

## Homework solutions From mechanics to statistical mechanics – Chapter 1

**Homework Problem S1.1:** For two dice, what is the probability of being in macrostate “7”? What function does the probability distribution approach when I roll many dice at once in each roll, and add up the numbers? Make a plot, starting with the uniform distribution (dice have equal probability of 1/6 for each face) for N=2 dice and N=20 dice using:

[http://195.134.76.37/applets/AppletCentralLimit/Apppl\\_CentralLimit2.html](http://195.134.76.37/applets/AppletCentralLimit/Apppl_CentralLimit2.html)

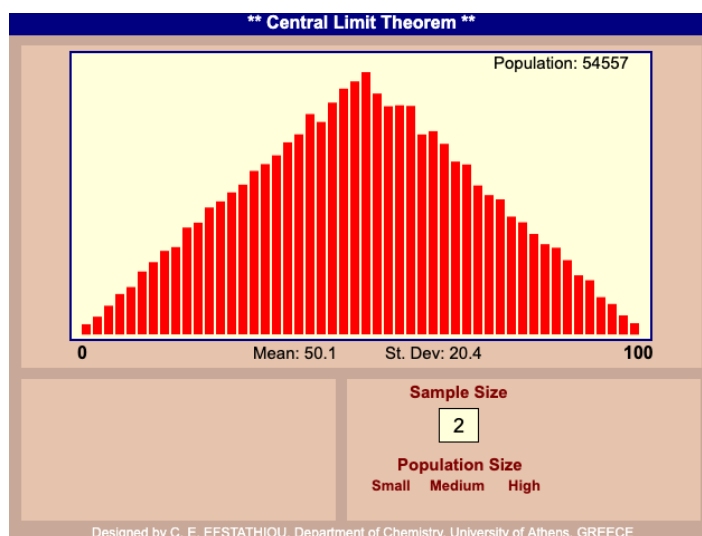
**Solution:** All the results of rolling two dice are given by the table

	1	2	3	4	5	6
1	2	3	4	5	6	7
2	3	4	5	6	7	8
3	4	5	6	7	8	9
4	5	6	7	8	9	10
5	7	8	9	10	11	12
6	7	8	9	10	11	12

where the top row and left column show the result for each die, and the entries the sum for that particular combination. The “7” shows up six times, e.g. 1+6, 2+5, etc. The macrostate “7” means the sum of the number on the dice faces pointing up is 7, so

$$P(\text{sum} = 7) = \frac{6}{36} = \frac{1}{6}$$

When rolling many dice at once, the probability distribution approach a normal distribution according to Central Limit Theorem.



**Figure 1:** Probability distribution of the sum of numbers on the dice faces pointing up (N=2)

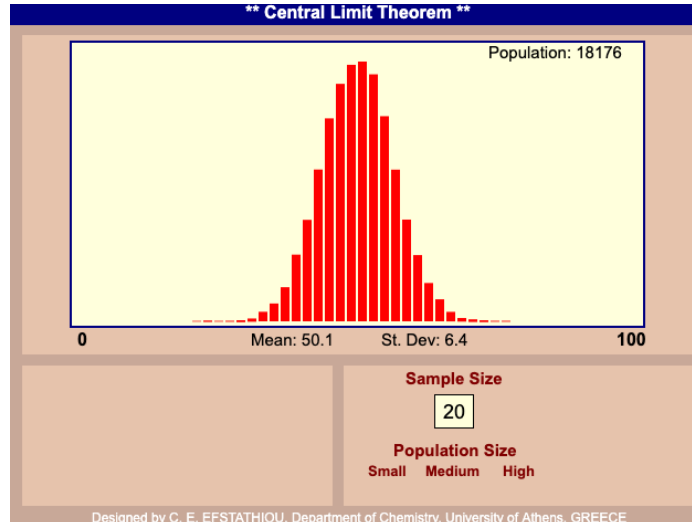


Figure 2: Probability distribution of the sum of numbers on the dice faces pointing up ( $N=20$ )

**Homework problem S1.2:** A bag contains two 1-dollar coins and 4 quarters. If you draw a single coin from the bag many times in a row, what is the average value of a draw? Could you ever draw that amount in a single attempt? If the bag contained a dollar coin, a half dollar and 2 quarters, what would be the answer to the same two questions? Beware: experiments can, but do not always, give the ‘average’ value as a result when you do them!

