Physics 112 - Intro to Statistical and Thermal Physics - Spring 2023
(Optional) Problem Set 12

Due Friday, May 5 at 11:59 PM (PDT), no late submissions
Last Update: May 2, 2023

- **Highlighted/Most Relevant Reading for the material on this week's problem set:**
  - Schroeder, Sections 7.6, 5.4, 5.5
- **Reading for next week (only bonus!):**
  - Schroeder, 8.2

Problem 12.1 - Bose-Einstein Condensation

In this problem we will explore the Bose gas and Bose-Einstein condensation. *Note: Throughout this problem we will set our energy scale so that the ground-state energy of our system is at $E = 0$.*

First we will look at temperatures above the critical temperature, before a BEC has formed. Consider a non-relativistic, 3D, spin-0 ($g_s = 1$) Bose gas at a temperature where the chemical potential is $\mu = -0.2 k_B T$. Recall that $g(E)\bar{n}_B(E)$ tells us the number of particles we have per unit energy and the area under the $g(E)\bar{n}_B(E)$-vs-E graph gives the total number of particles in the system N.

(a) Defining $\epsilon \equiv E/k_B T$, find and plot the density of states $g_\epsilon(\epsilon) = g(\epsilon k_B T)k_B T$ and the product $g_\epsilon(\epsilon)\bar{n}_B(\epsilon k_B T)$. You will have to set some value for N or you can divide both function by N. Shade the range of energies for which we will have *more than one* particle per state on average.
[*Note: You can do this last part with a simple visual analysis of the graphs you created - no algebra or numeric solving required.*]

In a Bose gas, we must have the chemical potential μ be less than the ground state energy $E_{g.s.} = 0$. In lecture we derived the ***critical temperature*** - the temperature at which μ becomes 0 - for a non-relativistic 3D gas of spin-0 identical bosons,

$$T_C = \left(\zeta\left(\tfrac{3}{2}\right)\right)^{-2/3}\frac{h^2}{2\pi m k_B}\left(\frac{N}{V}\right)^{2/3} \approx 0.527\frac{h^2}{2\pi m k_B}\left(\frac{N}{V}\right)^{2/3}.$$

The critical temperature provides a good, natural reference temperature for our system. When $T > T_C$, the chemical potential is given by the condition that there are a total of N particles in the gas,

$$N = \int_0^\infty g(E)\bar{n}_B(E)dE.$$

(b) When $T > T_C$, show that the chemical potential and temperature are related by

$$\int_0^\infty \frac{\sqrt{\varepsilon}}{e^{(\varepsilon-c)/t} - 1} d\varepsilon = \frac{\sqrt{\pi}}{2} \zeta(3/2) \approx 2.315,$$

where $t \equiv T/T_C$ and $\varepsilon \equiv E/k_B T_C$. Verify that $(t = 1, c = 0)$ solves this equation.

(c) Use the relation given in part (b) to find the temperature T that satisfies the condition $\mu = -0.2k_B T$ ($c = -0.2t$) that we explored in part (a). You will need to do some numerical work here.
Answer (highlight to reveal): [I found $T \approx 1.58 k_B T_C$.]
[*Supplementary Part (Not for Credit): Challenge! Make a graph of μ-vs-T for $T = 1.2T_C$ up to $T = 3T_C$.*]

Let's see how well our "non-interacting gas" approximation works for a system that's, well, really not that! Consider liquid Helium-4 (we explored this in Problem 11.1 as well). The density of this liquid is $\rho = 0.145 \, \text{gram/cm}^3$ and the mass of a single atom is approximately $4 \, \text{u}$.

(d) Calculate the condensation temperature for Helium-4 and compare it to the known value of $T_C = 2.17K$ of the transition between the fluid and superfluid phases of liquid helium-4.
Hint (highlight to reveal): [Your computed answer should be a bit higher than the known value, but within a factor of 2 of it.]

In lecture, we sketched a graph of the heat capacity of a Bose gas and showed that there was a kink (a discontinuity in the derivative) at the critical temperature - the calling card of a phase transition[1] Let's construct this now.

