Reif's Statistical Physics Book, Berkeley #5 PhL 4.16.07

Chapter 1: macroscopic systems 2

Talks about the ways that some molecules can be positioned in a box with two sides. C(n) is the number of ways that n of N molecules are on the left side. Then $P_n = C(n)/2^N$ since 2^N is all the ways. Page 18 shows a different situation, removing a partition and letting molecules flow, notion of **irreversible**. Fluctuations. **Brownian motion** on page 34. Page 36 starts on idea of **heat**. We have our two sides (later systems) called **A and A'** with N and N' molecules. Notation is always **A* = A+A'.**

Key idea is that we should expect E/N = E'/N' meaning the average energy of a molecule on either side should be the same if we are in **equilibrium**. When A and A' are first put into contact, the average energies might not be equal, and it is heat Q that flows to make them equal. Some Q = ΔE flows between to two systems to make them have **ε = ε'**. We are going to relate the idea of "temperature" to ε and say that in equilibrium we have T = T'.

Page 40 starts into **ideal gases**. Simple argument gives nv/6 as flux hitting a wall, v = average. If each bounce transfers 2mv, we then have **pressure** $p = 2mv*nv/6 = mnv^2/3$. But $\varepsilon = 1/2mv^2$ so can write that p = (2/3) nε. Then computes a simple estimate for **mean free path** $\ell = 1/(n\sigma)$ where $\sigma = 4\pi a^2$ and a is the radius of our atom.

Chapter 2: Basic Probability Concepts 56

The **"statistical ensemble"**. Page 64 says sum of probs of all outcomes is 1. Additive rule for the **OR** of chances of two events. The multiplicative rule for **joint probability** which is the **AND** case, the assumption that the two parameters are "statistically independent".

Binomial distribution: p = probability of something for one particle, q = 1-p. Up down system: Let n = up, n' = down, N = n + n'. P(n) = probability that n of N are up = $C_N(n)\, p^n\, q^{N=n}$ where C is the usual committee selection factor, so we get result on page 70 for P(n). This is the binomial distribution. Page 76 and the notion of a **mean value** of some parameter, you weight it with probability over **ensemble**. Various results from simple statistics like **dispersion**, mean. Here are the key results:

μ_0 = mag moment of one spin, p = prob that spin is up, N = number of spins, find that:

$$M_{av} = N(p-q)\mu_o \qquad \Delta M = 2\sqrt{Npq}\ \mu_o$$

Now apply all this to ideal gas.

Chapter 3: Statistical Description of Systems of Particles

In **QM**, you can do a **particle in a 1D box** and find that $E = (\pi^2\ \hbar^2 / 2m)\ (n/L)^2$ where n is the quantum number and L is box length. In 3D result has last factor replaced with sum see p 105.

Accessible states. If a system is equally likely to be found in any of its accessible states, the system is in **equilibrium**. If not in equilibrium, tend to move toward equilibrium if isolated system. **State density Ω(E)** = states from E to E+dE. So writes Ω(E) = **ρ(E)**dE. Use **Φ(E)** as total states at or below E. The get ρ(E) = dΦ(E)/dE.

Now back to box. We know in 1D that if we pick some E with its n, then there are n states below that E, and we have $\Phi(E) = n(E) = (28)$ on page 120, then differentiate to get (29) for $\Omega(E)$. For 3D results are as shown in (31) and (32) page 121.

In the 1D case, get $\Phi(E) \sim \sqrt{E}$ and $\Omega(E) \sim 1/\sqrt{E}$, but in 3D it is $\sim \sqrt{E}$ and $\sim E^{3/2}$. But this is the state of one particle, so think of this as lower case $\phi(\varepsilon)$. In large set of particles, each has some average energy ε and some number of states $\phi(\varepsilon)$ below ε. Then $\Phi(E) \sim \phi(\varepsilon)^f$ where f is some huge number like Avogadro. General idea for $\phi(\varepsilon)$ is $\sim (\varepsilon-\varepsilon_0)^\alpha$ like our 1/2 or 3/2 for α. In the end he sets $\alpha = 1$ and gets roughly $\Omega(E) \sim (E-E_0)^f$. This is a HUGE power increase (but still not expo). Due to the power, ln is useful, and we get that $S(E) = k\ln\Omega(E) \sim f\, f \ln(E-E_0)$. With large f, this is very good approx.]

