B \tanh(-1) = (N_B - N_A)\mu B \tanh(1)$$

We know that the final energy can be written as $U_f = 3U_B$, so:

$$U_f = 3U_B \implies U_B = \frac{N_B - N_A}{3} \mu B \tanh(1) = -25.38 \mu B$$

U_A is twice this value, so:

$$U_A = \frac{2(N_B - N_A)}{3} \mu B \tanh(1) = -50.77 \mu B$$

We can then solve for T_A algebraically by plugging our value for U_A at equilibrium and N_A back into the expression for U (I told Mathematica to simplify this expression and this is what it gave me):

$$T_A = \frac{2B\mu}{k \ln \left(\frac{200 + \frac{200 \tanh(1)}{3}}{200 - \frac{200 \tanh(1)}{3}} \right)}$$

Similarly for T_B :

$$T_B = \frac{2B\mu}{k \ln \left(\frac{100 + \frac{100 \tanh(1)}{3}}{100 - \frac{100 \tanh(1)}{3}} \right)}$$

Written in a nicer form, the algebraic ¹ expression for T_A and T_B is:

$$T_A = \frac{3.85 \mu B}{k} \quad T_B = \frac{3.85 \mu B}{k}$$

Numerically, we have:

$$T_A = 2.79 \times 10^{-21} \mu B$$

$$T_B = 2.79 \times 10^{-21} \mu B$$

These two values are identical, which makes sense, since from the start we claimed that $T_A = T_B$. □

- c) What is the change in the entropy ΔS_A , ΔS_B and ΔS_{AB} during this process? Is the 2nd law satisfied?

Solution: We can solve this problem by counting the number of microstates available to the paramagnet. We know that initially, we have the following:

$$U_A = -N_A \mu B \tanh(1) = -152.3 \mu B$$

$$U_B = -N_B \mu B \tanh(-1) = 76.15 \mu B$$

Since we're dealing with integer number of spins, I'm going to round down for both numbers, so we have:

$$U_A = -152$$

$$U_B = 76$$

For magnet A, this means that there are 152 spin down states, and 48 spins that cancel each other out. This means that half of the 48 spins are spin up, so there are a total of 24 spin up states in magnet A. There are 200 spins in magnet A, so:

$$S_A^i = k \ln \left(\frac{200}{24} \right)$$

Similarly, magnet B has 76 spin up states, so 24 spins cancel, hence 12 spin down states. Therefore, the entropy of magnet B is:

$$S_B^i = k \ln \left(\frac{100}{12} \right)$$

¹I wouldn't really call it an algebraic expression since we've already done some simplifications already; I'd argue that the initial equation for $\frac{1}{T_A}$ is the *true* algebraic expression.

Now recall our values for U_A and U_B at equilibrium:

$$\begin{aligned}U_A^f &= -50.77\mu B \\U_B^f &= -25.38\mu B\end{aligned}$$

Again, we need to round these numbers to the nearest integer. Since we need an even number of spins so that they cancel nicely, our rounding is going to be:

$$\begin{aligned}U_A^f &= -52\mu B \\U_B^f &= -24\mu B\end{aligned}$$

The reason we round from $-50.77\mu B$ down to $-52\mu B$ is because initially the system starts at a lower energy of $-152\mu B$ and it gains energy, since $-50\mu B$ is higher energy than $-50.77\mu B$, this system cannot have that much energy. Therefore, we're forced to round down to $-52\mu B$. Similarly, this means that system B goes to $-24\mu B$, since it lost energy, and can't possibly give away more energy since that doesn't contribute to the changing of a spin state in system A .

We then perform the same analysis as we did with the initial energy: there are 52 spin up states, and the remaining cancel out, meaning that there are 74 spin down states, so

$$S_A^f = k \ln \binom{200}{74}$$

Similarly, for magnet B we have 24 spin up states, so this corresponds to 38 spin down states, so

$$S_B^f = k \ln \binom{100}{38}$$

Now to calculate the entropy changes (done in Mathematica):

$$\begin{aligned}\Delta S_A &= S_A^f - S_A^i = 8.005 \times 10^{-22} \text{ J/K} \\ \Delta S_B &= S_B^f - S_B^i = 4.045 \times 10^{-22} \text{ J/K}\end{aligned}$$

Then $\Delta S_{AB} = \Delta S_A + \Delta S_B = 1.205 \times 10^{-21} \text{ J/K}$. Clearly, this value is positive, so the second law is satisfied. \square

Problem 2

A liter of air, initially at room temperature and atmospheric pressure, is heated at constant pressure until it doubles in volume. Calculate the increase in entropy during this process.