**Solution:** a) Set  $X$  the value in a single draw. The probability of drawing a dollar coin and a quarter at once is

$$P(X = 1) = \frac{2}{6} = \frac{1}{3}$$

$$P\left(X = \frac{1}{4}\right) = \frac{4}{6} = \frac{2}{3}$$

Therefore, the average value of a draw is calculated by the expectation

$$E(X) = \sum X_i P_i = 1 * \frac{1}{3} + \frac{1}{4} * \frac{2}{3} = \frac{1}{2}$$

Obviously, one cannot draw that amount in a single attempt. You would always get either 1 (dollar) or 0.25 (quarter), but there is no ‘1/2 dollar’ coin in the bag. So it can be deceiving to describe individual cases by averages.

b) Set  $Y$  the value in a single draw from the new bag.

$$P(Y = 1) = \frac{1}{4}$$

$$P\left(Y = \frac{1}{2}\right) = \frac{1}{4}$$

$$P\left(Y = \frac{1}{4}\right) = \frac{2}{4} = \frac{1}{2}$$

The average value is given by

$$E(Y) = \sum Y_i P_i = 1 * \frac{1}{4} + \frac{1}{2} * \frac{1}{4} + \frac{1}{4} * \frac{1}{2} = \frac{1}{2}$$

In this case, the average value can be gotten from a single attempt, with a 25% chance

### Homework solutions

#### Postulates of statistical mechanics, entropy, and thermodynamic laws – Chapter 2

**Homework problem S2.1:** A measurement of the ammonia out-of-plane bending angle by the “Coulomb explosion technique” yields values  $-27^\circ$ ,  $+16^\circ$ ,  $+20^\circ$ ,  $-12^\circ$ ,  $+8^\circ$ ,  $-12^\circ$ . Calculate the average by assigning a weight to each distinct value (e.g.  $1/6$  for  $+8^\circ$ ). Are any actual measurements near the average value? Remembering what you learned about tunneling in quantum mechanics, why are none of the measurements near the average?

**Solution:** Coulomb explosion is a technique used to determine the structure of simple gas phase. Molecules are held together by the balance of charge of negative electrons and positive nuclei. In Coulomb explosion, molecules are fully ionized first and then either laser irradiation or bombardment by highly charged ions is applied to disperse the nuclei which will be collected by a detector grid.

In this question, the out-of-plane bending angle are measured as  $-27^\circ$ ,  $+16^\circ$ ,  $+20^\circ$ ,  $-12^\circ$ ,  $+8^\circ$ ,  $-12^\circ$  so the average angle is calculated by

$$Avg = \frac{1}{6} * (-27) + \frac{1}{6} * 16 + \frac{1}{6} * 20 + \frac{1}{6} * (-12) + \frac{1}{6} * 8 + \frac{1}{6} * (-12) = -1.16$$

The average from the measurement is close to zero but none of the actual measured angles is near the average. Instead, they are either closed to  $+20$  or  $-20$  which corresponds to the angle pointing up or pointing down and conforms to two symmetric configurations of ammonia. So, from this question we can tell that when the probability distribution is bimodal, the average can be misleading.

**Homework problem S2.2:** How many distinguishable ways are there of arranging  $N=3$  different-colored balls in a box with three compartments? Draw all the configurations and express your answer in terms of a factorials. What if all balls are blue and you can't tell the difference between them, how many distinguishable ways are there then? Write your answer in terms of a ratio of factorials. What if 2 balls are red, and 1 is blue?

Solution: a) Let's assume the colors of the three balls are red, green, and blue. The ball in the first compartment can be in any of the three color, the second ball can only be in one of the two color left after the first ball is arranged and the color of the ball is determined right after the second ball is chosen. So the total number of the ways to arrange the three balls is  $3! = 6$ .

1	2	3
red	green	blue
red	blue	green
green	red	blue
green	blue	red
blue	red	green
blue	green	red

- b) if the three balls are all blue, there is only one way to arrange them, i.e. blue, blue, blue  
 c) if two of the three balls are red and one of them is blue, then the arrangements can be:

1	2	3
red	red	blue
red	blue	red
blue	red	red

The number of the arrangements is  $\frac{3!}{2!1!} = 3$ .

**Homework problem S2.3:** Using the boxed example two pages ago, show that  $S \approx Nk_B \ln(V/V_0) - Nk_B \ln N$  if  $M$  (number of volume elements  $V_0$  in the box) is much larger than  $N$  (the number of particles). If I double the size of a box containing  $6.2 \cdot 10^{20}$  molecules (roughly 1 mMole), by how much does the entropy increase in units of J/K? What if I increase the volume by a factor of 1000? As you can see, entropy grows very slowly with volume, but it does increase because more volume => more arrangements => more disorder is possible.

**Solution:** The number of arrangements for  $N$  particles in a box with  $M = V/V_0$  cells ( $N \ll M$ ) is

$$W = \frac{M!}{(M-N)! N!}$$

Apply the Stirling's formula  $\ln n! = n \ln n - n$ , thus

$$W = \frac{M!}{(M-N)! N!} \approx M^M (M-N)^{M-N} N^{-N} \approx \left(\frac{M}{N}\right)^N$$

