Physics 114 Statistical Mechanics Spring 2021
Week 8 Reading and Problem Assignment

Overview:

The big theme this week is systems where *particle numbers can vary* . We learn the third major ensemble: the *grand canonical ensemble.* The *grand canonical partition function* is noted as Z_G or $\not{Z}$. From $\not{Z}$(T, V, μ), all thermodynamic quantities can be calculated for a system in contact with a reservoir that can supply both energy and particles. The reservoir serves to establish both the smaller system's temperature, T (as for a canonical system) and its *chemical potential,* μ, whose importance we will probe this week.

Later in seminar, we will find that grand canonical statistics are essential for dealing with quantum particles which are not conserved in the universe (photons, phonons, ...). This week, we begin just past the part of G&T (p. 329) where they derive expressions for the *expected number of particles* $\bar{n}_k$ in any quantum state $\vec{k}$. We can exploit their results - sticking to examples with semiclassical particles - to find thermo averages, like energy $\bar{E}$. We'd find $\bar{E}$ by integrating the product $E(\vec{k}) \ \times g(\vec{k}) \ \times \bar{n}_k$, where $g(\vec{k})$ is the *density of states.* We've already calculated g in previous weeks for particles-in-a-box; we are reminded of its value this week for both matter particles and photons. This week we do problems that apply grand canonical statistics to ideal gasses, *absorption* on surfaces, *chemical reactions* and *osmosis.* Finally, we'll extend our understanding of how one simulates interacting particles via *Monte Carlo* for systems in which particle numbers can vary.

Note About reading: I'm not assigning Sections 6.3, 6.4 this week ... we will get to them later . Please *just take as true* Eqs. (6.85) and (6.86). These forms crop up once or twice in G&T Section 6.5. In the classical limit where $\bar{n}_k << 1$, this becomes (6.87), the good olde Maxwell-Boltzmann distribution :-)

Suggested Reading:

G&T Sections

- Section 4.12
- Sections 6.5, 6.6, and 6.11.1
- Sections 7.1, 7.2 and 7.5

B&B sections

- Ch. 22

Schroeder section

- Section 7.1

Warmup Problems:

1: Grand canonical statistics for an an ideal gas

G&T Problem 6.44 part a

2: The chemical demon algorithm

Explain in your own words the "Chemical Demon algorithm", which produces the Gibbs distribution: $P(E_d, N_d) \;\propto E^{-\beta(E_d-\mu N_d)}$

Problems to discuss in our meeting

Note: The * means that these problems are to be handed in. They are due the day after we meet.

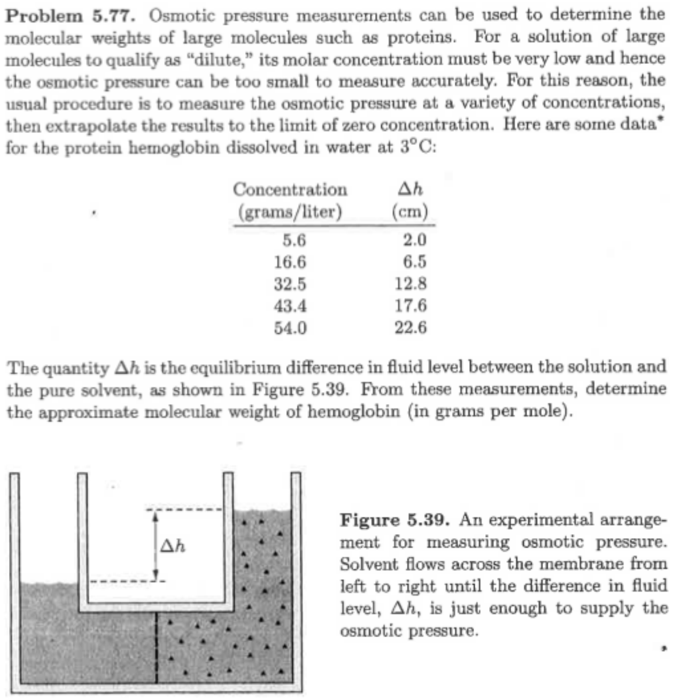
1*: Chemical reactions: production of Ammonia

The commercial production of ammonia from nitrogen and hydrogen is an example of a reaction that occurs the gaseous state:

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

a) Write down the equilibrium constant, K, in terms of the partial pressures of the nitrogen, hydrogen, and ammonia. (You may take $p^o = 1$ atm.)
b) Using the data tables at the back of Schroder (on our website under "Resources" link) please confirm that at $T = 298K$, $K = 5.9 \times 10^5$.
c) Please draw a quantitatively accurate plot of $logK$ vs. $1/T$. From this plot or in some other way, find K when $T = 773K$. (This is 500^oC which is apparently a good temperature at which to run this reaction, using a catalyst to speed it up.)
d) Will you drive the equilibrium toward more ammonia, or more nitrogen and hydrogen, if you increase T?
e) Same question, if you increase the pressure?