Solution: We begin first by verifying the table. For diatomic gases, since $f = 5$, we expect a C_P value of $\frac{7}{2}R \approx 29.1$. Looking at the table, we get that for oxygen, $C_P = 29.38$ and for Nitrogen, $C_P = 29.12$, exactly as expected.

Now solving the problem: We know that $Q = C_P dT$, and that:

$$(\Delta S)_P = \int_{T_i}^{T_f} \frac{Q}{T} = C_P \int_{T_i}^{T_f} \frac{dT}{T} = C_P \ln \left(\frac{T_f}{T_i} \right)$$

So now all we need to do is calculate T_f and T_i . This is relatively simple, we can use the ideal gas law:

$$T_i = \frac{P_0 V_0}{Nk}, \quad T_f = \frac{P_0 (2V_0)}{Nk} = 2T_i$$

Therefore:

$$(\Delta S)_P = C_P \ln \left(\frac{2T_i}{T_i} \right) = C_P \ln 2$$

This calculation for entropy gives us the change in entropy in one mole of air. We have one liter of air, which is $\frac{1}{22.4} = 0.044$ moles of air. (Here I used the fact that the molar volume is 22.4L). Therefore, the change in entropy is:

$$(\Delta S)_P = (29)(0.044) \ln 2 = 0.88 \text{ J/K}$$

□

Problem 3

Consider a monoatomic gas in which each particle experiences a constant potential energy v :

$$U = \sum_{i=1}^N \left[\frac{\mathbf{p}_i^2}{2m} + v \right]$$

- a) What is the entropy $S(U, N, V)$? Your result should be just a small modification of the Sackur-Tetrode equation coming from the potential v ; you don't need to derive the Sackur-Tetrode from scratch.

Solution:

With the given potential, we can write this instead as:

$$U_T = U_{\text{free}} + Nv$$

so rearranging, $U_{\text{free}} = U_T - Nv$. Since the free energy is really what the Sackur-Tetrode equation uses as its value for U , then we can just substitute this in for our entropy:

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m(U - Nv)}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right]$$

□

- b) What is $U(T, N, V)$?

Solution: We know that $U_{\text{free}} = \frac{3}{2}NkT$, so therefore:

$$U(T, N, V) = \frac{3}{2}NkT - Nv$$

□

- c) What is $P(T, N, V)$?

Solution: We have the relation $P = T \left(\frac{\partial S}{\partial V} \right)_{U, N}$ so all we need to do is take the derivative of S with respect to V . Note that in the equation for S , there is only one V term, so once we split the logarithm only the $\frac{V}{N}$ term matters. Therefore, taking the derivative:

$$\begin{aligned} P &= T \frac{\partial}{\partial V} \left[Nk \left(\ln \left(\frac{V}{N} \left(\frac{4\pi m(U - Nv)}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right) \right] \\ &= NkT \left(\frac{1}{V} \right) \end{aligned}$$

Therefore, we have:

$$P(T, N, V) = \frac{NkT}{V}$$

□

- d) Prove that

$$\mu(N, V, T) = -k_B T \ln \left(\frac{V}{N\lambda_T^3} \right) + v$$

where $\lambda_T = 1/\sqrt{2\pi m k_B T/h^2}$.

Solution: This problem has a lot of algebra so I won't bother going through it all, though I'll highlight the major steps. We know that to calculate the chemical potential,

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N}$$

Therefore, we have to take the derivative of S with respect to N . Here comes the algebra:

$$\begin{aligned} -\frac{\mu}{T} &= \frac{d}{dN} \left[Nk \left(\ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln \left(\frac{4\pi m(U - Nv)}{3Nh^2} \right) + \frac{5}{2} \right) \right] \\ &= k \left[\ln \left(\frac{V}{N} \right) + \frac{3}{2} \left(\frac{4\pi m(U - Nv)}{3Nh^2} \right) + \frac{5}{2} \right] + Nk \left[-\frac{1}{N} + \frac{3}{2} \frac{-4\pi mv}{4\pi m(U - Nv)} - \frac{3}{2} \frac{1}{3Nh^2} (3h^2) \right] \\ &= k \ln \left(\frac{V}{N} \left(\frac{4\pi m(U - Nv)}{3Nh^2} \right)^{3/2} + \frac{5}{2} \right) - Nk \left(\frac{1}{N} + \frac{3}{2} \frac{v}{U - Nv} + \frac{3}{2N} \right) \end{aligned}$$

