Physics 114 Statistical Mechanics Spring 2021
Week3 Conceptual Overview

Concept checklist from Readings:

- The idea of *free energy* is subtle; there are a couple of ways to describe free energy, and at first they seem to have nothing to do with each other. G&T tell us that in order to satisfy the first and second law for a *composite* made of system+bath:

  $$\Delta A = \Delta E + P_{bath}\Delta V - T_{bath}\Delta S \leq 0$$

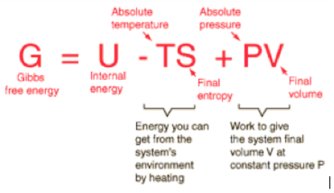
  The *availability*, ΔA is the energy *you* have to put in or get out in order to effect a change whose energy cost is ΔE . This is because you create (or destroy if $\Delta E < 0$) this amount of energy in contact with the bath. You provide ΔA and nature provides the rest, thanks to the the bath's *spontaneous* actions, in accord with the laws of thermodynamics.

- B&B says something very similar. Say that work $đW$ is done *on* the system ... where this work does not count the compression work $p_{bath}dV$ from the bath, which is written explicitly as a separate term. This work is always more than the change in A: $đW \geq dA$. In other words, when you do work *on* the system, *you have to do as much, or more work, than* dA. If there is work done *by* the system, then *the system's free energy will drop at least as much, and perhaps more, than the magnitude of the work it does*: $|\,đW| \leq |dA|$.

- When no work is done on the system, $dA \leq 0$ ... hence the system *minimizes* its availability. This suggests that availability can also be thought of as a *free energy* ... something that a system minimizes when it is allowed to come to equilibrium.

- The Helmholtz free energy, $F(T, V, N)$ is defined as $F = E - TS$. Here, E and S are averages chosen by the system at equilibrium, and T, V and N are fixed.

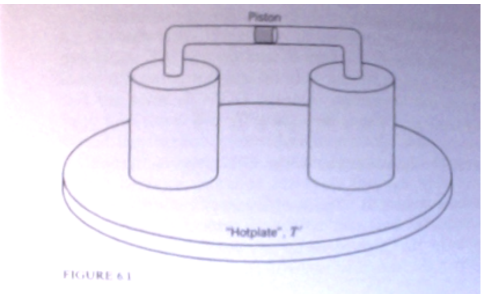
- Below is another one of Schroeder's magicians. U is the energy needed to create a rabbit at zero temperature in a vacuum. (Poor rabbit! Don't do it!) But G is the energy that the magician needs to supply to create the rabbit at finite temperature T and pressure P, assuming the rabbit has volume V.



- Yet another way to look at the different free energies: $F(T, V, N)$ is the *Legendre Transform* of $E(S, V, N)$. We know that $T = (\frac{\partial E}{\partial S})_{V,N}$. A Legendre Transform is $f(x) \to g(m)$ where $g(m) = f(x) - xf'(x)$. Thus $E(S, V, N)$ goes to $E - T(\frac{\partial E}{\partial S})_{V,N}$. We will hopefully get details about of Legendre Transforms in the intro to a problem this week.

- What does it mean for a free energy to be a minimum? If you remove an internal constraint, free energy it will decrease on its way to equilibrium. For example, if T, V, and N are constant, it is F that decreases. If T, P and N are constant, it is G that decreases. Entropy is weird just because of a sign difference: If E, V and N are held constant for a system, S tends to *increase*.

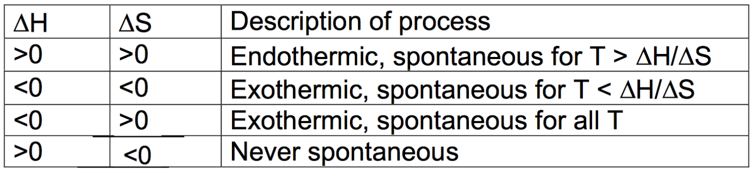
- Here is a good example involving F taken from Callen's Ch. 6: There are two subsystems, the L and R containers, and they share a bath, which is a hotplate beneath them. The combined volume $V_L + V_R = V$ is fixed.The plug cannot let energy or particles through, but it can move. This is a system with a constant total T, V, N, but it can adjust to have different amounts of V on the left or right. (We could play the game by letting the plug allow particles through instead, so N_L and N_R could adjust, but we won't do it now.) The plug will settle where the pressure between them is equalized: $P_L = P_R$. One can show



that $P = -(\frac{\partial F}{\partial V})_{T,N}$. One can thus argue that $F(T, V, N)$ is minimized when the plug is where it wants to be so the system is in equilibrium. Further, thermodynamic stability demands that also $(\frac{\partial^2 F}{\partial V^2})_{T,N} \geq 0$.