2: Osmosis (This is a Schroeder problem; but you'll be prepared to do it by the B&B reading (Ch. 22.9))



Problem 5.77. Osmotic pressure measurements can be used to determine the molecular weights of large molecules such as proteins. For a solution of large molecules to qualify as "dilute," its molar concentration must be very low and hence the osmotic pressure can be too small to measure accurately. For this reason, the usual procedure is to measure the osmotic pressure at a variety of concentrations, then extrapolate the results to the limit of zero concentration. Here are some data* for the protein hemoglobin dissolved in water at 3°C:

Concentration (grams/liter)	Δh (cm)
5.6	2.0
16.6	6.5
32.5	12.8
43.4	17.6
54.0	22.6

The quantity Δh is the equilibrium difference in fluid level between the solution and the pure solvent, as shown in Figure 5.39. From these measurements, determine the approximate molecular weight of hemoglobin (in grams per mole).

Figure 5.39. An experimental arrangement for measuring osmotic pressure. Solvent flows across the membrane from left to right until the difference in fluid level, Δh, is just enough to supply the osmotic pressure.

3*: Absorption onto a surface

Suppose a surface has M distinguishable sites, each of which can absorb at most one indistinguishable gas molecule. Say that an absorbed gas molecule has an energy of $-\epsilon$ compared with an unabsorbed molecule. The molecules have chemical potential μ both in the gas phase and on the surface. (This is what it means for the gas phase to be in equilibrium with the absorbed phase.)

a) Show that $\mathcal{Z}(T, V, \mu) = (1 + e^{\beta(\epsilon+\mu)})^M$

b) Find the equilibrium fraction, f, of sites that have absorbed molecules. In other words, if N_o molecules are absorbed, then $f = N_o/M$.

c) By equating μ with the chemical potential of an ideal gas at pressure P and temperature T, show that

$$f = \frac{P}{P + P_o(T)}$$

and find an expression for $P_o(T)$. *Hint: P_o will also depend on ϵ, the mass of the gas particles, and constants of nature.*

4: Chemical potential and equations of state of the monatomic ideal gas

i) G&T Problem 6.21
ii) G&T Problem 6.22

5*: Chemical potential and ionization of hydrogen

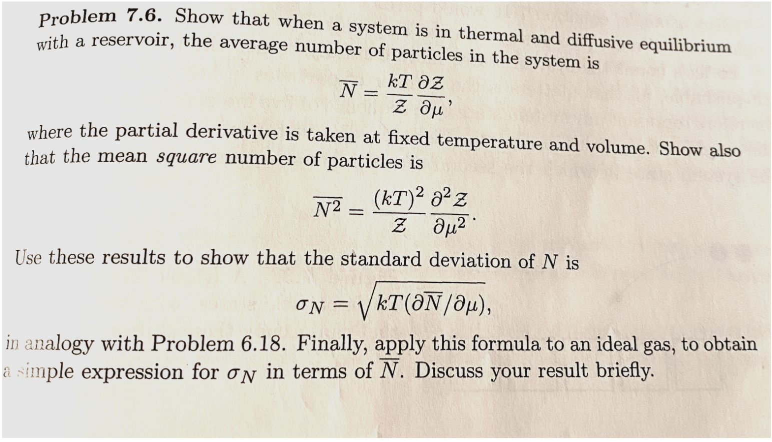
B&B Problem 22.6

6: Grand canonical statistics and fluctuations for an ideal gas

i) G&T Problem 6.44 Part b

ii) G&T Problem 6.44 Part c (Note: I think they mean "What is the $\bar{N}$ dependence ... ?")

In case it helps you ... see this similar problem, below, from Schroeder.



Problem 7.6. Show that when a system is in thermal and diffusive equilibrium with a reservoir, the average number of particles in the system is

$$\overline{N} = \frac{kT}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu},$$

where the partial derivative is taken at fixed temperature and volume. Show also that the mean *square* number of particles is

$$\overline{N^2} = \frac{(kT)^2}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}.$$

Use these results to show that the standard deviation of N is

$$\sigma_N = \sqrt{kT(\partial \overline{N}/\partial \mu)},$$

in analogy with Problem 6.18. Finally, apply this formula to an ideal gas, to obtain a simple expression for σ_N in terms of $\overline{N}$. Discuss your result briefly.

7: The chemical Demon algorithm

i) Begin with the familiar result that for a 3d semiclassical, noninteracting particles $\mu = -kT\ ln[(Z(T, V, 1)/N]$. Adapt it to 1d and show that with $k = 1,\ h = 1$, and $m = 1/2$, a Demon simulation should give:

$$\mu = -T\ ln[\frac{L}{N}\sqrt{\pi T}]$$

ii) Do G&T problem 7.7 (c) using their chemical demon applet to take data, and compare with the value of μ predicted in ii).

iii) This applet lets you go beyond the ideal gas by adding either a "hard core" close-range repulsion, or an attractive well. Do one of these variations, take data, and discuss how μ has changed.

8: Condition of chemical equilibrium

Please write down the conditions of chemical equilibrium for the following reactions:

i) $e^+ + e^- \longleftrightarrow 2\gamma$

ii) $CH_4 + 2O_2 \longleftrightarrow 2H_2O + CO_2$

iii) $2p + 2n \longleftrightarrow {}^4He$