The entropy  $S$  is calculated by its definition

$$S = k_B \ln W = k_B \ln \left(\frac{M}{N}\right)^N = Nk_B \ln M - Nk_B \ln N = Nk_B \ln \frac{V}{V_0} - Nk_B \ln N$$

a) If I double the size of the box,  $\Delta S = \left(Nk_B \ln \frac{2V}{V_0} - Nk_B \ln N\right) - \left(Nk_B \ln \frac{V}{V_0} - Nk_B \ln N\right)$

or  $\Delta S = (Nk_B \ln 2)$  after we cancel all the terms that don't change. For  $N = 6.2 \cdot 10^{20}$ ,

$$\Delta S \approx 6.2 \cdot 10^{20} \cdot 1.38 \cdot 10^{-23} \cdot 0.69 = 5.9 \cdot 10^{-3} \text{ J/K, a small change}$$

b) If I increase the volume by a factor of 1000,

$$\Delta S = (Nk_B \ln 1000) \approx 6.2 \cdot 10^{20} \cdot 1.38 \cdot 10^{-23} \cdot 6.9 = 5.9 \cdot 10^{-2} \text{ J/K, still a small change.}$$

### Homework solutions

#### Entropy, temperature, and the microcanonical partition function: how to calculate results with statistical mechanics – Chapter 3

**Homework problem S3.1:** Use the same logic to prove that  $P$  must be the pressure. Pressure is the quantity that is equalized when two systems connected by a movable wall reach equilibrium by changing their volumes. Note that the derivative  $\partial E/\partial V$  is defined as  $-P$  to agree with our intuition that volume decreases ( $dV$  is negative) by squeezing on the system, its energy increases ( $dE$  is positive) because we are doing work on the system.

**Solution:** Consider two subsystems  $\{\text{Sys}_1\}$  and  $\{\text{Sys}_2\}$  of a composite system  $\{\text{Sys}\}$  connected by a movable wall to reach equilibrium. The movable wall allows only the volume change of subsystem, so  $dn = 0$  and  $dE = 0$ . And at equilibrium, the number of microstates of the composite system is not changing, i.e.  $dS = 0$ .

$$dE = 0 = \left(\frac{\partial E_1}{\partial V_1}\right)_{S,n} dV_1 + \left(\frac{\partial E_2}{\partial V_2}\right)_{S,n} dV_2$$

or

$$dE = -P_1 dV_1 - P_2 dV_2$$

And because the total volume of the system is not changing,  $dV_1 = -dV_2$ ,

this equation can only be true if  $P_1 - P_2 = 0$  and therefore  $P_1 = P_2$ .

Thus,  $P$  is the intensive quantity that is equalized between two subsystems when volume change is allowed.

**Homework problem S3.2:** Now prove that  $\mu$ , the chemical potential, is the quantity that is equalized between two subsystems when particles flow back and forth (or react) and their particle numbers come to equilibrium. You could go on and on proving such relationships for other intensive (derivative) variables.

**Solution:** Same logic applies to the chemical potential. Consider two subsystems  $\{\text{Sys}_1\}$  and  $\{\text{Sys}_2\}$  of a composite system  $\{\text{Sys}\}$  connected by a wall that allows only the exchange of particles between the two subsystems, so  $dV = 0$  and  $dE = 0$ . At equilibrium, the number of microstates of the composite system is not changing, i.e.  $dS = 0$ .

$$dE = 0 = \left(\frac{\partial E_1}{\partial n_1}\right)_{S,V} dn_1 + \left(\frac{\partial E_2}{\partial n_2}\right)_{S,V} dn_2$$

or

$$dE = -\mu_1 dn_1 - \mu_2 dn_2$$

And because the total number of particles in the system is not changing,  $dn_1 = -dn_2$ ,

this equation can only be true if  $\mu_1 - \mu_2 = 0$  and therefore  $\mu_1 = \mu_2$ .

Thus,  $\mu$ , the chemical potential, is the intensive quantity that is equalized between two subsystems when the particle exchange is allowed.

**Homework problem S3.3:** Illustrate this for the two functions  $y(x)=x^2$  and  $z(x)=(x-5)^2$ . First, calculate  $m(x)=\partial y/\partial x$ , solve for  $x(m)$ , and insert back into  $y$  to get  $y(m)=?$ . Then do the same thing for  $z$ . The functions  $y(m)$  and  $z(m)$  are identical. So no way, if I give you  $y(m)$  or  $z(m)$ , can you tell me what the original different functions  $y(x)$  and  $z(x)$  were.

Solution: a)  $y(x)=x^2$

$$m(x) = \frac{\partial y}{\partial x} = 2x$$

Thus

$$x(m) = \frac{1}{2}m$$

Insert it back into  $y$ , so

$$y(m) = \frac{1}{4}m^2$$

b)  $z(x)=(x-5)^2$

$$m(x) = \frac{\partial z}{\partial x} = 2(x - 5) = 2x - 10$$

Thus

$$x(m) = \frac{1}{2}m + 5$$

Insert it back into  $z$ , so

$$z(m) = \frac{1}{4}m^2$$

which is identical to  $y(m)$ . So if you had  $y(m)$  or  $z(m)$ , you would never know whether the original function was  $y(x)$  or  $z(x)$ .

**Homework problem S3.4:** You already learned about the enthalpy  $H(S,P)=E+PV$ . Show that enthalpy is the heat flow when pressure is constant ( $dP=0$  and  $dn=0$ ), just like energy is the heat flow when volume is constant. To do so, use  $dH=TdS + VdP + \mu dn$  to write down a formula like the above one for  $S$ ,  $dq_{P,n}$  and  $T$  when pressure and mole number is constant. Look familiar compared to the equation above?