- The Gibbs free energy is $G = \mu N$, where μ is the chemical potential. In other words, μ is the Gibbs free energy per particle. (The generalization to a multicomponent system is also important ... we'll see this later.)

- Chemistry application: Chemical reactions. The sign of $\Delta H(S, P, N)$ tells you if a reaction is exothermic or endothermic. The sign of $\Delta G(T, P, N)$ tells you if a reaction will spontaneously proceed at a certain temperature T in a lab (so P is constant). Schroeder Ch. 5 talks about fuel cells and batteries. Though this is optional reading, we'll guide ourselves carefully through one of his problems this week. Hopefully, this is practical motivation for the seemingly arcane differences in thermodynamic potentials; all of chemistry and battery/fuel cell engineering depends on them!



ΔH	ΔS	Description of process
>0	>0	Endothermic, spontaneous for T > ΔH/ΔS
<0	<0	Exothermic, spontaneous for T < ΔH/ΔS
<0	>0	Exothermic, spontaneous for all T
>0	<0	Never spontaneous

- *Context is all.* Different free energies are useful for problem doing, and are minimized in different situations, where we hold different thermodynamic variables constant. For example, suppose we want a thermodynamic definition of temperature. Here are two, but the first is for a fixed P and the second for a fixed V system:

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad ; \left(\frac{\partial U}{\partial S}\right)_V = T$$

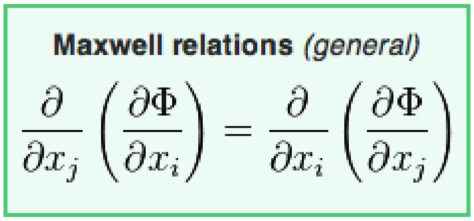
- Tables 2.2 in G&T and in section 16.4 of B&B are valuable summaries of how potentials are defined and their differential forms. Important thermodynamics potentials are *Helmholtz free energy* $F(T, V, N) = E - TS$, *Gibbs free energy* $G(T, P, N) = E - TS + PV$ and *enthalpy* $H(S, P, N) = E + PV$. There is also the *Landau potential* $\Omega = F - \mu N = -PV$ which will be less-used in what we do, until we get to Grand Canonical statistics.

- From the free energy definitions come differential forms, for example: $dG = -SdT + VdP + \mu dN$ and $dH = TdS + vdP + \mu dN$.

- From the differential forms of E, F, G, H, S and the fact that these are state functions, come partial derivative relations, for example:

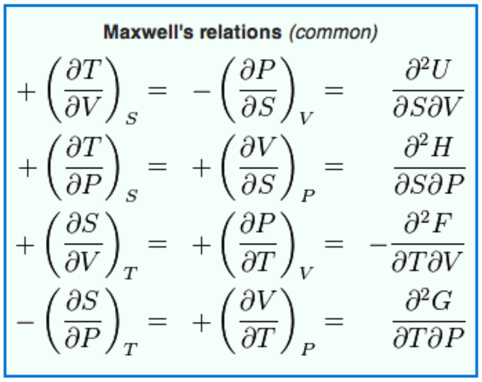
$$S = -(\frac{\partial F}{\partial T})_{V,N} \quad ; \; P = -(\frac{\partial F}{\partial V})_{T,N} \quad ; \; \mu = (\frac{\partial F}{\partial N})_{V,T}$$

- By equating *mixed second partial derivatives* of the thermodynamic potentials, we get the so called *Maxwell relations* . Below is the most general form for a Maxwell relation: Φ is a thermodynamic potential. The partials are taken with all other natural variables held constant.



