Physics 112 - Intro to Statistical and Thermal Physics - Spring 2023
Problem Set 04

Due Friday, February 24 at 11:59 PM (PST)
Last Update: February 16, 2023

- **Reading for the material on this week's problem set:**
  - Schroeder, Sections 1.7, 5.2, 5.3 (The van der Waals model), 2.1.
- **Reading for next week:**
  - Schroeder, Sections 2.1 - 2.6.

Problem 4.1 - Minimizing Gibbs Free Energy

Let's take a look at a gas of a single species (so we only have one N and μ to worry about). Recall that the thermodynamic relation for the Gibbs free energy is

$$dG = -S\,dT + V\,dP + \mu\,dN.$$

Let's say we have a fixed number of particles and are looking at our sample at a fixed temperature.

(a) Extra Part (*Not for Credit*) Show that for an ideal gas the Gibbs free energy is of the form $G(T,P,N) = Nk_BT\ln(P/P_0) + \gamma(T,N)$, where P_0 is some arbitrary pressure constant and $\gamma(T,N)$ is a yet-unknown function independent of pressure.

Now let's consider a van der Waals system. Recall that we introduced the non-dimensionalized variables $p \equiv P/P_c$, $t \equiv T/T_c$, and $v = V/V_c$ in Problem 1.2, where P_c, V_c, and T_c represented the pressure volume and temperature at the critical point. This yielded the non-dimensionalized van der Waals equation of state,

$$p = \frac{8t}{3v-1} - \frac{3}{v^2}. \tag{1}$$

We can play a similar game as in part (a) to derive a non-dimensionalized version of the Gibbs free energy,

$$g \equiv \frac{G}{k_BT_c} = N\left(-t\ln(3v-1) + \frac{t}{3v-1} - \frac{9}{4v} + \gamma(t)\right), \tag{2}$$

where $\gamma(t)$ is some temperature-dependent function independent of pressure.

Since v is *not* one of the natural variables of the Gibbs free energy, we can interpret the pair of equations Eq. 1 and Eq. 2 at some fixed temperature t as defining a parametric curve along one of the isotherms you generated in Problem 1.2(c).

(b) Plot the isotherm at $t = 0.85$ on a graph of p-vs-v for the range $0.5 \le v \le 5$. Then make a parametric plot of g-vs-p using Eqs. 1 and 2 for parameters $0.5 \le v \le 10$. In your parametric plot you can set $N = 1$ and $\gamma(t = 0.85) = 3$ for convenience.[1]

[1] Since we are just looking at minimizing g the overall scale and any additive factors don't affect anything.

(c) On both graphs identify the pressure $p = 0.45$. What are the three possible volumes consistent with Eq. 1? What are the three associated Gibbs free energies? Which point on the pv-isotherm will represent the equilibrium state at $t = 0.85$, $p = 0.45$? Then answer the same questions for $p = 0.55$. [*Note: I don't exect you to analytically solve the cubic here - just use a numerical solver for the volumes!*]

(d) **Extra Part** (*Not for Credit*) Use a numerical solver to determine the pressure at which the parametric plot of g-vs-p intersects itself.

Commentary: We can consider the "steep" part of the isotherm at low volumes the ***liquid phase*** of the van der Waals substance and the "shallow" part at high volumes the ***gas phase***. The point you found in part (d) represents the phase transition between gas and liquid. At this pressure and temperature both phases can coexist in equilibrium.

Problem 4.2 - Diffusion

In lecture we introduced ***Fick's law of diffusion***,

$$J_x = -D\frac{\partial n}{\partial x},$$

where n is the local concentration, $n = N/V$ in a region; J_x is the particle flux density, the net number of particles crossing a boundary per unit area per unit time; and D is the diffusion constant.

(a) Using similar logic to how we derived the thermal conductivity k_t in kinetic theory for an ideal gas, derive the diffusion constant for an ideal gas in terms of the mean free path ℓ and the rms speed v_{rms} of gas molecules. In the process you should find an equation that looks like Fick's law.
Hint (highlight to reveal): [Instead of the setup where we have temperature T on the left of the boundary and slightly higher temperature $T + dT$ on the right, use a setup where the temperatures are equal but we have a concentration n on the left and slightly higher concentration $n + dn$ on the right.] [*Hint: Remember your Taylor expansions! If* $\epsilon \ll 1$ *then* $(1+\epsilon)^p \approx 1 + p\epsilon$.]

