Physics 114 Statistical Mechanics Spring 2021
Week 5 Conceptual Overview

Concept checklist from Readings:

- *Conditional probabilities* are needed where experimental outcomes are *not independent*, as they relate to the question we ask. For example, suppose we toss two dice, look at the first but not the second, and ask about the sum of the values shown. The first die has value x_{seen}. Call this outcome Event B. We could ask for the probability that the total value shown on both die, $x_{seen} + x_{unseen}$, is greater than 7. Call this outcome Event A. What is $Prob(A\ occurs,\ given\ that\ B\ occurs)$? This is written $P(A|B)$. In general, $P(A|B) \neq P(A)$. This is because the information we received from Event B is meaningful. For example, it is more likely for the total to exceed 7 if Event B was $x_{seen} = 6$, as opposed the $x_{seen} = 2$.
- The completeness of our sample space implies
  - $P(A) = P(A|B) + P(A| \dashv B)$
    where $\dashv B$ is the situation where outcome B does *not* occur.
  - $P(A\ AND\ B) = P(A|B)P(B) = P(B|A)P(A)$
- *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
  $P(A_i\ and\ B) = P(A_i|B)P(B) = P(B|A_i)P(A_i)$. Bayes theorem is these last two equalities, re-written as:

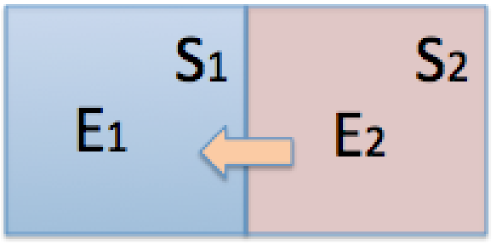
  $$P(A_i|B) = \frac{P(B|A_i)P(A_i)}{P(B)}$$

  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.
- *The methods of stat mech ...* (These are totally worth repeating from last week.)
  - 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.
  - Calculate statistical properties.

- *A small review of thermo topics ...* B&B Ch. 4 begins telling us about thermal equilibrium and the 0^{th} law of thermo: "thermometers work". It also talks about macro and micro states with coin-counting examples.

- *Statistical definition of entropy ...* B&B Ch. 4 presents a new definition of S. 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:

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

  $$\Delta E_1 = -\Delta E_2 = \Delta E$$

  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 definition reappears, but without the "i", in B&B section 14.5, where $S = dQ/T$ for a reversible process is equated with $k\ ln\Omega(E)$.)

- 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 $S(\{P_i\}) = -\Sigma_i P_i\ lnP_i$. 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*: $S = -k\Sigma_i P_i lnP_i$.

- In the context of information theory, $S =< Q >= -k\Sigma_i P_i\ lnP_i$, where Q is the information content of a statement. In B&B section 15.1, this is called the *Shannon entropy*. B&B Ch. 15 (and the optional readings on Moodle) expand on how entropy relates to encoding information, data compression, quantum information, and more. In G&T section 4.13, we read a compelling argument that "entropy is not disorder".

- *Entropy of mixing* : B&B section 14.6 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:

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

  (Spoiler alert: Next week, G&T section 6.1 will show us by explicitly using $S(T, V, N)$, that mixing identical gas particles results in $\Delta S = 0$, as it should be :-)

- *Maxwell's demon* can't exist. If they 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!

- *Einstein solids*: G&T section 4.2 discuss these collections of distinguishable objects which can store discrete quanta of energy. Two Einstein solids, A and B, with fixed numbers of energy-storing particles, N_A and N_B, are brought into thermal contact. They give a a concrete illustration of the idea of B&B section 4.4. Namely, the equilibrium energy of solid A, $\bar{E_A}$, corresponds to a maximum in the entropy for a 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 particles, N. One or both of these needs to be large in order for us to claim that stat mech works for this system.

- *Counting states* is done in G&T sections 4.2 and 4.3. Two systems whose states should be discretely counted are these:
  - The Einstein solid with energy E and number of particles N:

    $$\Omega = \frac{(E+N-1)!}{E!(N-1)!}$$

  - N distinguishable spins in a magnetic field, with n up, so that the energy is $-(2n-N)\mu B$.

    $$\Omega = \frac{N!}{n!(N-n)!}$$

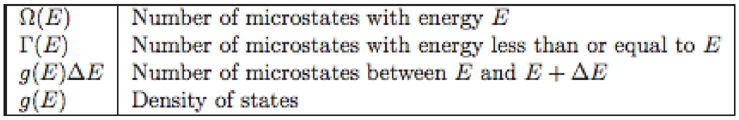
- 1-D Harmonic oscillator states are counted both classically and quantum mechanically in G&T Section 4.3.3.

