Physics 114 Statistical Mechanics Spring 2018
Seminar 5

Overview:

This is a big week, where we begin to do statistical mechanics in earnest. We talk about thermodynamic quantities, but they are all derivable from fundamental statistical arguments. One major topic this week is the statistical definition of entropy. Section 14.8 of B&B calls $S = -k\ P_i\ lnP_i$ the *Gibbs entropy* of a thermodynamic system. B&B Ch. 15 defines the *Shannon entropy*, which applies beyond thermodynamics, to fields like cryptography, data compression and quantum mechanics.

Another major concept is the *partition function.* Partition functions are "just" a normalizing factor ... but this is a crucial thing. We need the right normalization when taking thermodynamic averages. By counting states, the partition function and its derivatives tell us every thermodynamic quantity we might want to know.

We'll discuss 2 kinds of sets of states. (A set of states is an *ensemble.*) The first is the *Microcanonical ensemble*, in which E, V, N are the fixed quantities. Though sometimes people don't call it a "partition function" the total number of micro states, $\Omega(E, V, N)$, plays an equivalent role in this ensemble. The other is the *Canonical ensemble*, in which T, V, N are the fixed quantities. Such a system would have solid, diathermic walls and be immersed in a heat bath. In the canonical ensemble, the partition function is commonly written as $Z(T, V, N)$. The Canonical partition function is such a big player in stat mech that we will continue to study it next week. This week, we will use it for two important purposes: deriving the law of *equipartition of energy* and for the *Maxwell-Boltzmann* distribution of velocities.

Required Reading:

G&T Sections

- Section 3.4.2

- Sections 4.2-4.6

- Sections 6.1, 6.2

B&B sections

- Sections 4.1-4.6

- Sections 5.1 and 5.2 *(Optional - but good for experimentalists: 5.3)*
- Sections 14.5-14.8
- Section 15
- Section 19

Recommended Reading:

- The regular reading is so long, I hesitate to suggest anything else. For whenever you have time and interest, there are some very readable papers on information entropy linked to our Moodle Site.
- The original link to Claude Shannon's paper in information entropy is here: `http://math.harvard.edu/~ctm/home/text/others/shannon/entropy/entropy.pdf`

Concept checklist from Readings:

- This week, we do just a bit more with basic probability theory: *Bayes theorem*. Suppose there are multiple independent, exclusive outcomes of an experiment, $\{A_i\}$. B is anything else we know (a single outcome, a condition involving multiple outcomes, ...). A true statement is that $P(A_i \textit{ and } B) = P(A_i|B)P(B) = P(B|A_i)P(A_i)$. Bayes theorem is these last two equalities, re-written as:

  $$P(A_i|B) = \tfrac{P(B|A_i)P(A_i)}{P(B)}$$

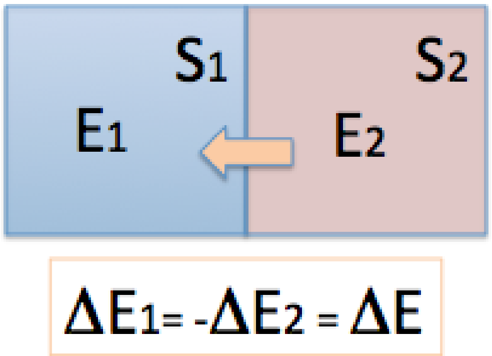
  This theorem can be counterintuitive but is very useful. Examples are found in G&T section 3.4.2 and B&B section 15.6.
- It is worth repeating from last week, that here are the methods of stat mech:
  - Specify macrostates and the microstates that contribute to each macrostate.
  - Choose the *ensemble*. This is a collection of identically-prepared systems, like the different trials from probability theory. For example, if energy is the same for all members, this is called the *microcanonical ensemble*
  - Calculate statistical properties.

- B&B Ch. 4 begins with a review of the 0^{th} law of thermo: Thermal equilibrium and thermometers exist. It also reviews macro and micro states with coin-counting examples.

