Physics 114 Statistical Mechanics Spring 2018

Seminar 8

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 Ƶ. From Ƶ(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.*

Catching up and moving on :-) We have a numerical and an analytical issue to catch up on ... both of which have to do with *probability.* In section Wed B, we did not hear a presentation about a classic *Monte Carlo* simulation of N particles, so Amy will do a short presentation on it this week. Finally, we will do a couple of problems on Bayesian statistics, for which we did not have time in Seminar 5.

Review Reading:

Bayesian statistics: G&T Section 3.4.2 and B&B Section 15.6
Canonical Monte Carlo simulation: Section 4.11

Required Reading:

G&T Sections

- Section 4.12
- Sections 6.5, 6.6, and 6.11.1
  Note: Parts of these Ch. 6 readings are tough going without having read Sections 6.3 and 6.4. For now, just use Section 6.4 equations like (6.85), (6.86) and (6.87). (We'll cover the derivations two weeks from now :-) .

- Sections 7.1, 7.2 and 7.5

B&B sections

- Ch. 22

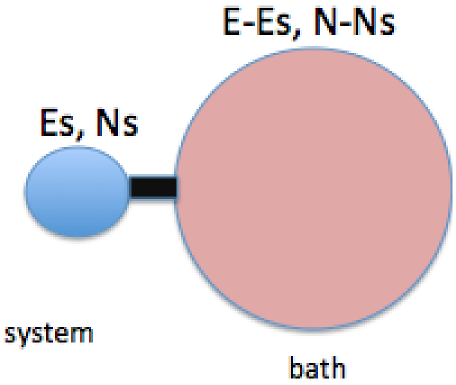
Schroeder section (scan is on our Moodle site)

- Section 7.1

Concept checklist from Readings:

- **The Grand canonical ensemble** has a probability distribution known as the *Gibbs distribution*:

$$P_s = \frac{1}{Z_G} e^{-\beta(E_s - \mu N_s)}; \quad where \quad Z_G = \Sigma_s \ e^{-\beta(E_s - \mu N_s)}$$



- Notation alert: The *grand partition function* is noted as Z_G in G&T and $\mathcal{Z}$ in both B&B and Schroeder.

- The proof that the Gibbs probability distribution is established equilibrium is very much like the one for the Boltzmann probability distribution. We argue that the system shown above has N_s particles and energy E_s , with energy and particles being exchanged with a $\huge{\text{huge}}$ bath. Thus:

$$ln\Omega_b(E - E_s, N - N_s) = ln\Omega_b(E, N) - \frac{d\ln\Omega_b(E,N)}{dE}E_s - \frac{d\ln\Omega_b(E,N)}{dN}N_s + ...$$

From earlier weeks, we recall that

$$\frac{d\ln\Omega_b(E,N)}{dN} \equiv \frac{1}{k}\frac{dS_b}{dN} \equiv -\mu/kT \ .$$

Because the equilibrium probability of observing a particular value of E_s and N_s is proportional to $\Omega_b(E - E_s, N - N_s)$ (which assumes $\Omega_s(E_s, N_s) = 1$) we are lead to the Gibbs distribution.

- The *chemical potential*, μ , will be very important this week, and we'll say more about it below.

- In the definition of the grand partition function,

$$Z_G(T, V, \mu) = \Sigma_s \; e^{-\beta(E_s - \mu N_s)}$$

you should infer that E_s depends on N_s . So to calculate $\cancel{Z}$ you might first sum over all states for a *given* N_s and then sum over all possible N_s:

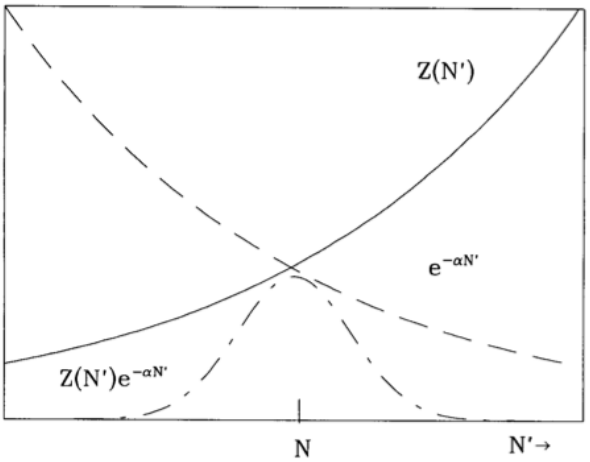
$$Z_G = \Sigma_{N_s} e^{\beta N_s \mu} \;\; \Sigma_{E_s, where\ s\ has\ N_s\ particles} \;\; e^{-\beta E_s}$$