Solution: Since

$$dH(S, P, n) = TdS + VdP + \mu dn,$$

for a system in which the pressure is constant ( $dn=0$  and  $dP=0$ ), adding heat to this system will (and is the only way to) change its energy. Therefore

$$dq_{P,n} = dH = TdS + VdP + \mu dn = TdS \text{ or}$$

$$dS = \frac{dq_{P,n}}{T}$$

This formula is analogous to the one derived in class using energy  $E$  if the volume is constant.

**Homework problem S3.5:** If  $S=S^{(0)}$  at the standard reference temperature  $T^{(0)}$  (e.g. 298 K) and constant pressure, show that at some other temperature,  $S=S^{(0)}+\int dTC_P(T)/T$  where the integration limits are from  $T^{(0)}$  to the other temperature. Derive a similar formula for  $H$ . We'll see later that this is useful for studying protein denaturation because disorder (entropy) of a protein increases as it unfolds at high temperature.

Solution: In the question, at the standard reference temperature  $T^{(0)}$  the standard reference entropy is  $S^{(0)}$ . These will be our lower integration limits where we start integrating over  $dS$  to get the entropy. The differential equation of entropy at constant pressure as a function of temperature is

$$dS = \frac{C_P(T)dT}{T}.$$

Integrate the left and right sides separately

$$\text{Left} = \int_{S^{(0)}}^{S(T)} dS' = \text{Right} = \int_{T^{(0)}}^T \frac{C_P(T')dT'}{T'}.$$

Note that we are renaming the integration variables  $S'$  and  $T'$  just so they don't get confused with the integration limits  $T$  and  $S(T)$ . Integration variables are 'dummy variables' that don't show up in the final result, so we could call them  $dx$ ,  $dt$ ,  $dT'$ , or anything we want.

$$S(T) - S^{(0)} = \int_{T^{(0)}}^T \frac{C_P(T')dT'}{T'}$$

$$S(T) = S^{(0)} + \int_{T^{(0)}}^T \frac{C_P(T')dT'}{T'}$$

Note that if you had a table of molar entropies  $s^{(0)}$  at the initial temperature (298 K in most tables), you could of course multiply by the number of moles of your substance,  $n$ , to get the initial entropy  $S^{(0)} = ns^{(0)}$ :

$$S(T) = ns^{(0)} + \int_{T^{(0)}}^T \frac{C_P(T')dT'}{T'}.$$

Also, if you had the molar heat capacity  $c_P$  instead of the total heat capacity  $C_P$ , you could just multiply  $C_P = n c_P$ .

Finally, we can derive the equation of enthalpy as a function of temperature at constant pressure in the same way, except  $dH = C_p(T)dT$ :

$$H(T) = H^{(0)} + \int_{T^{(0)}}^T C_p(T')dT'$$

**Homework problem S3.6:** By using  $H$ , so we have a variable that's a function of pressure, play the same game with the second derivative  $(\partial^2 H/\partial S^2)_{P,n,\dots}$  to derive the analogous formula for  $C_p$ .

Solution: Start from rewriting the second derivative  $(\partial^2 H/\partial S^2)_{P,n,\dots}$  using  $T = (\partial H/\partial S)_P$

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_{P,n} = \left(\frac{\partial T}{\partial S}\right)_{P,n} = \frac{T}{C_p(T)}$$

In going from the first to the second step, we are using that since  $\partial H/\partial S = T$ , if we take a derivative with respect to  $S$  again on both sides,  $\partial^2 H/\partial S^2 = \partial T/\partial S$ . In going from the second to the third step, we use that  $dS = dH/T = C_p dT/T$  (at constant pressure and mole number), or  $\partial S/\partial T = C_p/T$ . Then we just need to remember that  $\partial x/\partial y = 1 / (\partial y/\partial x)$ .

Thus

$$C_p(T) = T \left(\frac{\partial^2 H}{\partial S^2}\right)_{P,n}^{-1}$$

**Homework problem S3.7:** In the above formula,  $S_0 = ns_0$  in the last line lumps together all the constants. Derive  $S_0$  explicitly. Could  $S_0$  become negative? Should it be able to if we worked with the exact equation?

Solution: Start from the definition of entropy in terms of  $W$  and apply Stirling's approximation to the factorial

$$\begin{aligned} S &= k_B \ln W \approx -Nk_B \ln(V_0) + Nk_B \ln\left(\frac{V}{N}\right) \\ &\approx -Nk_B \ln V_0 - Nk_B \ln \frac{nA}{V} \end{aligned}$$

Rewrite the expression in terms of the gas constant by  $Nk_B = nR$

$$\begin{aligned} S &\approx -nR \ln AV_0 - nR \ln \frac{n}{V} \\ &\approx ns_0 - nR \ln \frac{n}{V} = ns_0 - nR \ln c \end{aligned}$$

where  $s_0 = -R \ln(AV_0)$  is the standard molar entropy. It is the entropy of 1 M pure substance ( $c=1$ ), and it provides a fixed reference point to calculate the entropy at any volume or temperature.  $S_0 = -nR \ln(AV_0)$  is the entropy for  $n$  moles of substance at 1 M concentration.