- B&B Ch. 4 then synthesizes a great new idea from material in earlier weeks. Consider two systems in thermal contact as below. Earlier, when we were purely doing thermo, we made an ad hoc definition of temperature as the thing that is equal when $S = S_1 + S_2$ is maximized:

$$dS = 0 \quad => \quad \frac{1}{T_1} = \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} = \frac{1}{T_2}$$

  Now, informed by stat mech, we can do better. We use definition that $S_i = k \; ln\Omega_i$. Thus $S = S_1 + S_2$ is maximized when $\Omega = \Omega_1\Omega_2$ is maximized. This happens for the Ω which is largest ... it embraces the most microstates for the combined system. This is equilibrium! So finally, the new idea this week - this *statistical definition of temperature* for any system i with energy E_i:



$$\frac{1}{kT_i} = \frac{\partial ln \; \Omega_i(E_i)}{\partial E_i}$$

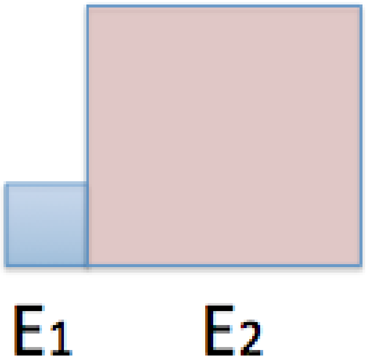
- This "statistical basis for entropy" is also discussed in B&B section 14.5. The bottom line is that

$$\frac{1}{T} = \frac{d \; (k \; ln\Omega)}{dE} = \frac{\partial S}{\partial E}$$

- G&T section 4.2 is about the *Einstein solid.* Two Einstein solids, A and B, with fixed numbers of energy-storing particles, N_A and N_B, are brought into thermal contact. This example is a concrete illustration of the idea of B&B section 4.4. Namely, equilibrium corresponds to a maximum in the entropy $S(E_A, E - E_A, N_A, N_B)$ for given E, N_A and N_B.

- We can further explore (via theory and simulation) fluctuations around the equilibrium value $\bar{E}_A$. There are two things that might be large in an Einstein solid: the total energy E and the number of oscillators, N. One or both of these needs to be large in order for us to claim that stat mech works for this system.

- G&T then goes on about counting states ... but we postpone that and now mention *ensembles*, as introduced in B&B 4.5 and 4.6. The *Canonical ensemble* is one where the system we care about is tiny, compared to the huge other system. They can exchange thermal energy (but not particles). E is conserved for the combination of the two, and we ask about the energy of the tiny system. The huge system hogs the energy because it can use energy to create more microstates than can the tiny system. For example, suppose they were set up each with half the total energy. They would be out of equilibrium since: $\Omega_1(E/2 - \Delta E)\Omega_2(E/2 + \Delta E) > \Omega_1(E/2)\Omega_2(E/2)$.



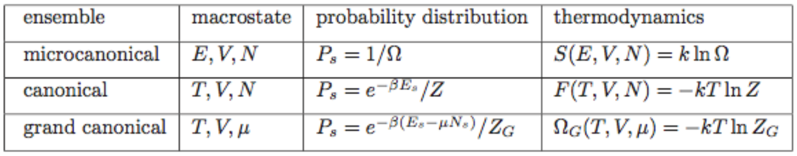
- What is the *Canonical ensemble*? It is an ensemble (group) of systems that are reflective of equilibrium. The probability $P(E_s)$ that any system has energy E_s is correct, given its temperature T equals that of the bath. G&T section 4.6, and B&B section 4.6 make the same argument (different notations unfortunately :-(The probability that the tiny system holds energy E_s is:

$$P(E_s) \propto e^{-E_s/kT} = \frac{1}{Z}\, e^{-E_s/kT}$$

where $\frac{1}{kT} = \frac{dln\Omega_b}{dE}$ ... the statistical definition of temperature. The heat bath maintains the small system and itself at a fairly steady temperature T by virtue of its hugeness. At the end of Section 4.6, B&B bring up the example of two Einstein solids, one huge (bath) and one tiny (system), as an example of canonical statistics.