Page 123 shows that in general we expect both $\Phi(E)$ and $\Omega(E)$ to be **extreme power functions of E** for macroscopic collections of particles.

Page 130 has notion of thermal interaction between systems A and A', or **"adiabatic" interaction** where they are **insulated** (so dQ = 0 between A and A'). In this latter case, work can perhaps be done by A on A' for example with a piston effect. In *general*, you have $\Delta E = Q + W$ as the total energy that might be exchanged between A and A', a thermal amount and the adiabatic amount. This is the famous **dE = dQ + dW** of thermo. [And dW should include all kinds of work you intend, not just -pdV]

Chapter 4: Thermal Interaction p 142

As usual, systems A* = A + A' and we get the famous result $\mathbf{\Omega^*(E) = \Omega(E)\, \Omega'(E^* - E)}$, the multiplication just because for each state of A, you get certain number of states of A'. Then
$P(E) = C\, \Omega(E)\, \Omega'(E^* - E)$ and $\ln P(E) = \ln C + \ln\Omega(E) + \ln\Omega'(E^* - E)$. We know that both Ω and Ω' are super-steep functions of argument. Where does P(E) have its max value? [see sharp peak idea in page 145 figure] Set $d\ln P(E)/dE = 0$ and conclude:

max prob occurs when $\partial\ln\Omega'(E')/\partial E' = \partial\ln\Omega(E)/\partial E$ or $\mathbf{\beta'(E') = \beta(E).}$

Since $\beta = (1/\Omega)\partial\Omega/\partial E$, its units are 1/energy. Come up with some constant which has units of energy, like Boltzmann's constant k. Then write $1/\beta = kT$ where in some sense T is now dimensionless and we have

$$1/kT = \beta = \partial\ln\Omega(E)/\partial E \qquad \text{or} \qquad 1/T = k\beta = \partial[k\ln\Omega(E)]/\partial E = \partial S/\partial E$$

where $\mathbf{S \equiv k\ln\Omega}$ = the **entropy** of system A. So we have **just defined "temperature" and "entropy"** of system A in terms of the state density of that system. Note that S has energy units. So now the situation that puts our P(E) at maximum is that T = T' . We also have S* = S + S' from our S definition, so we know that <u>T = T' maximizes S*</u> . [So "temperature" is merely a function of the state density at some energy E. In fact we have $1/T = \partial S/\partial E$. Written $\beta = [\, \partial\Omega/\partial E \,] / \Omega$, we see that β is the percentage increase in state density as you increase E slightly. The $\beta = \beta'$ situation means that this percentage increase is the same in both the A and A' systems, and this is what maximizes $\Omega^*(E^*)$.]

From earlier rough estimates, claim is that kT is *roughly* the energy per degree of freedom.

Now (page 156) suppose Q which moves into A is very small (but adds to E). If we move some Q between A and A', what happens to S? We find $\Delta \ln\Omega \approx \beta Q$ just keeping linear term in Q, so $\Delta S \approx k\beta Q = Q/T$. We end up with our famous little rule that **dS = dQ/T** for the change in entropy due to heat flow into

a system. [Add a little heat, so E increases a little, more states are accessible, S increases. Little means that you don't change T very much with dQ.]

Section 4.5 talks then about the **"heat reservoir" idea**. A' = reservoir and A = some small system in contact with the **reservoir** (a large system at some temperature T'). Suppose A has energy E_r in some state r. Then P_r = constant * $\Omega'(E^* - E_r)$ for this one state of A. Expand around E* to get:

$$f(E^* - E_r) = f(E^*) + f'(E^*)(-E_r) + \text{order } (E_r)^2$$

where the reservoir is huge so $E_r <<< E^\bullet$. Then let $f(x) = \ln \Omega'(x)$ so have:

$$\ln \Omega'(E^* - E_r) = \ln \Omega'(E^*) - E_r \beta(E^*) \qquad \text{since } \beta = \partial \ln \Omega'(E')/\partial E'$$

Now this says $\ln [\Omega'(E^* - E_r)/\Omega'(E^*)] = -\beta E_r$ so $\Omega'(E^* - E_r)/\Omega'(E^*) = \exp(-\beta E_r)$

$$\Omega'(E^* - E_r) = \Omega'(E^*) \exp(-\beta E_r) \qquad \Rightarrow P_r = \text{const} * \Omega'(E^*) \exp(-\beta E_r)$$

which is to say that $\mathbf{P_r(E_r) = constant' * \exp(-\beta E_r)}$. This says that, as you increase E_r, the probability of system A having that energy decreases exponentially. As you steal energy E_r from the reservoir, its number of states drops a lot, and that is where the $\exp(-\beta E_r)$ is coming from. This is the **Boltzmann factor** and then $\mathbf{P_r(E_r)} = C \exp(-\beta E_r)$ is the **Boltzmann Distribution**.