- What we have just written is:

$$Z_G(T, V, \mu) \equiv \Sigma_N e^{\beta N \mu} Z(T, V, N)$$

where $Z(T, V, N)$ is the canonical partition function. Cool! Z_G is a *transform* of Z, where the variable N is transformed to μ. Moreover, the Landau free energy, Ω, which is also known as the grand potential, is a transform of the Helmholtz free energy. They are related by a Legendre transform: $\Omega = F - \mu N$.

- Below is a figure (Clemson University website) which shows how multiplying $Z(N)$ by $e^{-\alpha N}$, produces a sharp peak at $\bar{N}$, the mean number of particles in the system. (Note: Their variable α is our -$\beta\mu$. For the semi-classical gas, $\mu << 0$. So with $\alpha > 0$, the shape of graph is sensible and relevant :-)



- **The grand potential** is proportional to the logarithm of the grand partition function; just as $F = -kTlnZ$ for the canonical ensemble.

- Notation alert: the *Grand potential* is written as $\Omega(T, V, \mu)$ in G&T, as $\Phi_G(T, V, \mu)$ in B&B and as $\Phi(T, V, \mu)$ in Schroeder.

- However you choose to write it, $\Phi_G(T, V, \mu) = -kT\ lnZ_G(T, V, \mu)$. As we learned in a problem in an earlier week, $\Phi_G = F - \mu N = -PV$. For similar mathematical reasons, $G = \mu N$.

- A nice summary of the three fundamental potentials: Entropy, Helmholtz, and Grand are shown in B&B:

  $\Omega = e^{\beta TS}$
  $Z = e^{-\beta F}$
  $\text{Ƶ} = e^{-\beta\Phi_G}$

- Like their partition functions, the potentials contain *all* equilibrium thermodymic information for their respective ensembles. For example, B&B section 22.4 shows

  $$S = -\left(\frac{\partial\Phi_G}{\partial T}\right)_{V,\mu}\ ,\ P = -\left(\frac{\partial\Phi_G}{\partial V}\right)_{T,\mu}\ ,\ N = -\left(\frac{\partial\Phi_G}{\partial\mu}\right)_{T,V}$$

  As ever, partial derivatives of a potential yield the "conjugate" quantities to its natural variables. Here: $(T, V\mu) \leftrightarrow (S, P, N)$.

- **Chemical potential** is discussed both in B&B and stat the start of G&T Ch. 7. We consider two systems, say 1 and 2, where particles can be exchanged. Guided by the idea that entropy is maximized, use of the definition $\mu/T = -(\frac{\partial S}{\partial N})_{U,V}$ leads to $\mu_1/T_1 = \mu_2/T_2$ at equilibrium

- Furthermore, using the idea that entropy must decrease when systems move toward equilibrium, we find that particles flow *down the gradient of chemical potential*, so if $\mu_1 > \mu_2$, particles flow from 1 to 2.

- On the topic of chemical potential, be sure you feel comfortable with

  - definitions of μ in other ensembles:

    $$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{T,P} = G/N$$

  - the example of Figure 7.1, where part of system is raised up in a gravitational field leading to $N_u = N_o e^{-\beta mgy}$

  - the example of two Einstein solids which can exchange particles ... leading to $\partial ln\Omega_A/\partial N_A = \partial ln\Omega_B/\partial N_B$ at equilibrium
  - Free energy arguments, like $dG = \Sigma_i \mu_i dN_i$ for a multi particle system. Such arguments
    - are the basic principle upon which chemical reaction problems (see below) rest
    - let us deduce that if we can destroy a species of particle completely (like a photon) then $\mu = 0$
  - the numerical *Widom particle insertion method* which relies on the fact that μ is the change in free energy, F, when we add a single particle to the simulation. A clever idea is to calculate only the addition to the ideal gas part of μ. This "excess" contribution is $\mu_{excess} = -kTln < e^{-\beta\Delta U} >$
  - the *chemical demon Monte Carlo algorithm* ... which appears in a presentation problem this week.