- *Counting states for particles in boxes* can also happen either classically or quantum-mechanically. G&T go through both kinds of calculation in the subsections of Ch. 4.3. They do this for a single particle 1-D, 2-D and 3-D boxes. Please hang in there; lots of counting this week ;-}

- In order to count states for the quantum mechanical particle-in-a-box (ideal gas atom) we can count 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:

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

- The functions that are most useful to count states are these, from Table 4.7 of G&T:



$\Omega(E)$	Number of microstates with energy E
$\Gamma(E)$	Number of microstates with energy less than or equal to E
$g(E)\Delta E$	Number of microstates between E and $E + \Delta E$
$g(E)$	Density of states

Table 4.7: Summary of the functions used to count microstates.

- It is often easier to calculate not $g(E)dE$ but $\Gamma(E)$ [1].
  $\Gamma(E) = \int_0^E g(E)dE$. Thus, $\frac{d\Gamma(E)}{dE} = g(E)$

  Note: This is not just a counting aid ... typically $\Gamma(E)$ is so huge that taking $ln \; \Gamma(E)$ is equivalent to taking $ln \; g(E)\Delta E$. This is like saying that the “volume” of state space is described by the outermost layer of the surface, when $\Delta E << E$.

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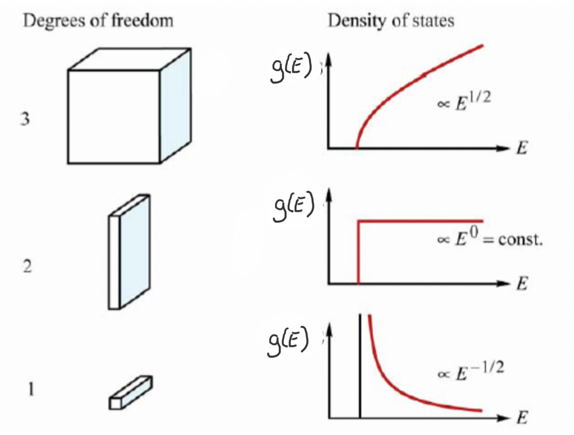
[1] In the language of probability theory, $g(E)$ is a probability distribution function and $\Gamma(E)$ is a cumulative distribution function.

- The formulae for Ω, Γ and g are complicated! A simple, important feature is how these states vary with energy E. This is neatly summarized in this picture below, showing densities of states $g(E)$ in $1d$, $2d$ and $3d$:



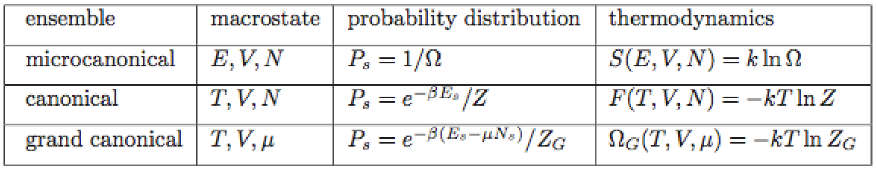
- An interesting thing happens if you try to find $\Gamma(E)$, the number of states with energy less than E, classically and quantum-mechanically. G&T do this for the harmonic oscillator and also particle-in-a-box (gas). In both cases, Γ_{cl} agrees perfectly with Γ_{qm} except that the former has $\Delta x \Delta p$ for the size of a small "box" in state-space, and the latter has h, Planck's constant. Before quantum mechanics was an established theory, statistical physicists had to leave this box-size unknown. Now we know the truth: we *should* identify $\Delta x \Delta p \equiv h$.

- So much emphasis on a single particle!? This is stat mech; what about many particles? G&T take this up in sections 4.3.6, 4.4 and refer to what they are doing as the *semiclassical limit.* With N particles in 3 dimension we have a $3N$-dimensional space in which the positions live. This is where G&T Section 4.14.1 or B&B Appendix C.8 come in ... they help us count up states in an “’n-dimensional hypersphere”.