The **first application** [p 163] is to consider a simple magnetic moment in B field situation where a given spin has one of two states, and we assume each spin is a system A, and the rest is system A' = the reservoir. Then we can easily compute $\langle \mu \rangle$ to be $\tanh(\Delta E/2kT)$ where $\Delta E = 2\mu_0 B$ in this case. If we then define $M = \chi B$, we come of with an actual derived expression for χ as in (65) page 166.

$$\chi = N_o \mu_o^2/kT \qquad \text{and this is } \textbf{Curie's law}$$

The **second application** [p 166] is our friendly ideal gas in 3D, monatomic. [In this situation, system A is a single molecule, system A' is the rest of the ideal gas which acts as a heat reservoir. The system A of a single molecule then has $E_r = \varepsilon_r$.] We know that the energy of a molecule state is given by (68) in terms of the quantum numbers, and then P_r is in (67). We later will learn how to turn the crank and get a useful result.

In fact that comes right now! Suppose we want to **compute mean ε_r** of a molecule in our 3D mono gas. This of course involves P_r which we have been talking about all this time, and we have (72). Then using the usual trick, we get ε_r written as derivative of **partition function Z** defined in (73), and shown for gas in (75). Reif shows how to evaluate Z and we end up with (83) which says $\langle \varepsilon \rangle = (3/2)$ kT, and we can see how we got 1/2 kT from each of the 3 dimensions.

Next, Reif computes the **mean force on a wall** of the 3D gas box using (88) which again involves P_r and he ends up with (90) for this force. Divide this by box-end area and you get **p = nkT** which is the famous **ideal gas law**. The pressure is linear in density and temperature.

Now you can write $N = \upsilon N_a$ where υ = number of moles and N_a is Avagadro. Then

$$\langle p \rangle = nkT = (N/V)kT = (\upsilon N_a/V)\, kT = (N_a k)\, \upsilon T/V = R\, \upsilon\, T/V \qquad \text{so } \mathbf{pV = \upsilon RT}.$$

This $\mathbf{R = N_a\, k}$ is just called "**the gas constant**". For fixed T, get pV = constant, Boyle's Law.

Comment: in these applications, we get to use the Boltzmann Distribution because we can regard each micro system like a molecule or spin as being in contact with a thermal reservoir consisting of all the other micro systems in the container.

Chapter 5: Microscopic Theory and Macroscopic Measurements p 192

Comments about absolute 0 and ideas that $E \to E_0$ and $T \to 0$ and $S \to 0$.

Next topic page 202 is dW = -pdV. The comes heat capacity $C = (dQ/dT)_y$ which is to say, how much Q to you add to change by dT, with parameters y held constant.

Now, for mono gas we know that $E = (3/2)kTN = (3/2)T\upsilon R$, so if we add dQ as small amount of E, and hold volume fixed so can do no work, then dE = dQ and $C_V = (3/2)$ R for one mole. So we get all the famous ideal gas results by trivial fiddling.

Page 201 mentions the **quasi-static** idea: think pdV piston motion. If you move it very slowly relative to time it takes for system to equilibrate, then always arbitrarily close to equilibrium and then you can use equilibrium results like the ideal gas law all the time. If you jerk the piston, there will be waves and other effects that lead to generation of heat more than the quasi-static process generates.

Chapter 6: Canonical Distribution in the Classical Approximation p 224

Question: in a non-quantum (classical) system, how do you count states near energy E? If a continuum, then always infinite. Solution is to divide up your energy function of p,q into little **phase space** squares of arbitrary but small dimension h, then you say like this:

$$P(q,p)\, dpdq = C \exp(-\beta E(p,q))\, dpdq$$

and you determine C such that $\int P(p,q)dpdq = 1 = C \int \exp(-\beta E(p,q))dpdq$. Of course this all depends on the details of the function E(p,q), and obvious how to extend to multiple dimensions.