- **About grand canonical statistics ... the backstory for B&B 6.5 and 6.6**

- How many particles do we expect to exist in *any single quantum state labelled by k*? This is the *occupation number* $\bar{n}_k$. Finding this quantity lends itself to *grand canonical* statistics, because we are not requiring a certain number of particles exist ... we are instead counting probable occupation of energy levels. In future weeks, we'll emphasize the fact that we must take into account the spin-related statistics of bosons and fermions. Fermions can only have $n_k = 0$ or 1 particles in state k. Bosons can have an infinite number.

- We write the grand partition function as $Z_G = \Sigma_k Z_{G,k}$ where

$$Z_{G,k} = \Sigma_{n_k} e^{-\beta n_k(\epsilon_k - \mu)}$$

G&T Section 6.4 goes through the two cases (fermions, bosons) to deduce that

$$Z_{G,k} = (1 \pm e^{-\beta(\epsilon_k-\mu)})^{\pm 1} \;\; with \; + \; for \; fermions \; ; \;\; - \; for \; bosons$$

- The Landau potential for each energy state is $\Omega_k = -kTlnZ_{G,k}$ and the expected occupation number is $\bar{n}_k = -\frac{\partial\Omega_k}{\partial\mu}$. These lead to

$$\bar{n}_k = \frac{1}{e^{\beta(\epsilon_k-\mu)} \pm 1} \;\; with \; + \; for \; fermions \; ; \;\; - \; for \; bosons$$

- What is interesting to us this week is the situation for semiclassical particles, where $\bar{n}_k$ is tiny. This is achieved in the limit that

$e^{\beta n_k(\epsilon_k-\mu)} >> 1$. While G&T call this the Maxwell-Boltzmann distribution in their Eq. (6.87). I find it odd ... I'm not sure why we don't call it the Gibbs distribution.

$$\bar{n}_k = e^{-\beta(\epsilon_k-\mu)}$$

- When we have many single-particle states close together, we can find thermodynamic averages by treating sums over states k as integrals. We use $\bar{n}_k\ g(\epsilon_k)$ as the *weighting factor* for the quantity we want to average. For example, the mean energy would be

  $$\bar{E} = \int_0^\infty \epsilon_k \bar{n}(\epsilon_k) g(\epsilon_k) d\epsilon_k$$

  while the expected number of particles is

  $$\bar{N} = \int_0^\infty \bar{n}(\epsilon_k) g(\epsilon_k) d\epsilon_k$$

  As in previous weeks, particle-in-a-box counting yields the density of states $g(k)$:

  $$g(k)dk = \frac{Vk^2}{2\pi^2}dk \ \ the\ number\ of\ waves\ with\ wave\ vector\ k;$$

  Then one can convert from k to energy, ϵ for the cases of matter particles or photons:

  $$g(\epsilon) = n_s \frac{V}{4\pi^2\hbar^2}(2m)^{3/2}\epsilon^{1/2} \ \ matter\ particles\ with\ n_s\ internal\ states;$$

  $$g(\epsilon) = \frac{V\epsilon^2}{\pi^2\hbar^3 c^3} \ \ photons\ with\ two\ polarizationstates$$

- **Chemical reactions** are a key application of chemical potential. A typical reaction might be: $|\nu_A|A + |\nu_B|B \leftrightarrow |\nu_C|C + |\nu_D|D$. The ν_i are *stoiciometric coefficients*. We translate this to math as

  $$\Sigma_i \nu_i N_i = 0$$

  with N_i the number of molecules of type i. By convention, $\nu_i > 0$ if i is a product molecule; $\nu_i < 0$ for a reactant.