(b) Based on your answer to (a), show that the diffusion constant D should scale with temperature and pressure via

$$D \propto (k_B T)^{3/2}, \qquad D \propto P^{-1}.$$

The ***diffusion equation*** shows how concentrations even out over time in response to a gradient,

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}.$$

(c) **Extra Part** (*Not for Credit*) Following a procedure similar to what we did in lecture, derive the diffusion equation from Fick's law.

(d) Show that $n(x,t) = n_0 + \frac{c}{\sqrt{t}}e^{-x^2/4Dt}$ is a solution to the diffusion equation, where c is any constant.
[*Note: At* $t = 0$, *this is represents a gas of uniform concentration with a delta function spike in concentration at* $x = 0$.]
[*Supplementary Part (Not for Credit): Try graphing the diffusion at some different times. For an extra challenge, try animating it!*]

Order-of-Magnitude Physics! Let's do some quick order-of-magnitude estimations involving diffusion.

(e) Use the ideal gas law to determine the concentration n for air molecules (basically N_2) at STP (standard temperature and pressure)[2]. From this estimate the mean free path ℓ and thus the diffusion constant D for air molecules at standard temperature and pressure.
Answer (highlight to reveal): [You should find to within an order of magnitude that $D \sim 10^{-5}\text{m}^2/\text{s}$.]

(f) A perfume bottle is opened at one end of a classroom. Using the diffusion equation, *estimate* how much time it would take the perfume to diffuse across the room. Assume that diffusion is the *only* method of transport for this problem (as opposed to convection currents/bulk motions of the air). Based on you answer, is this a reasonable assumption to make in practice?
Hint (highlight to reveal): [This is an order-of-magnitude estimation problem involving a differential equation. A good way to approach this is to replace the partials with scales for the quantities. That is, we can replace something like $\frac{\partial^2 n}{\partial x^2}$ with N/x^2, where N is a typical number scale for the number of particles involved (sub-spoiler: this will wind up canceling out!) and x is the typical length scale for distances involved. Our goal is to find a time-scale.]
Hint (highlight to reveal): [Some chemistry! The "fruity" smell of perfume is from the compound ethyl octanoate, $C_{10}H_{20}O_2$. You can use this to estimate the relative mass and size of the perfume molecules as compared to air.]

Problem 4.3 - Biased Random Walks and Binary State Systems

In class we introduced the idea of a ***random walk*** which we will explore in more depth in this problem. Each "step" i of the walk, the displacement Δx_i is given by the probability distribution

$$\Delta x_i = \begin{cases} +\ell, & \text{Probability } p_R, \\ -\ell, & \text{Probability } p_L = 1 - p_R. \end{cases}$$

The total displacement from the origin after N steps is then

$$X = \sum_i \Delta x_i = (2N_R - N)\ell,$$

where N_R is the total number of steps to the right taken. A given ***microstate*** will be a specification of the path walked, e.g. if $N = 3$, one microstate could be written "RLR", meaning "step 1 was to the right, step 2 was to the left, and step 3 was to the right." A given ***macrostate*** for an N-step random walk will be a specification of the number of steps to the right N_R or, equivalently, the total displacement X. For example, if $N = 3$, the macrostate $X = +\ell$ consists of three microstates: RRL, RLR, LRR. If $p_R = p_L = 1/2$ the random walk is unbiased and the system is equivalent to tossing a set of N fair coins. If $p_R \neq 1/2$ then we call this a ***biased random walk***.

(a) Extra Part (*Not for Credit*) For an N-step random walk, determine the total number of microstates of the system. Also determine the number of macrostates and the multiplicity of each macrostate. Check your results explicitly against the case $N = 4$.
Hint (highlight to reveal): [In the $N = 4$ case there are 16 microstates with macrostates and multiplicities $X = \pm 4\ell$ with $\Omega = 1$; $X = \pm 2\ell$ with $\Omega = 4$; $X = 0$ with $\Omega = 6$.]