Application: ideal gas has $\varepsilon = \mathbf{p}^2/2m$ where **p** is a vector. But p = mv, so express in terms of v instead, since this is usual **Maxwell Distribution form**, and you get $P \sim \exp(-\beta mv^2/2)$. Integrate over volume constant, so really $Pd^3v = P(v)d^3v = C * \exp(-\beta mv^2/2)d^3v$ and I know how to do this Gaussian integral and I could evaluate C. He defines f(v) as distribution such that integral gives density n(molecules/cm^3) and we end up with result 21. Argues that this applies for molecules as well, where you treat p,q as applying to the entire molecule in obvious manner, and the internal degrees of freedom pass just get into the constant.

Calculations: computes $g(v_x)dv_x$ and gets $C' \exp(-\beta mv_x^2/2)d^3v$. These are **Normal** or **Gaussian** distributions, the σ is shown page 235, increases with $\sigma = \sqrt{kT/m}$. If you want the ***speed*** **distribution**, you get the extra factor of v^2 in the usual solid angle integration manner, so no longer a Gaussian function exactly, have this power in there, see graphs page 238. If you set derivative to 0, you get the speed of the curve peak which is the "most probably speed".

Reviews the **classical limit conditions**, so need large T, large m, small n. Then talks about how you might do an experiment to measure the distribution!

Page 246 starts on the **equipartition theorem**. You assume that your energy function has the special form shown in (23) [for a given particle i] where E' is not a function of p_i. In this case, you get a nice

cancellation and if you compute the mean energy ε_i you get (45) which can be transformed using the usual log trick into a sort of partition function form (46). Then we assume further than the ε_i term is **quadratic**. In this case, a variable change to y shows that $<\varepsilon> = -\partial/\partial\beta\ [\ -1/2\ \ln\beta\ ] = kT/2$! Now suppose you had 3 quadratic terms in (47) instead of the one shown. You would get the product of three equal integrals, and end up with $\beta^{-3/2}$ and then -3/2 lnβ and then 3/2 kT. The general conclusion is that each quadratic term in the energy for a particle (or system) contributes 1/2 kT and this is the equipartition theorem. Each quadratic term is called a **degree of freedom**.

The Maxell distribution predicts a certain σ for the v_x curve which peaks at 0, so the theory predicts the Brownian motion. Another example is the **harmonic oscillator** with 2 quadratic coordinates, so get ε = kT. You can model the energy of a solid as a sum of harmonic oscillators and get the fact that ε = 3kT so then $\mathbf{c_V = 3R}$ ~ 25 in mks units. Table shows this is a reasonable estimate for many elemental solids, but not for diamond. As shown p 255, diamond has a very large spring constant so this pushes it out of the classical limit at room temperature.

Chapter 7: General Thermodynamic Interaction p 266

Reif now adds, in addition to energy, some arbitrary extra parameter x, and defines a **generalized force X** that goes with it. Then dW = X dx = work, and $-\beta X = [\partial \ln\Omega/\partial x]_E$, but we also have $X = \partial E_r/\partial x$. Notice that $-\beta X = (1/k)(\partial S/\partial x)_E = -X/kT$ so $X = -T\ (\partial S/\partial x)_E$

One example is x = volume V, then -X = pressure p, and then $p = T(\partial S/\partial V)_E$. [Another example is X = voltage V and x = charge q, so Vdq, again has units of energy.]

Reif now shows that if you do little differential changes like dx, meaning quasi-static change, and if you are adiabatic so dQ = 0 (insulated) then he has already proven that dS = 0 ! So it is possible to do a smooth change and not increase entropy.

On page 272 we sort of start over thinking of things as functions of E and V, an example of an **extra parameter**. We look for the maximum of the lnΩ* function of E as before and find that you will be at it if *two conditions are met*: A and A' have the **same T and the same p**! You then have thermal and mechanical equilibrium.

Next, Reif shows that dS = dQ/T even when you have an extra parameters x_i. This just follows really from the fact that dQ = dE - dW. Again, you have to be **quasi-static** to get this. So:

$$dQ = dE - dW \quad => \quad TdS = dE + pdV$$

The main thing here is that if you allow some dQ to happen, you are increasing your entropy by dS.

Example 1: Reif computes the entropy S of an ideal gas by throwing in c_V to get desired forms. The result is the integral (48) on page 278. If c_V is a constant, you get a simple result (50).