- Conservation principles and the minimization of the Gibbs free energy at a given temperature and pressure lead to

  $$dG = -SdT + VdP + \Sigma_i \mu_i dN_i = 0 \ \ => \ \Sigma_i \nu_i \mu_i = 0 \qquad (1)$$

  This is the condition of *chemical equilibrium.*

- What is a *equilibrium constant* , K? It sets the ratio of reagents to products. Its definition depends on the specific reaction, as well as P and T. We will only deal with *gas phase* reactions in this seminar - though liquid ones aren't much harder once you get the procedure down. K is defined as

  $$K = \Pi_i (N_i/N)^{\nu_i} \equiv \Pi_i (P_i/P)^{\nu_i}$$

  K is a *constant* when the reagents and products are in equilibrium. The relationship above is also called the *law of mass action.*

- How do we find the value of K? The arguments in B&B and G&T begin with

  $$\mu_i(T, P, N_i) = \mu_i^o(T, P) - kTln(N_i/N) \qquad (2)$$

  Using Eqs. (1) and (2), we find K via

  $$-kT\ lnK = \Sigma_i \nu_i\ \mu_i^o(T, P)$$

  where μ_i^o is the chemical potential of a system of molecules of type i at temperature T and pressure P. (Remember that μ for an ideal gas is one of the many things you know how to find from Z_{ideal}.)

- Sometimes chemists standardize μ^o by finding it at a standard temperature and pressure. They often note the standard pressure as $P^{\ominus}$. This leads to writing, as in B&B, $\mu^o \equiv \mu^{\ominus}$ and

  $$K = \Pi_i (P_i/P^{\ominus})^{\nu_i}$$

- Yet another way to write the equilibrium constant is derived from Eqs. (1) and (2) above:

  $$K = e^{-\Delta_r G^{\ominus}/RT} \qquad (3)$$

  The subscript r means that we take the difference between reactants and products, and we measure these quantities in moles. To find $\Delta_r G$, a table like the one at the back of Schroeder is just the thing!

- Another game we can play with K leads to *Le Chatellier's principle.* Using Eq. (3) and the definition $H = G + TS = G - T(\frac{\partial G}{\partial T})_P$ we find

  $$\frac{d\ lnK}{dT} = \frac{\Delta_r H^{\ominus}}{RT^2}\ ; \quad or\ \frac{d\ lnK}{d\ (1/T)} = \frac{-\Delta_r H^{\ominus}}{R} \qquad (4)$$

- How does Eq. (4) help us? Since *exothermic* reactions have $\Delta_r H^{\ominus} < 0$, it tells us how K *drops* as temperature increases. Similarly, it tells us how K *rises* with T for *endothermic* reactions. This is *Le Chatelier's principle* ... reactions adjust their equilibrium to try and minimize the disturbance. If you raise temperature for an exothermic reaction, it goes less strongly, thereby releasing less heat!

- Another name for the second identity in Eq. (4) is the *van't Hoff equation*. There is a linear relationship between lnK and $(1/T)$, with the slope equal to $-\Delta_r H^{\ominus}/R$.
- *Osmosis* is a very useful phenomenon involving particle exchange. A membrane dividing two containers of an A and B mixture is permeable to only one species, A say. This will result in a pressure higher by an amount Π, on the the side containing more B. Eventually, Π will reach an equilibrium value.
- What is this equilibrium value? The question is answered for "dilute, ideal" solutions in B&B section 22.9. Example 22.8 shows that the chemical potential of a solvent A with a tiny amount of solute B added is *lowered* from the value of the pure liquid. The amount by which it is lowered is $RTlnx_A$. Using this fact and equating chemical potentials on either side of the membrane, leads to

  $$\Pi = n_B RT/V$$

  where n_B/V is the concentration of B.
- On the way to deriving the osmotic pressure, B&B mention *Raolt's law*. (We will probably see it again when we study phase transitions.) Raolt's law states that the vapor pressure of A is lowered from its pure liquid by a factor x_A, if there is a fraction $x_B = 1 - x_A$ mixed in.
- **Fluctuations** are discussed in G&T 6.11.1. Number fluctuations are directly proportional to κ, the isothermal compressibility. This is going to be important when we think about a critical phase transition later ... fluctuations go wild as a gas becomes so compressible it falls into a liquid state!
  - Don't worry about a "new Maxwell relation". Eq. (6.235) does not have the right form.
  - Do follow the logic that leads to Eq. (6.238), with the take-home message that $\kappa = \frac{1}{\rho kT}\frac{<\Delta N^2>}{<N>}$
  - Do take home the message of Eq. (6.240), that $\frac{<\Delta N>}{<N>} \propto \frac{1}{\sqrt{<N>}}$