I skipped quite a bit of from the second to third step, but I also can't be bothered to write out all the algebra. From here, we can substitute $U = \frac{3}{2}NkT + Nv^2$ into both places, eventually getting us:

$$-\frac{\mu}{T} = k \ln \left(\frac{V}{N} \left(\frac{4\pi m}{3Nh^2} \frac{3}{2} NkT \right)^{3/2} \right) - \frac{3}{2} \frac{Nkv}{\frac{3}{2}NkT}$$

From here we multiply the T and the negative sign over, and we get:

$$\mu = -kT \ln \left(\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right) + v$$

We now recognize that everything inside the logarithm beside the $\frac{N}{V}$ is our λ term, so we finally get the desired equation:

$$\mu(N, V, T) = -kT \ln \left(\frac{V}{N\lambda_T^3} \right) + v$$

□

- e) Two boxes of gas with differing potentials $v_A \neq v_B$ are brought into contact. Particles and number flow to achieve chemical and thermal equilibrium, with their volumes V_A, V_B fixed. They equilibrate to density $n_A = \frac{N_A}{V_A}$ and $\frac{N_B}{V_B}$ and temperature T . Find the expression for $\frac{n_A}{n_B}$ that depends on $v_A - v_B$ and T .

Solution: We have the following expressions for the chemical potentials:

$$\begin{aligned} \mu_A &= -kT_A \ln \left(\frac{V_A}{N_A \lambda_{T_A}^3} \right) + v_A \\ \mu_B &= -kT_B \ln \left(\frac{V_B}{N_B \lambda_{T_B}^3} \right) + v_B \end{aligned}$$

Our end goal is to set these two equal to each other to find an expression for n_A and n_B . Note that at thermal equilibrium, $T_A = T_B = T$, and since λ is only dependent on T , then $\lambda_{T_A} = \lambda_{T_B} = \lambda$. Now we set these equal to each other:

$$kT \ln \left(\frac{V_A}{N_A \lambda^3} \right) - v_A - kT \ln \left(\frac{V_B}{N_B \lambda^3} \right) + v_B = 0$$

²I'm omitting the T subscript I used in part (a), but it's the same U I'm referring to

Simplify this by pulling v_A and v_B to one side and combine the logarithm:

$$\begin{aligned} kT \ln \left(\frac{V_A/(N_A \lambda^3)}{V_B/(N_B \lambda^3)} \right) &= v_A - v_B \\ \ln \left(\frac{n_B}{n_A} \right) &= \frac{1}{kT} (v_A - v_B) \\ \therefore \frac{n_A}{n_B} &= e^{-(v_A - v_B)/kT} \end{aligned}$$

□

f) How can this problem be used to give an alternative explanation to Schroder 1.16c from HW1?

Solution: Problem 1.16c was discussing the relationship between the pressure and altitude, assuming that T remained constant throughout the Earth's atmosphere. In that problem we reasoned the equation for pressure by considering the volume of air at height z and $z + dz$.

Notice that in these two volumes of air, the particles have different potentials, just like the system described in part (e). Furthermore, notice that the pressure of a gas is proportional to the density via the relationship:

$$P = \frac{NkT}{V} = nkT$$

where n is the density. Since T is constant, $P \propto n$. Therefore, up to some constants, we can write:

$$\frac{P_A}{P_B} = e^{-(v_A - v_B)/kT} \implies P_A = P_B e^{-(v_A - v_B)/kT}$$

If we let P_B be the lower of the two volumes, then this final equation gives us a relationship between the pressure at a higher altitude in terms of the pressure at a lower altitude. This matches exactly the equation we derived in 1.16c:

$$P(z) = P(0)e^{-mgz/kT}$$

where the pressure at a height z is related to the pressure at sea level $P(0)$. Note that the potentials also match, since $v_A - v_B$ is the difference in potential energy and if B is at sea level then $v_B = 0$ so $v_A - v_B = mgz$, exactly as in the equation for $P(z)$. □