The third law of thermodynamics states that the entropy of a system approaches constant value as its temperature approaches absolute zero. At 0 K the system must be in a unique state with



minimum possible energy (i.e. the ground state) and at any temperatures above absolute zero the number of accessible microstates is greater than one, thus the sign of the entropy is always positive. If  $V_0$  gets big, then obviously  $\ln(AV_0)$  could become a positive number, and  $s_0$  or  $S_0$  would be negative, which is not possible. The reason is that if  $V_0$  gets big, our approximation for  $W$  is not correct, and we really need to use  $W=M!/(M-N)!/N!$  in that case.

**Homework problem S3.8:** Mechanical work  $dw=PdV$ . Show that  $w=T\Delta S$  when only the volume of an ideal gas, not its temperature, is changed. [Hint: integrate  $dw$  from  $V_1$  to  $V_2$  using the ideal gas law, and show that  $\Delta S = S_2 - S_1 = nR\ln(V_2/V_1)$ , then combine the two equations.]

Solution: The mechanical work done to the system depends only on the volume change

$$dw = PdV$$

Rewrite it by the ideal gas law  $PV = nRT$  so

$$dw = \frac{nRT}{V} dV$$

Integrate the left and right sides

$$w = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \int_{V_1}^{V_2} \frac{1}{V} dV = nRT \ln\left(\frac{V_2}{V_1}\right)$$

Now go back to the expression of entropy

$$S \approx nS_0 - nR \ln \frac{n}{V}$$

since the amount of substance  $n$  is not changing during the process so the term  $nR \ln n$  is constant

$$\Delta S = S_2 - S_1 = (nS_0 - nR \ln n + nR \ln V_2) - (nS_0 - nR \ln n + nR \ln V_1) = nR \ln \frac{V_2}{V_1}$$

Compare the equations of  $w$  and  $\Delta S$  so

$$w = T\Delta S$$

**Homework solutions**  
**Working at constant temperature - the Canonical Ensemble – Chapter 4**

**Homework problem S4.1:** What is the microcanonical partition function of an electron spin, when there is no magnetic field applied? (spin up and spin down have the same energy)?

**Solution:** When no magnetic fields are applied to the electron, the energy of spin-up and spin-down states have the same energy. According to the definition, a partition function of a system is the average number of microstates accessible to the system, which is two (spin up and spin down) in the electron case.

**Homework problem S4.2:** Derive a simple formula for the average energy of a system at constant temperature. Start with  $Z=e^{-\beta F}$ , write out  $F$  in terms of  $E$  and  $S$  in the exponent, then take the derivative of  $Z$  with respect to  $\beta$  and solve for  $E$ .

**Solution:** Recall the equation of expectation:

$$\langle E \rangle = \sum_k E_k P_k = \frac{1}{Z} \sum_k E_k e^{-\beta E_k}$$

Notice that  $E_k e^{-\beta E_k} = -\frac{\partial e^{-\beta E_k}}{\partial \beta}$  so

$$\begin{aligned} \langle E \rangle &= \frac{1}{Z} \left[ -\frac{\partial (\sum_k e^{-\beta E_k})}{\partial \beta} \right] \\ &= \frac{1}{Z} \left[ -\frac{\partial Z}{\partial \beta} \right] = -\frac{\partial \ln Z}{\partial \beta} \end{aligned}$$

**Homework problem S4.3:** Derive a formula for average pressure in a system at constant temperature that directly related  $P$  to  $Z$ . Hint: remember from chapter 3 that  $P=-(\partial E/\partial V)$ . The analogous formula is still true for the Helmholtz potential  $F$ , and  $F$  is related to  $Z$  as we proved earlier in this chapter.

**Solution:** The partition function of the canonical ensemble is related to the Helmholtz potential  $F$  by  $Z=e^{-\beta F}$  so

$$F = -\frac{\ln Z}{\beta}$$
$$\langle P \rangle = -\frac{\partial F}{\partial V} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}$$

**Homework problem S4.4: Derive a formula for the entropy of a system at constant temperature in terms of  $Z$ .** Hint: Once we have  $E$  and  $A$ , it is easy to obtain  $S$ !

Solution: The entropy can be calculated if the energy  $E$  and the Helmholtz free energy  $A$  is known:

$$S = \frac{\langle E \rangle - F}{T} = \frac{1}{T} \left( -\frac{\partial \ln Z}{\partial \beta} + \frac{\ln Z}{\beta} \right)$$

**Homework solutions**  
**Chemical equilibrium and the free energy Ensemble – Chapter 5**

**Homework problem S5.1:** When a visible solar photon of energy  $h\nu \sim k_B T_{\text{solar}}$  ( $T_{\text{solar}} \sim 6000$  K) hits the Earth's surface, it is absorbed, but the energy does not disappear. Instead, it is re-emitted as several 'thermal' photons with energy  $\sim k_B T$  ( $T \sim 300$  K), or transferred as heat energy, also in packets  $\sim k_B T$  by the equipartition principle. Let's assume for a moment the photon just splits into equal lower energy  $\sim k_B T$  photons. The reaction here is  $\nu_{\text{solar}} \rightarrow N \nu_{\text{solar}}$ . How many  $N$  'thermal' photons can be made from a solar photon by energy conservation?