(e) Extra Part (*Not for Credit*) Find an integral expression for the expected value of total energy $\langle U \rangle$ for a Bose gas in a box of volume V.
[*Note: This is very similar to what we did for the photon gas, phonon gas, and Fermi gas, so you should be familiar with the procedure by now!*]
Answer (highlight to reveal): [$\langle U \rangle = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \frac{E^{3/2}}{e^{\beta(E-\mu)}-1} dE$]

(f) Find $\langle U \rangle$ as a function of T in the case $T < T_C$. Use this to find $C_V(T)$. What is the limit as $T \to T_C$? Plot of C_V/Nk_B-vs-T/T_C for $T < T_C$.
Hint (highlight to reveal): [Recall that $\mu \approx 0$ when $T < T_C$.]

(g) Find the entropy as a function of temperature for this system when $T < T_C$. From this and the previous part, find the Helmholtz free energy and then the pressure of the system.

Challenge! In part (c), I challenged you to graph μ when $T > T_C$. Let's put that to use!

(h) Extra Part (*Not for Credit*) Using numerically computed values for μ when $T > T_C$, numerically integrate your expression from (f) and then take a numerical derivative to find data points for C_V/Nk_B. Plot these. What is the limit as $T \to T_C$?

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[1]In particular, a kink in the graph of the heat capacity indicates this is a **second-order phase transition**. If it were a first-order phase transition there would have been a discontinuity in C_V itself.

Problem 12.2 - Water and Water Vapor

Note: These problems are adapted from Schroeder Chapter 5

In this problem we will explore the phases of water. The phase diagram is shown below.
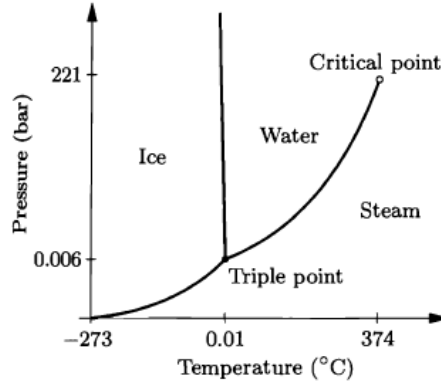
(a) *Qualitatively* sketch graphs of the Gibbs free energy G-vs-T at 1 atmosphere of pressure for the three different phases of water: solid (ice), liquid, and gas (vapor).
[*Note: The features we are most interested in are the signs of the slopes, the* relative *magnitudes of the slopes, qualitatively accurate relative values of the Gibbs free energy (in particular, having the appropriate curve represent the minimum in the appropriate region), and the temperatures at which graphs intersect (for the intersections that are physically important).*]
Hint (highlight to reveal): [What I mean by "physically important": There will be an intersection point for the curves between solid-and-liquid and liquid-and-gas which represent the phase transitions (we jump from one curve to another when minimizing G). The intersection point for the solid-and-gas curve is not physically meaningful at this pressure since the liquid curve is the important one, having the smallest G in this region.]
[*Supplementary Part (Not for Credit): Do the same for graphs of G-vs-P at $T = 0°C$.*]

Recall that the ***Clausius-Clapeyron equation*** gives an expression for the slope of a phase boundary curve between two phases in a phase diagram,

$$\left(\frac{\partial P}{\partial T}\right)_{\substack{\text{phase} \\ \text{bndry}}} = \frac{L}{T\Delta v} = \frac{\ell}{T\Delta\tilde{v}},$$

where L is the specific latent heat (energy-per-unit-mass), ℓ is the molar latent heat (energy-per-mole), v is the specific volume (volume-per-unit-mass) and $\tilde{v}$ is the molar volume (volume-per-mole). The density of ice is $\rho_{\text{ice}} = 917\,\text{kg/m}^3$. At a pressure of 1 atm, the freezing point of water is $0°C$ and the latent heat for the liquid-solid transition is $L = 334\,\text{kJ/kg}$.

(b) Why does the fact that solid ice tends to have a greater volume than an equal mass of liquid water imply that the slope of the phase boundary betwen liquid water and ice is negative? Find the slope of this curve at standard pressure and use this slope to estimate the pressure at which freezing point of water lowers to $-1°C$.