- A *notation* everyone uses is $\beta = \frac{1}{kT}$.
- In the expression $P(E_s) \propto e^{-E_s/kT} = \frac{1}{Z}\ e^{-E_s/kT}$ the quantity Z is called the *Canonical partition function.* It shows up innocently as a normalization. But really, as we will emphasize next week, it is the *key to all of equilibrium stat mech*, for a system of constant N and V in contact with a bath at temperature T.
- Last week, we read that the method of *Lagrange's undetermined multipliers* is a clever way to maximize a function subject to a constraints like normalization, and it works for multiple constraints. Last week we had a problem about a loaded die, where the mean value of the die, $\bar{n}$ was a second constraint. In Example 14.7 of B&B (p. 152), a very similar second constraint is applied: the mean of the energy is known. This leads us back to Canonical statistics. Another name for the canonical probability distribution is the *Boltzmann distribution* of states: $P_j \propto e^{-\beta E_J}$.
- The Boltzmann distribution can be applied, as in G&T section 6.2.2 and 6.2.3 to gas velocities. In that case, it is often known as the *Maxwell-Boltzmann (MB) distribution* and the speed distribution $p \propto v^2 e^{-mv^2/2kT}$ is called a *Maxwellian.*)
- Ch. 5 of B&B is a short, excellent reference for the MB distribution of velocities.
- We can also apply the Boltzmann distribution to derive the beautiful *equipartition theorem.* This is done in G&T section 6.2.1 and B&B Ch. 19. This presumes particles are classical; it breaks down for low enough temperatures. On the other hand, if $kT >> \Delta E_q$, where ΔE_q is a typical separation between quantum levels, then equipartition applies. In this case, every squared "degree of freedom" in the Hamiltonian gets $\frac{1}{2}kT$ of energy.
- Please be sure that you can use equipartition to find how much energy, on average, is contained in
    - a single harmonic oscillator
    - a solid with N atoms (modeled as harmonic oscillators :-)
    - a mole of monatomic gas
    - a mole of diatomic gas
- A system like two same-size boxes of gas, isolated from the world, would be a member of the microcanonical ensemble. On the other hand, a tiny box within a big bath would be a member of the canonical ensemble. In any ensemble, one wants to know the *partition function.* Table

4.9 of G&T is a good summary. We see the natural variables written in $\Omega(E, V, N)$ and $Z(T, V, N)$ respectively; these are the microcanonical and canonical partition functions. (Math note: It's a *Legendre transform* taking us from E to T .)



ensemble	macrostate	probability distribution	thermodynamics
microcanonical	E, V, N	$P_s = 1/\Omega$	$S(E, V, N) = k \ln \Omega$
canonical	T, V, N	$P_s = e^{-\beta E_s}/Z$	$F(T, V, N) = -kT \ln Z$
grand canonical	T, V, μ	$P_s = e^{-\beta(E_s - \mu N_s)}/Z_G$	$\Omega_G(T, V, \mu) = -kT \ln Z_G$

Table 4.9: Summary of the three most common ensembles. P_s is the probability that the system is in microstate s.

- G&T section 4.5 shows us that we can talk about two systems using the micro canonical ensemble, and do the counting to find the way energy divides between them in equilibrium. This leads us to this $S(E, V, N)$ for a monatomic ideal gas:

  $$S(E, V, N) = Nk[ln\frac{V}{N} + \frac{3}{2}ln\frac{mE}{3N\pi\hbar^2} + \frac{5}{2}]$$

  Now we aren't limited to merely knowing ΔS between two states ... we have an absolute entropy. Some good things we can do with it:

  - Take partial derivatives w.r.t. E, V and N to find T, P and μ. '
  - Derive $PV = NkT$
  - Derive $E = \frac{3}{2}NkT$
  - Swap T for E to get another expression for entropy: $S(T, V, N)$ which is called *Sackur-Tetrode*
  - Use $S(T, V, N)$ to confirm the third law of thermodynamics

- Things that you can get from the Canonical partition function (a partial list ... we will get more next week):

  - The expectation value of the *energy*: $\bar{E} = -\partial\ lnZ/\partial T$
  - The expected size of mean squared *fluctuations in the energy*:

    $$< E^2 - \bar{E}^2 >= kT^2 C_V$$

    This is pretty interesting. First off, it's an example of a "fluctuation-dissipation" theorem; these occur in other places in physics. Also, it's a way to find heat capacity, without adding any heat to a system! Just measure the natural fluctuations ... the larger they are, the bigger the heat capacity!