Solution: A solar photon with energy  $h\nu \sim k_B T_{\text{solar}}$  splits into lower energy  $\sim k_B T$  photons. According to the energy conservation, the total energy of the lower-energy photons should be the same as the solar photon so

$$k_B T_{\text{solar}} = N k_B T$$

$$k_B * 6000K = N k_B * 300K$$

so

$$N = 20$$

**Homework problem S5.2:** Assume that the photons behave like an ideal gas in a box, which we'll take to be unit volume  $V=1$ . Use the formula for  $Z$  of a gas from the last chapter, Planck's law  $E=h\nu$ , and Einstein's formula  $E/c^2 = m$  to write down the partition function for a photon per unit volume in terms of only  $k_B$ ,  $T$ ,  $c$ , and  $h$ . [Note: your formula is a ballpark estimate because photons really are massless and  $E/c^2 = \sqrt{(m^2 + (p/c)^2)}$ ; but it will be very close to the right answer.]

Solution: Derived in the last chapter, the partition function  $Z$  of an ideal gas in a box is given by

$$Z = \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} V$$

Combine Planck's law and Einstein's formula so

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2}$$

Substitute it into the formula for  $Z$  and set  $V=1$  to get the partition function per unit volume,

$$Z = V \left( \frac{2\pi k_B T}{h^2} \left( \frac{h\nu}{c^2} \right) \right)^{\frac{3}{2}} = V \left( \frac{2\pi \nu k_B T}{c^2} \right)^{\frac{3}{2}} = \left( \frac{2\pi \nu k_B T}{c^2 h} \right)^{\frac{3}{2}}$$

This is the approximate partition function for photons in a box. We call such light 'black body radiation.' This answer is off from the exact answer by an additional numerical constant, but otherwise it looks the same. The reason is that photons are really massless, and one should use the correct Hamiltonian for photons and Einstein's more general formula  $E = [m^2 c^4 + p^2 c^2]^{1/2}$ .

**Homework problem S5.3:** On the figure above, mark with an arrow a place where the reaction spontaneously makes more ammonia, and a place where it makes more nitrogen and hydrogen. What is the slope of  $G$  in each case, positive or negative? Are there more places in the plot where ammonia will be made, or hydrogen will be made. So if I pick random concentrations between 0 and 1 moles/l of hydrogen, nitrogen and ammonia as starting conditions, will the reaction most likely go forward or backward?

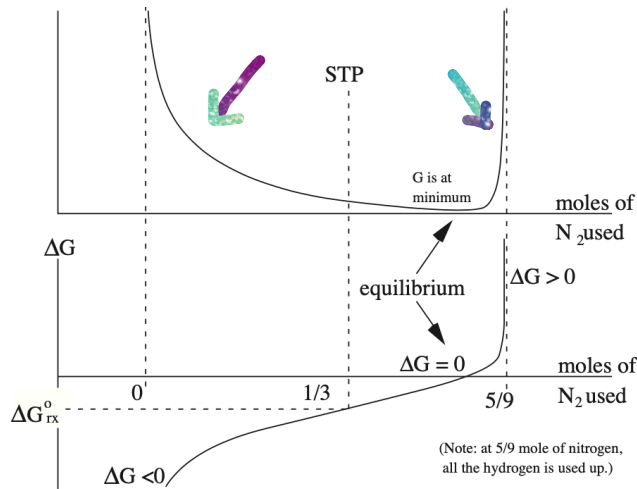
**Solution:** For a reaction at constant temperature and pressure, the free energy change  $\Delta G$  follows that

$$\partial G/\partial x = \Delta G(P,T) < 0 \text{ (spontaneous reaction) [x is the number of moles } N_2 \text{ used]}$$

$$\Delta G(P,T) = 0 \text{ (equilibrium)}$$

$$\Delta G(P,T) > 0 \text{ (spontaneous reverse reaction)}$$

In the figure, on the left side of the minimum at  $\Delta G=0$ , the reaction goes forward and spontaneously make more ammonia. The slope of  $G$  in this region is negative. On the right side of the minimum, it makes more nitrogen and hydrogen and the slope of  $G$  in this region is positive: there the reaction goes backward.



The plot of  $G$  and  $\Delta G$  will change if we add more hydrogen into the system or remove the product ammonia from the system. That means the direction of the reaction depends on the relative concentration of the molecules as we have learned from our general chemistry course.

**Homework problem S5.4:** Since  $\mu_i = h_i - Ts_i$ , insert the formula for  $s_i = s_i^{(0)} - R \ln(c)$  to show directly that the chemical potential for chemical species “i” can be written as  $\mu_i = \mu_i^{(0)} + RT \ln(c)$ , and what is the constant  $\mu_i^{(0)}$ . Note that this strictly applies only for ideal solutions or gases we discussed at the end of Chapter 3.