Amy's Presentation (Wed Section B): Metropolis Monte Carlo

Sydney and Emma's Presentations (Wed Sections A and B): A new Demon algorithm

i) Explain the “Chemical Demon algorithm”, which produces the Gibbs distribution: $P(E_d, N_d) \ \propto E^{-\beta(E_d - \mu N_d)}$

ii) 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:

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

iii) 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).
iv) 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.

Warmup Problem: B&B 22.3

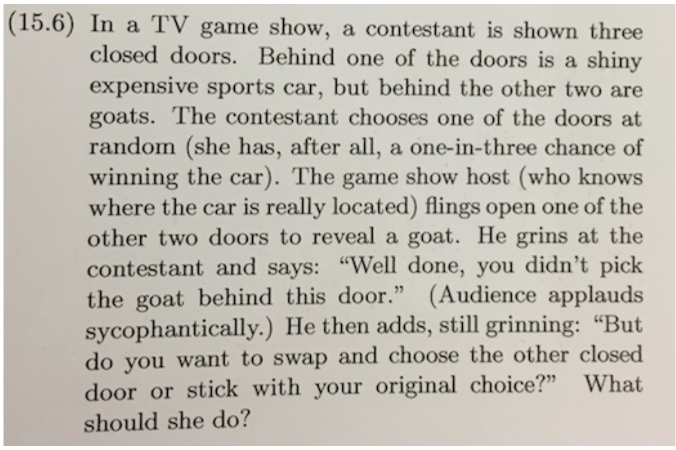
It is OK this week to hand this problem in during seminar if needed. I know some folks are taking the test late, and others are working on corrections.

Regular problems:

1: Bayesian Statistics

i) B&B Problem 15.6 (see copy below ... it may be missing in some editions)

Note: This B&B problem is done as example 3.15 in G&T. Feel free to use this as a guide, but also look at G&T Problems 3.23, 3.24. Problem 3.23 asks us to do the problem the “simple way”, by making a table and imagining our space of outcomes is reduced once the host opens a door. Let’s do the problem in this simple way, as well as the more elegant way using Bayes’ theorem. Problem 3.24, which asks us to answer assuming that the host was not informed, and picked the door which they chose completely at random. It happened to not have a car behind it. Let’s decide if in this case - an ignorant host - should the the contestant stick with their original choice, or switch to the remaining unopened door? ii) G&T Problem 3.25



(15.6) In a TV game show, a contestant is shown three closed doors. Behind one of the doors is a shiny expensive sports car, but behind the other two are goats. The contestant chooses one of the doors at random (she has, after all, a one-in-three chance of winning the car). The game show host (who knows where the car is really located) flings open one of the other two doors to reveal a goat. He grins at the contestant and says: "Well done, you didn't pick the goat behind this door." (Audience applauds sycophantically.) He then adds, still grinning: "But do you want to swap and choose the other closed door or stick with your original choice?" What should she do?

2: Grand canonical statistics and fluctuations in an ideal gas

G&T Problem 6.44

3: PV = 2/3 E the hard way

Do G&T Problem 6.19, but please feel free to specialize to the semiclassical particle case, where $\bar{n}(\epsilon)$ is described by Eq. (6.87)

4: 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?

5: 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 $Ƶ(T, V, \mu) = (1 + e^{\beta(\epsilon+\mu)})^M$
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.*

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

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

7: Chemical potential and ionization of hydrogen

B&B Problem 22.6

8: Condition of chemical equilibrium

Please write down the conditions of chemical equilibrium for the following reactions:
i) $e^+ + e^- \longleftrightarrow 2\gamma$
ii) $CH_4 + 2O_2 \longleftrightarrow 2H_2O + CO_2$