

Physics 352: Problem Set 9

**Due date:** Wednesday, Mar. 12, 5pm. In order to promptly post the solutions, **no late homework will be accepted.**

**(1, 2 pts.) Osmotic Pressure.** In class we derived the equation of state for an ideal gas by considering the “non-degenerate,” “classical” limit of quantum-mechanical particles-in-a-box<sup>1</sup>. We found that  $PV = Nk_B T$ , where all the symbols have their usual meaning. This equation applies to any dilute, non-interacting, non-relativistic particles, including molecules in solution (e.g. a dilute solution of salt in water.)  $N/V$  is the concentration of solute,  $n$ , so the **osmotic pressure**  $P = nk_B T$ . A typical solute concentration in your cells is 0.15 M, where 1 M is 1 mole per liter. (1 mole is  $6.02 \times 10^{23}$  particles.) Suppose one injects pure water into someone’s blood vessels, so a red blood cell with 0.15 M solute inside is surrounded by plain water. What is the osmotic pressure difference between the inside and the outside of the cell? Express your answer in units of atmospheres (1 atm = 101,000 Pa). The blood cell membranes, by the way, can’t withstand this; they will rupture and the resulting mess can clog the blood vessel. People have died in hospitals by having water mistakenly injected into them.

**(2, 7 pts.) A 2-state system, revisited.** Consider a two-state system, in which one state has energy 0 and the other has energy  $\varepsilon$ .

**(a, 2 pts.)** Calculate the **Helmholtz free energy**,  $F$ , as a function of temperature and  $\varepsilon$ . There are various ways to figure out  $F$  – think of one, based on what we’ve done in class, that doesn’t require doing part (b) first.

**(b, 3 pts.)** Calculate the **entropy** of the two state system. There are several ways to do this. I find that it’s not at all apparent how to write the “number of available states” at various temperatures – instead, take the seemingly less direct path of relating  $\sigma$  to other parameters.

**(c, 1 pt.)** As  $\varepsilon/\tau \rightarrow 0$ , and  $\varepsilon/\tau \rightarrow \infty$ , what values would you expect  $\sigma$  to approach? (This doesn’t involve calculations.)

**(d, 1 pt.)** Calculate  $\sigma$  in the limits  $\varepsilon/\tau \rightarrow 0$  and  $\varepsilon/\tau \rightarrow \infty$  -- which hopefully agrees with your answers to (c).

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<sup>1</sup> We could have taken a purely classical approach, but this would get us into trouble when considering interesting quantum systems later in the course.

**(3, 5 pts.) Relating  $F$  and  $Z$ .** We showed in class that the Helmholtz Free Energy,  $F$ , is in general related to the partition function,  $Z$ , and temperature,  $\tau$ , by  $F/\tau = \ln(Z) + B$ , where  $B$  is a constant of integration. **Show that  $B = 0$** , and therefore  $F = \tau \ln(Z)$ .

To do this: (i) Note that as  $\tau \rightarrow 0$ , the entropy  $\sigma \rightarrow \ln \Omega_0$ , where  $\Omega_0$  is the degeneracy of the ground state. (ii) Calculate  $\sigma_{\tau \rightarrow 0}$  using an expression we derived that relates entropy and derivatives of  $F$ , using  $F/\tau = \ln(Z) + B$ . (Note from an earlier problem set what must happen to  $Z$  as  $\tau \rightarrow 0$ .) The two  $\sigma$ 's must agree, from which you'll be able to show that  $B$  must be zero.

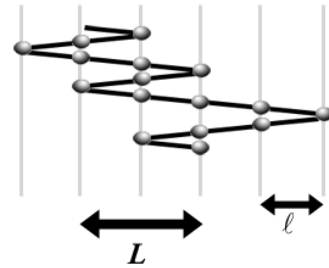
**(4, 7 pts.) A one-dimensional gas.** In class we examined a three-dimensional ideal gas. Consider here an ideal gas of  $N$  non-relativistic particles of mass  $m$  confined to a **one-dimensional** box of size  $L$ . (One can find one-dimensional systems in, for example, carbon nanotubes – materials we saw earlier.) Derive expressions for

**(a, 5 pts.)** The energy  $U$  as a function of  $N$  and  $\tau$ , and

**(b, 2 pts.)** The heat capacity at constant volume ( $c_v = \left. \frac{\partial U}{\partial \tau} \right|_v$ ).

You can use either the “entropy-based” or “partition-function-based” approaches we used in class.