**Solution:** Start from the equation  $\mu_i = h_i - Ts_i$  and rewrite the molar entropy in terms of  $h_i$ ,  $\mu_i$  and  $T$

$$s_i = \frac{h_i - \mu_i}{T}$$

Substitute it into the formula for  $s_i = s_i^{(0)} - R \ln(c)$  so

$$\frac{h_i - \mu_i}{T} = s_i^{(0)} - R \ln(c)$$

Multiply times  $T$  on both sides of the equation and rearrange the terms so

$$h_i - \mu_i = T s_i^{(0)} - RT \ln(c)$$

$$\mu_i = h_i - T s_i^{(0)} + RT \ln(c)$$

$$= \mu^{(0)} + RT \ln(c)$$

where we  $h_i = h_i^{(0)}$  so  $\mu^{(0)} = h_i^{(0)} - T s_i^{(0)}$  because we are under standard conditions. Of course, then we should pick  $T = 298$  K (standard temperature). Note we can correct the formula for different temperatures using the heat capacity formulas we derived, that tell us how  $h$  and  $s$  depend on temperature.

**Homework problem S5.5:** Let's do one simple example, the folding of the RNA from macrostate U to macrostate F in the reaction  $U \rightleftharpoons F$  in the previous chapter, so  $\nu_F = +1$  and  $\nu_U = -1$  for the stoichiometric coefficients going towards folded product. Using the partition function  $Z$  for the folded RNA in the previous Chapter as  $Z_F = W_F$ , and for the unfolded RNA as  $Z_U = W_U e^{-\epsilon/RT}$ , write down the formula for  $\Delta G \approx \Delta F$  and the equilibrium constant  $K_{eq}$ . These are two of the most important equations to describe at what temperature an RNA molecule or a protein folds.

Solution: Recall the simple model discussed in chapter 4 for the reaction that interconverts an unfolded RNA hairpin to a folded RNA hairpin. The figure below shows a simple 2-D lattice model for an RNA with four bases, two of which can base pair in the "stem."

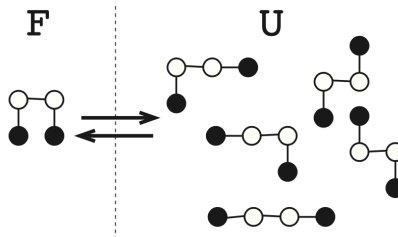


Figure: Folding/unfolding reaction of an RNA hairpin in a simple 2-D lattice model that allows only  $90^\circ$  hinge motions of the bases, and counts only one interaction energy (base pairing energy), between the two black bases.

As we did before, renormalizing the minimum energy to 0, we have  $E_F = 0$   $W_F = 1$  and  $E_U = +\epsilon$  and  $W_U = 5$ . So the partition functions for the folded RNA are  $Z_F = W_F$  and for the unfolded RNA as  $Z_U = W_U e^{-\epsilon/RT}$ .

The next step is to calculate the chemical potential using the formula we derived in lecture on page 27:

$$\mu_i = -RT \ln \frac{z_i}{N_i}$$

Inserting the specific answers for  $z$  for the folded and unfolded states,

$$\mu_F \left( \frac{\text{J}}{\text{mole}} \right) = -RT \ln \frac{Z_F}{N_F} = -RT \ln \frac{W_F}{N_F}$$

and

$$\mu_U \left( \frac{\text{J}}{\text{mole}} \right) = -RT \ln \frac{Z_U}{N_U} = -RT \ln \frac{W_U e^{-\frac{\varepsilon}{RT}}}{N_U}.$$

The latter can be simplified to

$$\mu_U \left( \frac{\text{J}}{\text{mole}} \right) = -RT \ln \frac{W_U}{N_U} + \frac{\varepsilon R}{R} = -RT \ln \frac{W_U}{N_U} + \varepsilon,$$

Now we can calculate the free energy. Note that the canonical partition function is at constant temperature and volume (*not* constant pressure), so strictly speaking we are calculating  $\Delta F_{rx}$ , not  $\Delta G_{rx}$ . However, this does not make much of a difference in this case because the volume change during a folding reaction is small and so  $\Delta G_{rx} = \Delta F_{rx} + P\Delta V_{rx} \approx \Delta F_{rx}$ . Thus

$$\begin{aligned} \Delta G_{rx} &= \sum v_i \mu_i = v_F \mu_F + v_U \mu_U = \mu_F - \mu_U \\ &\approx -RT \ln \frac{W_F}{N_F} + RT \ln \frac{W_U}{N_U} - \varepsilon \\ &= RT \ln \frac{W_U}{W_F} + RT \ln \frac{N_F}{N_U} - \varepsilon \\ &= RT \ln \frac{W_U}{W_F} - \varepsilon + RT \ln \frac{c_F}{c_U} \end{aligned}$$