- You may be wondering how we know a gas can be treated semi classically? More on this next week, but the nutshell is we we calculate the *thermal deBroglie wavelength*, $\bar{\lambda}$. If this is much smaller than the mean distance between particles, the semiclassical limit is good.

- *Ensembles* are introduced in B&B 4.5 and 4.6. An *ensemble* is a group of systems that are reflective of equilibrium. A system like two same-size boxes of gas, isolated from the world, would be a member of the energy-conserving *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 as arguments of $\Omega(E,V,N)$ and $Z(T,V,N)$ respectively. (Math note: It's a *Legendre transform* which takes 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.

- *Using the micro canonical ensemble...* Two B&T discrete-state examples are the Einstein solid and spins in a magnetic field. (These can also be treated with canonical statistics, which we'll do next week.)
- G&T section 4.5 leads us to an expression for $S(E,V,N)$ for a monatomic ideal gas:

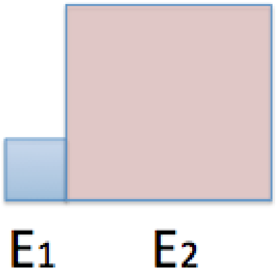
$$S(E,V,N) = Nk[ln\frac{V}{N} + \frac{3}{2}ln\frac{mE}{3N\pi\hbar^2} + \frac{5}{2}]$$

  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. To wit

$$\frac{1}{T} = (\frac{\partial S}{\partial E})_{V,N} \;\; ; \;\; \frac{P}{T} = (\frac{\partial S}{\partial V})_{E,N} \;\; ; \;\; \frac{\mu}{T} = -(\frac{\partial S}{\partial N})_{E,V}$$

  - 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 the *Sackur-Tetrode* entropy
- *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, E_1, of the tiny system. The huge system hogs the energy because it can use energy to create more microstates than can the tiny system.
- What does equilibrium look like in the *Canonical ensemble*? We seek the probability $P(E_s)$ that any system has energy E_s, 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 :-(They find

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

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 invoke the example of two Einstein solids, one huge (bath) and one tiny (system).

- The quantity Z is called the *Canonical partition function*. Above, it appears innocently, as just a normalization for $P(E_s)$. But as we will emphasize next week, $Z(T, V, N)$ 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.
- *Names and notations* : A *notation* everyone uses is $\beta = \frac{1}{kT}$. The weighting factor $e^{-\beta E_s}$ is called a *Boltzmann factor*. Another name for the Canonical probability distribution is the *Boltzmann distribution*.
- 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. We had a problem about a loaded die, where the mean value of the die, $\bar{n}$ was a constraint. In Example 14.7 of B&B (p. 152), a very similar constraint is applied: the mean of the energy is known. This leads us to Canonical statistics.
- *The Canonical partition function: its uses and some useful facts:*
- One can find the expectation value of the *energy*: $\bar{E} = -\partial\, lnZ/\partial T$
- One can find 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. Finally, the mean and variance of energy gives us another example of relative fluctuations in an observable going like $1/\sqrt{N}$. (You may recall that this was true of fluctuations in particle number, in a problem we did last week. It involved adjacent volumes V_1 and V_2 and $N = N_1 + N_2$ particles. We found $\frac{\sigma_{N_1}}{\bar{N_1}} = \sqrt{N}\sqrt{\frac{V2}{V1}}$.)

- G&T section 4.14.2 has the details about *energry fluctuations* mentioned above. There are two problems: G&T 4.25 and 4.26, both of whose answers turn my head around. The answers are both "It's a gaussian". Why? The Boltzmann distribution says that $P_s \propto e^{-\beta E_s}$. Why isn't the answer "It's an exponential."? Please take a look at Eq. (4.161) to see that yes, while there is a Boltzmann factor, it is the density of states $g(E)$ that broadens the distribution, peaked around $\bar{E}$.

- 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,what plays the role of degeneracy, g_J, is the *density of states* $g(E)$. Finding Z in these two cases is much like last week when, when we sometimes wanted to normalize probabilites $p(x_i)$ for discrete variables x_i; and sometimes probability densities $p(x)$ for continuous variables. Now,

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

- A final cool idea from G&T section 4.6: The first law of thermodynamics is $dE = TdS - PdV$. The term TdS comes from a change in the probability distribution P_s which says how the quantum states $\{E_s\}$ are occupied. When dS is positive, the distribution becomes more random!