**(5, 11 pts.) A one-dimensional polymer.<sup>2</sup>** As discussed earlier, polymers are long, chain-like molecules. (Rubber is an everyday example.) As a crude model of a polymer molecule, consider a chain of  $N$  links, each of length  $\ell$ , with each link able to point only either left or right – a “one-dimensional” polymer. The end-to-end distance is  $L$ .  $N_R$  links point to the right, and  $N_L$  to the left. (See figure.)



A “1D” POLYMER, DRAWN SLIGHTLY EXTENDING INTO TWO-DIMENSIONS. FOR THE SYSTEM CONFIGURATION SHOWN,  $N = 16$ ,  $L = 2\ell$ , AND  $N_R = 9$  LINKS POINT TO THE RIGHT.

For parts **a** and **b**, you may wish to consult the handout or your lecture notes on Brownian Motion.

**(a, 1 pt.)** Treating the polymer as a 1D random walk, where each link takes a random “step” left or right, how would you expect  $L$  to scale with  $N$ ? (In other words, if  $L \propto N^p$ , what is  $p$ ?)

**(b, 1 pt.)** Show that for large  $N$ ,  $L \ll N\ell$ . (We’ll consider large  $N$  in this problem.)

**(c, 3 pts.)** Write an expression for the entropy of the system as a function of  $N$  and  $L$ . (*Hint:* You should realize that this system is eerily similar to the binary spin system whose entropy we already considered in great detail. Map this system onto that. Express  $L$  in terms of  $N$  and  $N_R$ .)

<sup>2</sup> Much of this problem is based on Problem 3.34 in “Thermal Physics,” by David Schroeder (2000).

- (d, 2 pts.) For a one-dimensional system,  $L$  plays the role the volume ( $V$ ) plays in 3D. Similarly, the tension force  $f$  replaces the pressure ( $P$ ). (Note that  $P dV$  has the same dimensions as  $f dL$ .) Taking  $f$  to be positive when the rubber band pulls inward, write and explain the appropriate thermodynamic identity, i.e. the relation between  $dU$ ,  $\tau\sigma$ , and mechanical work, for the system.
- (e, 3 pts.) Using the thermodynamic identity, express  $f$  in terms of a partial derivative of the entropy. From this, **determine**  $f$  in terms of  $L$ ,  $\ell$ , and  $\tau$ . You should find that the tension force is linearly proportional to the extension,  $L$  – i.e. the polymer obeys Hooke’s Law. This is quite remarkable: In our model there is no energetic difference between different conformations. *Solely* due to entropy, rather than any “restoring force” from molecular bonds, the polymer behaves as a spring!
- (f, 1 pt.) Discuss the force dependence of the tension force on the temperature (at fixed  $L$ , for example). If you increase the temperature of a rubber band, should it expand or contract?

(6, 2 pts.) **Diffusion.** We showed in class that for a one-dimensional random walk, the mean-squared distance traveled,  $\langle x^2 \rangle$ , is proportional to the travel time:  $\langle x^2 \rangle = 2Dt$ , where  $D$  is the diffusion coefficient. Show that for a particle moving in two-dimensions,  $\langle r^2 \rangle = 4Dt$ , where  $r = \sqrt{x^2 + y^2}$ . (*Hint:* For a **random** walk, are the motions in the  $x$  and  $y$  directions related to one another?)

(7, 2 pts.) **Hypersphere volumes.** The concept of a sphere in three-dimensional Euclidean space can be generalized to that of a “hypersphere” in  $n$ -dimensional Euclidean space. (For example, an  $n=2$  hypersphere is a disk.) The volume of a hypersphere of radius  $R$  in  $n$ -dimensional

Euclidean space is:  $V_n = \frac{\pi^{n/2}}{2 \Gamma\left(\frac{n}{2}\right)} R^n$ , where  $\Gamma(x)$  is the gamma function (see Problem Set 6).

- (a, 2 pts.) Verify that the boxed equation gives the expected volume expressions for  $n=2$  and  $n=3$ . You may use the results of Problem 1 of Problem Set 6.
- (b, 0 pts.) Prove the boxed equation. [*Note: This problem is quite difficult. I’m assigning it zero points because I don’t want it to distract you from the more “essential” problems in the assignment. If you’re mathematically inclined, you may enjoy the challenge of proving it, and I’d be happy to look at your solution. If you skip this problem, I won’t mind at all -- really. There’s more than one way to prove this relation, by the way.*]