- Let's write some definitions for Z because they capture subtle things that are easy to get wrong:
  - If we use a label α to signify a microstate, then

    $$Z = \Sigma_\alpha E^{-\beta E_\alpha} \tag{1}$$

  - If a macrostate whose energy is E_J has got multiple microstates , we need to count them ... to find the *degeneracy* g_J. Then we can write:

    $$Z = \Sigma_J \; g_J E^{-\beta E_J} \tag{2}$$

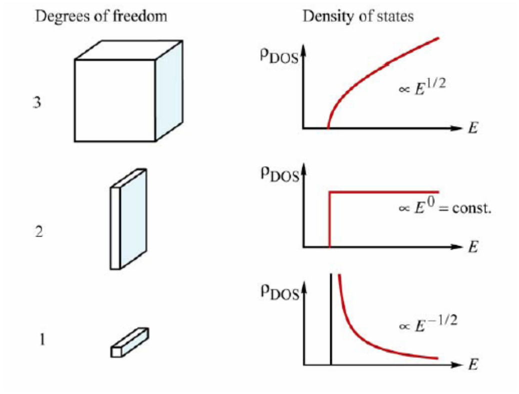
    Please note that Eqs. (1) and (2) are *calculating the same thing in two different ways.*
  - Sometimes energy is a continuous variable. Even if discrete, sometimes energy states are so closely spaced that there is a huge number in any interval ΔE we could measure. An example is the *semiclassical ideal gas.* In this case, the degeneracy is called the *density of states* g(E). This is much like last week when we had probabilities, $p(x_i)$ for discrete variables x_i, and probability densities $p(x)$ for continuous variables. In the continuous case:

    $$Z = \int g(E) e^{-\beta E} dE$$

  - In order to count states for the quantum particle-in-a-box (ideal gas atom) we often go through the stage of counting the allowed wave numbers, k, that fit in the box of length L in 1d (or area L^2 in 2d or volume L^3 in 3d). The way to translate between these two representations of states is:

    $$\hbar^2 k^2/2m = E \;\; thus \;\; \hbar^2 k/m \; dk = dE \; . \;\; Also \;\; g(E)dE = g(k)dk$$

  - Formulae are derived in your book, and the gist of our counting is shown in this picture:



- Other aids to counting are to calculate not $g(E)dE$, which is like a probability distribution function, but $\Gamma(E)$, is like a cumulative distribution function: $\Gamma(E) = \int_0^E g(E)dE$. Thus, $\frac{d\Gamma(E)}{dE} = g(E)$ This is not just a counting aid ... typically $\Gamma(E)$ is so huge that taking $ln\Gamma$ is equivalent to taking $ln\Omega$, but this is minutia.

- Z(T,V,N) is the partition function for N particles, but we read a lot about the *single particle partition function.* Why care about one particle? Because if we have N distinguishable particles, it is the case that

$$Z(T,V,N) = Z(T,V,1)^N \;\; distinguishable \;\; particles$$

- In a related way, if we have two completely different degrees of freedom (like A = rotations and B = translations) then partition functions just multiply

$$Z = Z_A \; Z_B$$

- What about N indistinguishable particles?
  - The *right way*: Find out if they are bosons and fermions and do the correct counting arguments
  - The *not-totally-right way*: This works for classical ideal gasses, and in fact it is essential to get the entropy of mixing correct:

$$Z(T,V,N) = \frac{1}{N!} Z(T,V,1)^N \;\; dilute, \; semiclassical \;\; particles$$

  This approach is predicated on the idea that there are so many states, and so few particles (N is few? Well ... N is few compared to the number of available quantum states.) that it would be extremely unlikely to find any two particles occupying the same quantum state.