Maxwell relations *(general)*

$$\frac{\partial}{\partial x_j}\left(\frac{\partial \Phi}{\partial x_i}\right) = \frac{\partial}{\partial x_i}\left(\frac{\partial \Phi}{\partial x_j}\right)$$



Maxwell's relations *(common)*

$$\begin{aligned}
+\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V} \\
+\left(\frac{\partial T}{\partial P}\right)_S &= +\left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial S \partial P} \\
+\left(\frac{\partial S}{\partial V}\right)_T &= +\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V} \\
-\left(\frac{\partial S}{\partial P}\right)_T &= +\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial T \partial P}
\end{aligned}$$

- Though you can see a table of Maxwell relations below, you should know how to derive them ... memorizing them is annoying. (Chemists sometimes use mnemonics :-) My way is to start with the differential form of a free energy, and take mixed partials as shown above. This is done in example 16.3 of B&B. *Optionally* for people who know about Jacobeans, reviewed in B&B Appendix C.9, there is an elegant alternative in the box on B&B p. 181.

- *Thermodynamic response functions* which are also called *generalized susceptibilities* are important. Useful ones are the *expansivity* which tells how volume changes with temperature, the *compressibility* which tells how volume changes with pressure, and *heat capacity* which tells how energy changes with temperature. The *bulk modulus* B is the inverse of compressibility.

- Here are definitions of these response functions:
  - compressibility $\kappa_X = -\frac{1}{V}(\frac{\partial V}{\partial P})_X$
    (If $X = T$, this is the "isothermal compressibility".)
  - isobaric volume expansivity $\alpha_P = \frac{1}{V}(\frac{\partial V}{\partial T})_P$
    (This is also called " thermal expansion coefficient". B&B uses symbol β not α.)
  - heat capacity: $C_X = T(\frac{\partial S}{\partial T})_X$

  Maxwell relations help us derive relationships between thermodynamic response functions.

- What happens to a real gas during different kinds of expansions or contractions? This is the subject of G&T 2.23.1 (in last week's reading, and the subject of a problem we did: G&T Problem 2.29) and also G&T 2.23.2 and B&B Ch. 27. We find out about three key cases:
  - **Free expansion:** Irreversible! Constant energy, but the temperature can change. It does this in a way controlled by the *Joule coefficient* μ_J. (It looks like a constant, but in general coefficients like this, like specific heats, are functions of T.) Its definition is: $\mu_J = -\frac{1}{C_V}((\frac{\partial P}{\partial T})_V - P)$ and it is the case that $\Delta T = \int_{V_1}^{V_2} \mu_J \, dV$.
  - **Isothermal expansion:** Reversible! Constant temperature, but the energy can change. Again the story is told by μ_J. B&B Eq. (27.11) can be rewritten as $\Delta U = -C_V \int_{V_1}^{V_2} \mu_J \, dV$.
  - **Joule-Kelvin expansion:** Irreversible! Constant enthalpy, but the entropy and temperature can change. Now the story is told by the *Joule-Kelvin* coefficient μ_{JK}. Its definition is:
    $\mu_{JK} = \frac{1}{C_P}((\frac{\partial V}{\partial T})_p - V)$ and it is the case that $\Delta T = \int_{V_1}^{V_2} \mu_{JK} \, dP$.

- *Note about the real world:* The Joule-Kelvin process is also known as "Joule-Thompson" or a "throttling process" b/c it happens when you push a fluid through a porous plug, or a narrow aperture known as a "throttle valve". The point is to obstruct the flow. In a car engine, the throttle is a valve that directly adjusts the amount of air entering the engine, controlling the fuel+air ratio, giving more or less power to the engine via the burning fuel. Throttling is important for liquifying gases for research, and also important to refrigeration and air conditioning systems. The circulating refrigerant is at medium temperature and high pressure when then it enters the throttling valve. Passing through the throttling valve, the pressure and the temperature of the refrigerant are reduced drastically. Afterward, it is able to do the necessary cooling within the fridge or room.

- The *Joule-Kelvin* process is a constant-enthalphy process. $H_{P\ high} = H_{P\ low}$ on the two sides of the porous plug or narrow throttle valve through which gas is being pushed from high to low pressure. While in a free expansion, we seek $(\partial T/\partial V)_E$, in throttling we want $(\partial T/\partial P)_H$. These are both equal to zero for an ideal gas - not so for a non-ideal gas. The Maxwell relations prove their utility by showing that the temperature may rise or fall depending on the size of the volume expansivity α. Please be sure you follow the argument leading to $T\alpha \geq 1$ implying the temperature *drops* for the gas during throttling.

- We define an *inversion temperature* T_{inv}, below which a real gas cools when it is throttled, and above which it warms. The Joule Kelvin coefficient, $\mu_{JK}(T)$, changes sign at that temperature: $\mu_{JK}(T_{inv}) = 0$