[2] https://en.wikipedia.org/wiki/Standard_temperature_and_pressure

(b) Given a biased random walk of N steps, argue that the probability for each microstate *within* a given macrostate is the same. Then find the probability $P(X)$ (or, equivalently, $P(N_R)$) for each macrostate.
[*Note: The "counting" you need to do will be easier if you use the number of steps to the right* N_R *rather than the net displacement* X*.*]

Before doing more general analysis, let's look at a specific tractable case of a biased random walk of $N = 5$ steps with $p_R = 3/5$. There are a total of 32 microstates in this system.

(c) Determine the macrostates X, the multiplicities $\Omega(X)$, and the probabilities $P(X)$. Which *individual microstate(s)* is/are most likely to occur and which is the least likely to occur? Which *macrostate* is the most likely to occur?
[*Supplementary Part (Not for Credit): Verify that your probabilities add up to 1.*]

(d) Using your probabilities from part (c), determine the average position $\langle X\rangle$ after 5 steps. What is the standard deviation $\sigma_X \equiv \sqrt{\langle X^2\rangle - \langle X\rangle^2}$ of your results?
[*Note: The standard deviation will be a measure of how spread out our results are.*]
Hint (highlight to reveal): [Remember that the expectation value/average of some function $f(X)$ of our variable X is given by $\langle f(X)\rangle = \sum_i f(X_i)P(X_i)$.]

Since each step Δx_i is independent of the previous step, we can treat the expectation value using

$$\langle X\rangle = \left\langle \sum_i \Delta x_i \right\rangle = \sum_i \langle \Delta x_i\rangle.$$

(e) Determine $\langle X\rangle$ for a biased random walk of N steps given a bias of p_R.
[*Supplementary Part (Not for Credit): Verify your answer agrees with part (d) in the case* $N = 5$ *and* $p_R = 3/5$*.*]
Hint (highlight to reveal): [Since the Δx_i are all independent, $\langle \Delta x_i\rangle$ will be the same for all values of i.]

The expectation value of X^2 can be expressed as

$$\langle X^2\rangle = \left\langle \Big(\sum_i \Delta x_i\Big)\Big(\sum_j \Delta x_j\Big)\right\rangle = \sum_{ij} \left\langle \Delta x_i \Delta x_j\right\rangle.$$

Make sure you understand why we had to use different indices in the two sums! This sum has N^2 terms. We can separate these into the cases where $i = j$ in which case the summand becomes $(\Delta x_i)^2$ and the case $i \neq j$ in which case Δx_i and Δx_j represent independent (and therefore uncorrelated) variables.

(f) Find $\left\langle \Delta x_i \Delta x_j\right\rangle$. Use your results to find $\langle X^2\rangle$ and σ_X.
[*Supplementary Part (Not for Credit): Verify your answer agrees with part (d) in the case* $N = 5$ *and* $p_R = 3/5$*.*]
Hint (highlight to reveal): [You can express $\langle \Delta x_i \Delta x_j\rangle$ using the Kronecker delta as δ_{ij}(answer when $i = j$)+ $(1-\delta_{ij})$(answer when $i \neq j$).]
Answer (highlight to reveal): [You should find $\langle \Delta x_i \Delta x_j\rangle = \ell^2\left(\delta_{ij} + (1-\delta_{ij})(p_R - p_L)^2\right)$.]

(g) **Extra Part** (*Not for Credit*) Show that the relative width of the probability distribution $\sigma_X/\langle X\rangle$ shrinks as N grows.
[*Note: This shows that in the limit of large* N *the peak becomes very sharp.*]

Finally, let's consider a random walk with a very large number of steps. When n is large we will use ***Stirling's approximation*** for the factorial $n!$,

$$n \gg 1 \quad \Longrightarrow \quad n! \approx n^n\, e^{-n}\, \sqrt{2\pi n} \quad \Longrightarrow \quad \ln n! \approx n \ln n - n + \mathcal{O}(\ln n).$$

Also recall that the binomial coefficient "a choose b" in terms of factorials is

$$\binom{a}{b} = \frac{a!}{b!(a-b)!}.$$

For simplicitly, you might want to define $n \equiv N_R$, $m \equiv N - N_R = N_L$, $p \equiv p_R$, and $q \equiv 1 - p_R = p_L$.