- For semiclassical particles (now we are being more general than just talking about ideal gasses) G&T Section 6.2 tells us that we can cut through all the "particle in a box" counting. There is one quantum state per "box" of size $dxdp/h$. To find Z amounts to taking an integral over $x_1, y_1, z_1, x_2 .... p_{x,1}, p_{y,1} ...$. We integrate over the $3N$ coordinates of N particles in $3D$. Thus

$$Z_{N,classical} = \frac{1}{h^{3N}\ N!} \int e^{-\beta E(x_1, y_1, ..., p_{y,N}, p_{z,N}) dx_1, ..., p_{z,N}}$$

- How do we know a gas can be treated semi classically? For this, we calculate the *thermal deBroglie wavelength*, $\bar{\lambda}$. If this is much smaller than the mean distance between particles, the semiclassical limit is good.

- G&T section 3.4.1 (last week's reading) said that *uncertainty* in a system with probabilities $\{P_i\}$ can be characterized by a function $S(\{P_i\}) = -\Sigma_i P_i ln(P_i)$. In the special case that $P_i = 1/\Omega$ for all i, one has $S = ln\Omega$. This week, we read in B&B 14.8 that inserting a k to get units right, this is the *Gibbs expression for entropy*: $S = -k\Sigma_i P_i ln(P_i)$.

- In the context of information theory, $S =< Q >= -k\Sigma_i P_i ln(P_i)$, where Q is the information content of a statement. In B&B section 15.1, this is called the *Shannon entropy*. We have some recommended readings as well as B&B Ch. 15 which talk expand on how entropy relates to encoding information, as applied data compression, quantum information, and more.

- *Entropy of mixing* hearkens back to the red and white beans I showed in Week 1. B&B Ch. 14 shows that two distinguishable gasses, totaling N molecules and initially occupying volumes xV and $(1-x)V$, when mixed in volume V, experience this change in entropy:

  $$\Delta S = -Nk\ [x\ lnx\ +\ (1-x)\ ln(1-x)]$$

  G&T section 6.1 shows us how it is the case that identical particles have $\Delta S = 0$, as it should be :-)

- *Maxwell's demon* can't exist. If he/she could, the 2nd law of thermo would crumble. We also read that even a cyber-demon can't do the job of reversing an irreversible process. It would increase the entropy of the universe whenever it destroyed information, e.g. to erase files on its hard drive. Entropy and information are deeply intertwined in our universe!

Presentation: Entropy

Tell us about different definitions entropy we encounter in the reading (statistical, thermodynamic, Gibbs, Shannon, ...) Are they all talking about the same quantity? xkcd thinks not ... see `https`://xkcd.com/1862/ . Once you have covered the basics, if you would like to branch out (say talk about data compression? See some references I've put on our Moodle site ...) go ahead. Just please be mindful of our very limited time this year ... 15 minutes is a good length for a presentation!

Warmup Problems: *Due Monday ideally ... Tuesday OK*

1: Demon thermometer and ideal gas: G&T problem 1.8 parts (a), (b), (c), (d), and (g)

2: Statistical definition of entropy
B&B Problem 14.8

Regular problems:

1: Counting states for gas particles in a box
i) G&T Problem 4.11
ii) G&T Problem 4.14

2: Einstein solids in thermal contact G&T Problem 4.7

3: An isolated Einstein solid: G&T Problem 4.22

4: Relative abundance of isomers: G&T Problem 4.24

5: Maximizing the Shannon entropy B&B Problem 15.3

6: Semiclassical limit of ideal gasses
i) G&T Problem 6.2
ii) What is the thermal deBroglie wavelength, $\bar{\lambda}$, for nitrogen N_2 gas at room temperature? At what density, ρ would room temperature nitrogen need to be treated with quantum mechanics? At this temperature and atmospheric pressure, is nitrogen a solid, liquid or gas?

7: Entropy of mixing G&T Problem 6.9

8: Equipartition
i) B&B Problem 19.5
ii) G&T Problem 6.47

9: Maxwell-Boltzman velocity distribution
G&T Problem 6.11

10: Maxwellian speed distribution
G&T Problem 6.12

Optional: Bayesian Statistics
i) G&T Problem 3.25
ii) See example 15.6 in B&B and also at the"Let's make a deal" (Monte Hall) problem of example 3.15 in G&T. Can we challenge ourselves to do these problems two ways? First, the more simpleminded way of considering how the sample space changes as we receive prior info. Second, using the formalism of Bayesian statistics?