In the first step we inserted the stoichiometric coefficients  $\pm 1$ ; in the second step we inserted the values of the chemical potentials for folded and unfolded state calculated above; in the third term we collected the  $W$ 's and the  $N$ 's into the same logarithm using  $\ln(a) - \ln(b) = \ln(a/b)$ ; in the fourth step we made use of the fact that the ratio of number of molecules is the same as the ratio of concentrations, since  $N = Ac$ , where  $A$  is Avogadro's number. You have just derived the mass action law from the partition function, with

$$\Delta G_{rx} = \Delta G^{(0)} + RT \ln \frac{c_F}{c_U}$$

and  $\Delta G^{(0)} = -\varepsilon + RT \ln \frac{W_U}{W_F}$  being the standard free energy. Note that  $\Delta E_{rx} = -\varepsilon$  and  $\Delta H = \Delta E + P\Delta V \approx \Delta E$  because the volume change is small, and that  $RT \ln \frac{W_U}{W_F} = -T(S_U - S_F)$ .

Therefore  $\Delta G_{rx} = \Delta H_{rx} - T\Delta S_{rx}$ , just as we would expect.

Finally, the equilibrium constant is

$$K_{eq} = e^{-\Delta G^{(0)}/RT} \approx e^{-\ln \frac{W_U}{W_F} + \frac{\varepsilon}{RT}} = \left( \frac{W_F}{W_U} \right) e^{\frac{\varepsilon}{RT}}.$$

Voilà! You just calculated the equilibrium constant for RNA folding from first principles. Think about it intuitively: the bigger  $\varepsilon$ , the bigger the equilibrium constant: if the unfolded state is at higher energy, you're going to get more of the low-energy folded state; if  $W_U$  gets smaller,  $K_{eq}$  also increases: the fewer conformations the unfolded state has, the less likely the RNA will be in it. And finally,  $K_{eq}$  decreases at higher temperature: when you heat up the RNA, it tends to unfold. All of this makes intuitive sense, but thanks to stat mech and thermo we can have an accurate formula for it.

**Homework solutions**  
**Out of equilibrium: Brownian motion and drift velocity – Chapter 6**

**Homework problem S6.1:** A protein has a diffusion coefficient of  $10 \mu\text{m}^2/\text{s}$ . A human cell has a diameter of  $30 \mu\text{m}$ . On average how long does it take a protein to diffuse across a cell?

**Solution:** In three dimensions, the equation of Brownian motion is written as

$$\langle \delta x^2 \rangle = 6Dt$$

Consider the diffusion of a protein across a cell with a diameter  $R = 30 \mu\text{m}$

$$R^2 = 6Dt$$

$$(30 \mu\text{m})^2 = 6 * \frac{10 \mu\text{m}^2}{\text{s}} * t$$

so the time for protein diffusion across cell is

$$t = 15 \text{ s}$$

**Homework problem 6.2:** A voltage of  $-100 \text{ V}$  is applied to an electrophoresis gel of  $10 \text{ cm}$  length. The protein phosphoglycerate kinase has charge  $+2e$  and in a  $1\%$  polyacrylamide gel at room temperature, its diffusion coefficient is  $D=100 \mu\text{m}^2/\text{s}$ . What is the drift velocity of PGK in  $\text{mm}/\text{s}$ ? How long should you plan on running the gel if you want the protein to move across half the length of the gel? Let's assume room temperature is  $293 \text{ K}$  for this problem.

**Solution:** First, let's sort out the value of variables given in the question. We have

- Electric field  $\mathcal{E} = -V/L = 100 \text{ V}/10 \text{ cm} = 1000 \text{ V}/\text{m}$
- Protein charge  $q = +2e$

To calculate the drift velocity  $v_{drift}$  by the equation  $v_{drift} = \frac{q}{\gamma} E$ , we also need to know the friction coefficient  $\gamma$ . The good news is we know that at room temperature  $T = 293\text{K}$ , the diffusion coefficient of the  $1\%$  polyacrylamide gel is  $D = 100 \mu\text{m}^2/\text{s}$  so

$$\gamma = \frac{k_B T}{D} = \frac{1.38 * 10^{-23} \text{ J} \cdot \text{K}^{-1} * 293 \text{ K}}{100 \mu\text{m}^2/\text{s}} = \frac{1.38 * 10^{-23} \text{ J} \cdot \text{K}^{-1} * 293 \text{ K}}{1 * 10^{-10} \text{ m}^2/\text{s}} = 4.04 * 10^{-11} \text{ kg} \cdot \text{s}^{-1}$$

Therefore

$$v_{drift} = \frac{q\mathcal{E}}{\gamma} = \frac{2 * 1.602 * 10^{-19} \text{ C} * 1000 \text{ V} \cdot \text{m}^{-1}}{4.04 * 10^{-11} \text{ kg} \cdot \text{s}^{-1}} = 7.9 * 10^{-6} \text{ m} \cdot \text{s}^{-1} = 7.9 * 10^{-3} \text{ mm} \cdot \text{s}^{-1}$$

(Be careful with unit conversion!)

So you would have to wait for an hour to run the gel to get the protein to move a  $\text{cm}$  or so, and be able to see separate lanes on the gel.