Next, he derives the **"adiabatic gas law"** which is (56) on page 280, all quasi-static. The result is much different from the reservoir constant T result which is shown in (58), ie, a different V power. The adiabatic law applies to sound wave compressions if frequency high enough so any little volume dV changes so fast that there is not time for a dQ. This lets you measure the power γ.

Now finally we are going to state the three **laws of thermo**:

(0) If A eq B and B eq C, then A eq C thermo, so you can have the notion of a "thermometer".

(1) If A is isolated, E = constant. Otherwise $\Delta E = W + Q$ = work done on it + heat added to it. This law is really just conservation of energy.

(2) For quasi-static, $dS = dQ/T$, otherwise $\Delta S \geq 0$. T is called the absolute temperature. For an isolated system, macrostate changes result in $\Delta S \geq 0$ because system always moves to macrostate which has more accessible states. That is $S = k\ln\Omega$. This would be a non-equilibrium change since system is not in the most probably state when you start.

(3) As $T \rightarrow 0$, $S \rightarrow$ some S_0.

(4) From our definition of S, we can write **probability ~ $e^{S/k}$** . I think this idea was discovered before any microtheory existed in terms of number of quantum states.

Now, on to page 288 where we now have a reservoir which stabilizes both temperature and pressure as shown in the figure. It is easy to compute ΔS^* as in (75). If we define the **Gibbs free energy** as shown, which is G = E - TS + pV, then we get $\Delta S^* = -\Delta G/T$. So if we want to max S^* , we want to **minimize G**. This is boxed on page 291, and is very general!

Now, in (71) we claimed that $P(y) = P(y_0) \exp(\Delta S/k)$ where $\Delta S = S(y) - S(y_0)$. So now with our G definition we get $P(y) = P(y_0) \exp(-\Delta G/kT)$ where $\Delta G = G(y) - G(y_0)$, so we get $P(y) \sim \exp[-G(y)/kT]$ and this then shows that we max P when we min G.

[Comment: Reif has omitted to say something that cost me lots of time. The Gibbs Free Energy has that name because it is the max amount of work that can be extracted from a system. I have shown this now elsewhere, and this relates to electrochemistry.]

Reif on page 294 looks at a system A (in touch still with reservoir T,p) but which has **two phases**, like water and water vapor. He defines g_i as the Gibbs free energy per molecule in phase i. He then shows what you might expect, that equilibrium means $g_1 = g_2$ so when molecule changes phases, total G does not change and you are at the min of G. [And this is a key idea for **chemical reactions**.]

Next, we consider a **phase diagram** with a boundary between two phases drawn in p,T space page 294. The curve itself is determined by the **Clausius-Clapyron equation** (92) which Reif derives here using just what we know so far. If we change a chunk of stuff from phase 1 to phase 2, we get $\Delta S = dQ/T$ where dQ is now the **latent heat of the phase change** (which went into the reservoir). So we get (95). If we assume a constant latent heat L, we can integrate to get (98) which shows how **vapor pressure** in a liquid-gas system depends on L and on T.

Next he comments that you can reduce the entropy of system A only if you at least compensate by increasing entropy in S'. You can increase order locally in this manner.

Page 302 then starts into **"engines"**. The workable plan is shown page 303 where you extract heat from a higher temperature T region, and exhaust it to a lower temperature T' region. Some of the heat extracted from the T region can be converted to work, and the efficiency limit is given in (108). So you want $T' << T$ is possible. Need quasi-static to get close to theory.

Now finally Reif actually has a **biochemistry example**! He points out that chemical reactions all have constant T and pressure p, so they fit right in with the Gibbs free energy stuff. His example is making sucrose as shown. The reaction has a positive ΔG so won't want to go. But if you **couple** it with ATP $\rightarrow$ ADP, you can make it go. That is his only point. He quotes ΔG values as .24 eV at standard 1 molar concentrations.

Remember that G really does have units of energy so OK to use eV. This might be a per-molecule of reaction energy amount.

Chapter 8: Kinetic Transport Processes p 318

This is about viscosity, diffusion, conductivity and so on. I skip it for now.

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Now, I want to apply the above to understand the presentation on this web page:

http://en.wikipedia.org/wiki/Nernst_equation

This was the entire motivation for today's review of Reif's 300+ page book.