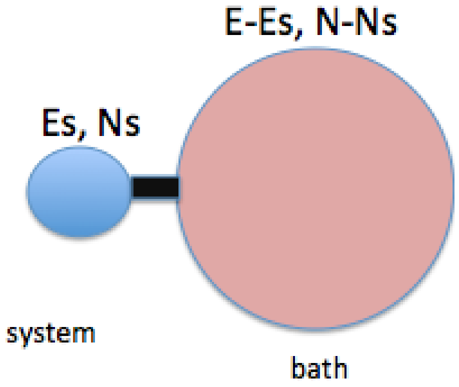
Physics 114 Statistical Mechanics Spring 2021
Week 8 Conceptual Overview

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 Ƶ you might first sum over all states for a *given* N_s and then sum over all possible N_s:

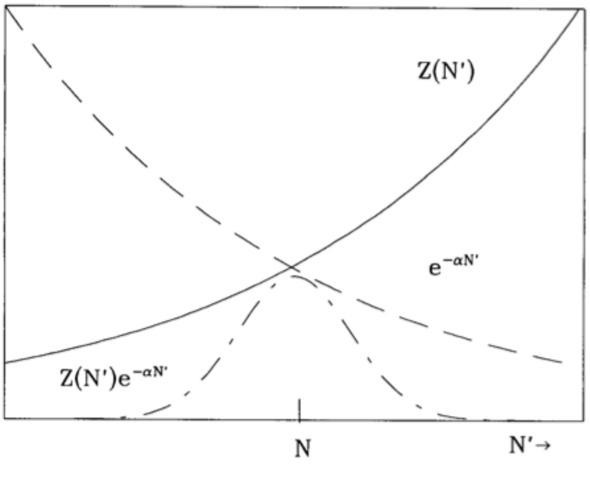
$$Z_G = \Sigma_{N_s} e^{\beta N_s \mu} \ \ \Sigma_{E_s, where\ s\ has\ N_s\ particles} \ \ e^{-\beta E_s}$$

- 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:

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

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

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

  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 problem this week.

- We will read B&B 6.3 and 6.4 soon. These do the explicit counting needed for bosons and fermions. Below is a nutshell summary which sets us up to use grand canonical stats as they are used in B&B 6.5 and 6.6... which is *the limit where semiclassical stats hold.*

- 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 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 $Z_G = \Pi_k Z_{G,k}$ where

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

  is the partition function for *one* quantum state with label k ... which could be occupied by n_k particles ... and we sum over n_k. When we read G&T Section 6.4, we'll see that it goes through the two cases (fermions, bosons) to deduce that

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

  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

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

- Theh equation abve was G&T 6.85. Currently relevant is semiclassical particles, where $\bar{n}_k$ is tiny. This is achieved in the limit that $e^{\beta n_k(\epsilon_k - \mu)} >> 1$. G&T call this the Maxwell-Boltzmann distribution in their Eq. (6.87). (I do find this 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 $g(k)$:

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

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

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

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

- *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
$$\mu_i(T,P,N_i) = \mu_i^o(T,P) - kTln(N_i/N) \tag{2}$$
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:
$$K = e^{-\Delta_r G^{\ominus}/RT} \tag{3}$$
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
$$\frac{d\ lnK}{dT} = \frac{\Delta_r H^{\ominus}}{RT^2}\ ; \quad or\ \frac{d\ lnK}{d\ (1/T)} = \frac{-\Delta_r H^{\ominus}}{R} \tag{4}$$

- 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.

- *Numberfluctuations* are discussed in G&T 6.11.1. These 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". To me, Eq. (6.235) does not have the right form.
  - Please do follow the logic that leads to Eq. (6.238), with the take-home message that $\kappa = \frac{1}{\rho kT}\frac{<\Delta N^2>}{<N>}$
  - Please do take home the message of Eq. (6.240), that $\frac{<\Delta N>}{<N>} \propto \frac{1}{\sqrt{<N>}}$