(c) One last order-of-magnitude question for the semester! Estimate the pressure under the blade of an ice skate and using the results of part (b) estimate the melting temperature of ice at this pressure. Some sources have claimed that ice skating is possible because a thin layer of water forms under the skate at the surface of the ice. Based on this order-of-magnitude estimate, does the

pressure cause the melting point to lower significantly enough to explain this layer of water?
[*Note: Of course we are ignoring a* lot *of things, such as the huge difference that surface effects cause,*]

The ***vapor pressure*** is the pressure exerted by water vapor when it is in equilibrium with liquid water and/or ice. This means that the equation for the vapor pressure is just the equation $P_v(T)$ of the phase boundary between vapor and liquid water. Let's find this! Note that we can treat the specific/molar volume of the gas phase to be much much larger than for the liquid phase (the density of water vapor is roughly five orders of magnitude smaller than that of liquid water). We will also approximate the latent heat as roughly constant at $\ell = 40.66 \, \text{kJ/mol}$.[2] In the temperature and pressure range under consideration, we can approximate water vapor to be an ideal gas.

(d) Apply these approximations to the Clausius-Clapeyron equation to get a differential equation for $P_v(T)$ and then solve that equation with initial condition $P_v(100°\text{C}) = 1\,\text{atm}$. Use this to determine the boiling point when the pressure is 0.9 atm. Why does it take longer to properly make hard-boiled eggs at higher altitudes?

At $T = 25°C$, the latent heat has changed significantly enough that we should redo our calculations. We find that near this temperature,

$$P_v(T) = A \, e^{-\ell/RT}, \qquad A = 1.626 \times 10^{11} \, \text{Pa}, \qquad \ell = 43.99 \, \text{kJ/mol}.$$

We interpret the vapor pressure now as the partial pressure of water vapor in the air when the air is ***saturated***. In some senses this is a poor choice of words - "saturated" air is just air whose water vapor content is in equilibrium with liquid water and thus neither evaporation nor condensation is preferred.

The partial pressure of water vapor in the air is typically less than the vapor pressure at the ambient temperature (this is why a cup of water will spontaneously evaporate.) The ratio of the actual partial pressure of water vapor in the air to the vapor pressure is called the ***relative humidity***. Saturation occurs when the relative humidity is 100%. For a given actual partial pressure of water vapor in air, we define the ***dew point*** to be the temperature at which saturation would occur. Therefore knowing the dew point[3] allows us to calculate the actual partial pressure of water in air and knowing the temperature allows us to calculate the vapor pressure. Knowing both of these allows us to compute the relative humidity![4].

(e) Find a formula relating the temperature T, dew point T_d and relative humidity h. At the time of this writing, it is $18°\text{C}$ in Berkeley, California with a dew point of $7°\text{C}$. What is the relative humidity?

(f) As the temperature increases, what happens to the vapor pressure? Assuming the partial pressure of water in the air (i.e. the water content in the air) remains roughly constant, how does an increase in temperature affect the relative humidity? Applying this to the climate, would this make rainfall more or less likely if global temperatures were to rise?[5]

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[2]The latent heat does vary but this will be a decent approximation for us.

[3]The dew point is actually relatively straightforward to measure, using a ***hygrometer***. The hygrometer has a polished metal mirror which is cooled as air is passed over it. The temperature at which dew forms on the mirror is the measured dew point.

[4]Really, knowledge of any two of these would let us find the third

[5]There are a *lot* of approximations and assumptions going into this exercise but it is an important first (and very elementary/unsophisticated) toy model for climate change.

Commentary A few things! First, it is entirely possible for the relative humidity to be greater than 100%. This just means that the air is **supersaturated** and that introduction of nucleation sites might cause precipitation. From Wikipedia, "Relative humidity is an important metric used in weather forecasts and reports, as it is an indicator of the likelihood of precipitation, dew, or fog. In hot summer weather, a rise in relative humidity increases the apparent temperature to humans (and other animals) by hindering the evaporation of perspiration from the skin." For example, on an already-hot summer day of 32°C (90°F), if the relative humidity is 70% then the heat index says it feels like 41°C (106°F).