(h) Use Stirling's approximation to approximate the probability $P(X)$ you found in part (b). Note that you may ignore the factor of $\sqrt{2\pi n}$ in your approximations.[3] Given an N, for what value of X (or, equivalently, for what value of N_R) is the macrostate probability maximized?
[*Note: I would recommend working with $P(N_R)$ - that is, taking N_R as the independent variable - at the start and only converting back to X at the end.*]
Hint (highlight to reveal): [The X that maximizes $P(X)$ will also be the X that maximizes $\ln P(X)$. The logarithm will be easier to work with!]
Answer (highlight to reveal): [You should find that the maximum occurs when $n = pN$.]

Problem 4.4 - DataHub - Biased Random Walks

Now let's *simulate* a biased 1D random walk for an equivalent problem: the ***binary spin model*** or ***two-state paramagnet*** as detailed in Schroeder, Section 2.1. Instead of the "walk" being N subsequent steps to the left or right, our 1D paramagnet model will consist of a set of N "spins" which can point either up ($\uparrow$, which we give value +1) or down ($\downarrow$, which we give value -1). We will let σ_i tell us the value of the i-th spin[4], with

$$\sigma_i = \begin{cases} +1, & \text{Probability } \theta, \\ -1, & \text{Probability } 1-\theta \end{cases} .$$

Rather than talk about total displacement X (the sum of all individual displacements), in the paramagnet we talk about ***magnetization***, the sum of all spins[5],

$$M = \sum_i \sigma_i.$$

A given ***microstate*** will be a specification of all individual spins, e.g. if $N = 3$, one microstate could be written $\uparrow\downarrow\uparrow$. A given ***macrostate*** for an N-spin paramagnet will be a specification of the number of up-spins $N_\uparrow$. This is equivalent to specifying the value of M, since

$$M = +N_\uparrow - (N - N_\uparrow) = (2N_\uparrow - N).$$

For example, if $N = 3$, the macrostate $M = +1$ consists of three microstates: $\uparrow\uparrow\downarrow, \uparrow\downarrow\uparrow, \downarrow\uparrow\uparrow$.

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[3] In Schroeder's language, we would say $n^n e^{-n}$ is a "very large number" while $\sqrt{2\pi n}$ is merely "large" and when we multiply a large factor with a very large factor we can effectively ignore the large factor. This is justified by looking at the logarithms.

[4] We are ignoring factors of 2 and $\hbar$ here at the moment. We can absorb these into other constants that we will subsequently set to 1 as we prepare to analyze this system via code.

[5] Technically, the magnetization is the sum of all spins times a constant μ which converts the spin value to a magnetic moment value.

In the DataHub problem you will first create a function that generates a microstate for a given N and θ and computes its magnetization. By repeatedly running this function we can get a distribution of M values for a given N and θ. We will plot this distribution and compare it to a Gaussian distribution.

Hint (highlight to reveal): [For part (a), you can generate the random walk by first generating an array of N random numbers chosen uniformly between 0 and 1. Numpy has a function that does this nicely. Once you have the array of numbers, you can convert that to a microstate by, for example, saying if a given number is less than θ then we will call that "spin up" and otherwise call it "spin down." Think about why that works!]

http://datahub.berkeley.edu/user-redirect/interact?account=ajh38&repo=phy112-001_spring_2023&branch=main&path=Sp23-112-Hw04-Python

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Not for Credit - DataHub - Large N Effect

I have added a second problem to the data hub, titled "*Large N Effect*". This is a straightforward graphing problem that shows how $e^{-Nf(x)}$ becomes sharply peaked around the global maximum of $f(x)$ as N grows large. This problem is ***not for credit*** and is just something to play around with to support some of the claims we will make in class. Solutions to this will be released so even if you never get around to doing it you can see some of the results and how the solution was implemented.

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