Physics 313 Problem Set 8

Important concepts from lectures 24-27

Under conditions of constant T, V and N, the equilibrium configuration is determined by minimizing the Helmholtz free energy. (ie, the entropy, pressure and chemical potential adjust to minimize F).

Under conditions of constant T, P and N, the equilibrium configuration is determined by minimizing the Gibbs free energy. (ie, the entropy, volume and chemical potential adjust to minimize G).

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The best way to think about phase transitions is in terms of P and T. The relevant quantity is then the Gibbs free energy, G(P,T,N).

A phase transition line (where the two phases can coexist in equilibrium) is where the Gibbs free energies **per molecule** of the two phases are equal. Since G = Nμ, this is the same as having the same chemical potential in both phases.

At the phase transition point, fixed T and P, volume can usually be adjusted by changing the relative amount of the substance in each of the two phases.

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You should be able to sketch and explain the phase diagram of a typical substance with solid, liquid and gas phases, including the triple point (where all three forms coexist) and the critical point (where the boundary between gas and liquid ends).

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Clausius-Clapeyron equation gives you the slope of the phase transition line on the P-T diagram in terms of the latent heat L and the difference in volumes between the two phases.

$$\frac{\partial P}{\partial T} = \frac{L}{T\Delta V}$$

When using this equation, make sure that the latent heat L and the volume difference ΔV are for the same amount of the substance (for example, 1 kg or 1 mole).

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You are not responsible for the Van der Waals model.

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If a particle is held in equilibrium with a heat reservoir, at constant temperature T and fixed volume V, the probability of finding it in a state s with a particular energy E(s) is proportional to the Boltzmann factor

$$\text{prob}(s) \sim \exp\left(-\frac{E(s)}{kT}\right)$$

The probability of finding the particle in any state with energy E is

$$\text{prob}(E) \sim \Omega(E) \exp\left(-\frac{E}{kT}\right)$$

where $\Omega(E)$ is the number of states with energy E (its multiplicity).

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Useful notation:

$$\beta \equiv \frac{1}{kT}$$

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Partition function definition:

$$Z(T) \equiv \sum_{\text{all states s}} e^{-\beta E(s)}$$

This is equivalent to

$$Z(T) = \sum_{\text{all energies E}} \Omega(E) e^{-\beta E}$$

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The probability of finding the particle in a **particular** state s with energy E(s) is

$$\boxed{P(s) = \tfrac{1}{Z} \, e^{-\beta E(s)}}$$

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To calculate the expectation value (the average) of any quantity X, simply compute the following sum over states

$$\overline{X} = \sum_{s} X(s) P(s)$$

For example, the average energy is

$$\overline{E} = \sum_{s} E(s) P(s)$$

The total internal energy for N identical particles is $U = N\overline{E}$. There is a very useful formula

$$U = N\overline{E} = -\frac{N}{Z}\frac{d}{d\beta} Z(\beta)$$

Problem Set

Due at the end of class, Wednesday November 12th (late assignments will not be accepted).

1. Consider a system enclosed in cylinder closed with a movable piston and immersed in a heat bath. The piston keeps pressure P constant and the bath keeps temperature T constant. There is one kilogram of H_2O molecules in the cylinder. Assume that P and T are adjusted so that there is both some liquid water and water vapor in the cylinder, at equilibrium with each other.

(a) Take T=50°C and use Table 4.1 in the book. What is P? what is the total Gibbs free energy of the liquid and gas together (relative to liquid water at the triple point)? what is the chemical potential of the molecules in the liquid? what is the chemical potential of the molecules in the gas?

Note: there are (naturally) some rounding errors in the Table. Please make sure that these are not causing you to give answers which make no sense (like claiming that two quantities which should be equal are not).

(b) What is the latent heat of evaporation of water at 50°C? (make sure you specify the units!)

(c) The piston is slowly pulled out, increasing the volume by $\Delta V = 10^{-2}m^3$. How much work is done **on** the system?

(d) Assuming water vapor is an ideal gas, how many molecules are evaporated as the volume increases? how much heat enters the system?

(e) Put (c) and (d) together to obtain the difference in the internal energy of the system, ΔU.

(f) Compute ΔS, the increase in entropy of the system, two ways: from $dS = Q/T$ together with your answer to (d), and from from values of S in Table 4.4. Do your answers agree (within some rounding errors)?

(g) How does the total Gibbs free energy of the system change during the volume increase and why?

(h) Compute ΔG from your answers in parts (e) and (f) and the definition $G = U + PV - TS$. Does your answer agree with your reasoning in part (g)?

2. Schroeder 5.32, pg 174

3. (a) Schroeder 5.35, pg 175
(b) Use the data in Table 5.11 and your result in part (a) to calculate the boiling temperature of water at 0.8 atm, the atmospheric pressure at 6000 feet above the sea level. Why does it take longer to cook noodles in the mountains?

4. For each of the partition functions below, write down the spectrum (the allowed values of energies) and the multiplicities. For parts (d) and (e) you will need to use a Taylor expansion.

(a) $Z = e^{-\epsilon\beta} + 2e^{-2\epsilon\beta} + 5e^{-4\epsilon\beta}$

(b) $Z = e^{2\epsilon\beta} + 3 + 2e^{-3\epsilon\beta} + e^{-5\epsilon\beta}$

(c) $Z = \left(e^{-\epsilon\beta/2} + e^{\epsilon\beta/2}\right)^3$

(d) $Z = \frac{1}{1-e^{-\epsilon\beta}}$

(e) $Z = \frac{1}{\left(1-e^{-\epsilon\beta}\right)^N}$ [Write down just the first 3 energy levels only for this one.]

5. What is wrong with the following partition functions?

(a) $Z = e^{-\epsilon\beta/2} - e^{\epsilon\beta/2}$

(b) $Z = e^{-\epsilon\beta/2} + \frac{1}{3}e^{\epsilon\beta/2}$

6. The hydrogen atom spectrum is given by $E(n) = -E_R/n^2$ where $E_R = (13.61eV)$ is the Rydberg energy and where n is a positive integer ($n = 1, 2, 3, \ldots$). The multiplicity of each state is $2n^2$.

(a) Write down the formula for the partition function Z in terms of β and E_R. Don't try to evaluate the sum.

(b) For $T = 5800K$ (the temperature at the surface of the sun, evaluate the first 3 terms of Z. Is it reasonable to approximate Z with just the first term?

(c) Compute the probability of finding a hydrogen atom in any of the $n = 2$ and any of $n = 3$ states.

7. In class we saw that the partition fuction for a single quantum harmonic oscillator with spacing $\epsilon = hf$ is

$$Z = \frac{1}{1 - e^{-\beta\epsilon}}$$

Find the total energy of N identical QHO at temperature T. Notice that this computes the exact internal energy in an Einstein solid, a problem we could not tackle using tools from chapters 2 and 3.

Extra (not for credit): Problems 5.33 and 5.55 are both very nice, if you are looking for more practice with phase transitions. 6.14 is another look at the exponential formula for the density of the atmosphere.