Problem 12.3 - Critical Exponents

You've made it to the final homework problem of the semester! In this problem we will discuss the behavior of a van der Waals gas near its **critical point**. Things get weird and neat near critical points and the behaviors of many properties become **power laws**.[6] If quantities A and B obey a power law then they are related by $A \propto B^{-k}$, where k is some exponent. Note that there is a *monomial* on the right - polynomial relationships are *not* considered power laws. One key feature of power-laws is their **scale invariance** - scaling quantity B produces a result that is proportional to A. This can be seen by graphing a log-log plot of A-vs-B in which case a power law appears as a straight line.

Recall from earlier problem sets the van der Waals equation of state,

$$\left(P + \frac{aN^2}{V^2}\right)(V - bN) = Nk_BT.$$

The critical point of this system occurs at

$$P_c = \frac{a}{27b^2}, \qquad V_c = 3Nb, \qquad k_BT_c = \frac{8a}{27b}.$$

We define non-dimensionalized variables and re-express the equation of state,

$$p \equiv \frac{P}{P_c}, \qquad v \equiv \frac{V}{V_c}, \qquad t \equiv \frac{T}{T_c} \quad \Longrightarrow \quad p = \frac{8t}{3v - 1} - \frac{3}{v^2}.$$

Note that the critical point now occurs at $p = v = t = 1$. We will explore the behavior of several power-law relationships near the critical point. The exponents that appear in these power-law relationships are called **critical exponents**. It is believed (but surprisingly *not yet proven*) that all critical exponents exhibit **universality** - that is, they only depend on general features of a system rather than specific details. For example, universality of a relationship for a van der Waals gas would imply that none of the critical exponents can depend on the parameters a or b.

(a) Extra Part (*Not for Credit*) Find the combination P_cV_c/Nk_BT_c, which is a dimensionless constant and independent of the van der Waals parameters a and b (and thus a universal property of a van der Waals gas).

As our first power-law, let's consider the shape of the $T = T_c$ isotherm (the **critical isotherm**) near the critical point.

(b) Show that $(P - P_c) \propto (V - V_c)^\delta$ and determine the critical exponent δ.

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[6]https://en.wikipedia.org/wiki/Power_law

Another critical exponent occurs along the phase boundary relating the difference in volume between the liquid and gas phases as we approach the critical point.

$$(V_g - V_\ell) \propto (T_c - T)^\beta.$$

Experiments show that β has a universal value of around $1/3$. Unfortunately the van der Waals model doesn't quite agree with this result. Let's see...

(c) Taylor expand the (non-dimensionalized) van der Waals equation of state about the point $v = 1$ keeping terms through order $(v - 1)^3$.

(d) **Extra Part** (*Not for Credit*) Argue that when $(v - 1)$ becomes comparable in size to $(t - 1)$, the term linear in $(v - 1)$ will be the dominant term. Then argue that when $(v - 1)^2$ becomes comparable in size to $(t - 1)$ the cubic term and linear terms in $(v - 1)$ become comparable in size and larger than the term quadratic in $(v - 1)$. Therefore, we can approximate to third order that the coexistence curve follows

$$(p - 1) \approx 4(t - 1) - 6(t - 1)(v - 1) - \frac{3}{2}(v - 1)^3. \tag{1}$$

(e) Use Eq. 1 to plot some isotherms for temperatures slightly below $t = 1$. Argue that the Maxwell equal-area construction implies that the vapor pressure is equal to the pressure at $v = 1$. From this, determine the slope $\frac{\partial P}{\partial T}$ for the coexistence curve at the critical point.
Answer (highlight to reveal): [You should find that, in the dimensionless variables, $\frac{\partial p}{\partial t} = 4$.]

(f) Using the equations for isotherms from part (d) and the vapor pressure curve $P(T)$ found in part (e), determine the difference in the volumes of the liquid and gas phases as a function of temperature and thus determine the critical exponent β.
Answer (highlight to reveal): [In the dimensionless variables, $\Delta v = 4\sqrt{1 - t}$.]

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