Physics 114 Statistical Mechanics Spring 2018
Seminar 6

Overview:

This week, we'll continue to work with the *Canonical ensemble.* We'll see the simple relationship between $Z(T, V, N)$ and the Helmoltz free energy, $F(T, V, N)$. We'll practice calculating other thermodynamic variables, both ones that are easy to measure and control (like P), easy to measure but not control (like C_V) and difficult to control (like E and S) from $Z(T, V, N)$. We'll do problems that bridge the gap between micro canonical and canonical statistics - showing that for thermodynamically large systems, these provide two roads to the same destination. Finally, via a presentation,we will study how one simulates a system of interacting particles using *Monte Carlo.*

Required Reading:

G&T Sections

- Section 4.7-4.11

- Sections 4.13

B&B sections

- Section 4.7
- Ch. 20
- Ch. 21

Recommended Reading:

- Every book on our Cornell library reserve shelf has a section on the Canonical ensembles, with good explanations and examples.
- Vis a vis our discussion last week on erasing bits and entropy: `https://arstechnica.com/science/2012/03/information-and-entropy-finally-linked-through-experiment/`

Concept checklist from Readings:

- **From Z comes the free energy, and more ...** Last week in B&B problem 14.8 we saw that

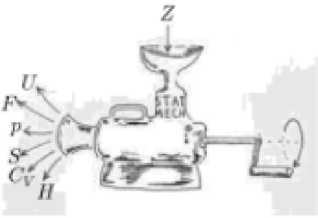
  $$S/k = \beta \bar{E} + ln\ Z$$

  (except that B&B used U, not $\bar{E}$ for energy.) This week, this equation reappears; moreover we learn that Helmholtz free energy is the "natural" free energy for the Canonical ensemble:

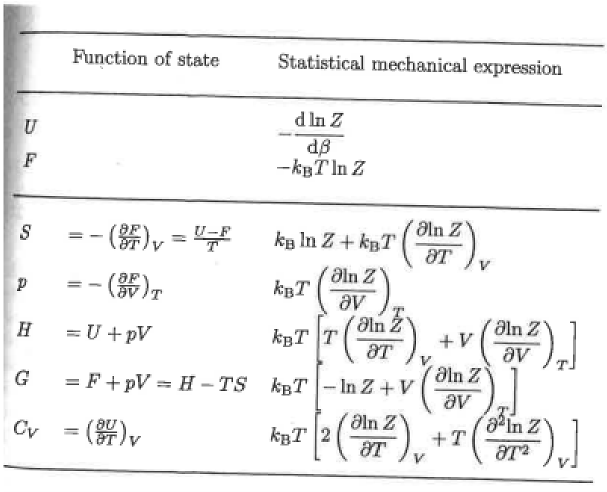
  $$F(T, V, N) = -kT\ ln\ Z(T, V, N) \quad \textit{or equivalently} \quad Z = e^{-\beta F}$$

  As the logarithm of a "master function", free energy is also a master function. Either produces all thermodynamic information.

- This sausage machine:

  produces, via explicit formulae we already know, all useful functions of state.



	Function of state	Statistical mechanical expression
U		$-\dfrac{\mathrm{d}\ln Z}{\mathrm{d}\beta}$
F		$-k_B T \ln Z$
S	$= -\left(\frac{\partial F}{\partial T}\right)_V = \frac{U-F}{T}$	$k_B \ln Z + k_B T \left(\dfrac{\partial \ln Z}{\partial T}\right)_V$
p	$= -\left(\frac{\partial F}{\partial V}\right)_T$	$k_B T \left(\dfrac{\partial \ln Z}{\partial V}\right)_T$
H	$= U + pV$	$k_B T \left[T \left(\dfrac{\partial \ln Z}{\partial T}\right)_V + V \left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
G	$= F + pV = H - TS$	$k_B T \left[-\ln Z + V \left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
C_V	$= \left(\frac{\partial U}{\partial T}\right)_V$	$k_B T \left[2 \left(\dfrac{\partial \ln Z}{\partial T}\right)_V + T \left(\dfrac{\partial^2 \ln Z}{\partial T^2}\right)_V\right]$

Table 20.1 Thermodynamic quantities derived from the partition function Z.

- Analogy: $\Omega(E,V,N)$ and its logarithm $S(E,V,N)$ contain all thermodynamic information in the micro canonical ensemble.

- The protocol for the Canonical ensemble is simply described in a box in Ch. 20 of B&B

  1. Write down Z
  2. Go through standard procedures to obtain functions of state you want from Z

- **Applications of Canonical ensemble to single-particle systems, with easy extension to N particles ...**

- As mentioned last week, often partition functions for N particles are simply derived from 1 particle ones. This is possible if the particles don't interact! This explains why many of the examples this week are pitched in terms of finding $f = -kT\ lnZ(T,V,1)$, $s = -(\partial f/\partial T)_V$, $\bar{e} = -\partial\ lnZ(T,V,1)/\partial\beta$, ... and so on. These are the free energy, entropy, and expected energy *per particle*. For N non-interacting particles, you just *multiply by N*.

- Many examples are done this week, which are good "toy" models for realistic systems. Please be sure that for the models listed below, you feel comfortable finding both single-particle and N-particle quantities like $\bar{E}$, S, C, ...

  - 2-level system
  - N-level system
  - 1d harmonic oscillator
  - Rotating diatomic molecule
  - Chemical reactions: dependence of products on temperature
  - The isothermal atmosphere
  - The spin 1/2 paramagnet
  - The ideal gas

- The specific heat $C = \partial E/\partial T$ is of particular interest this week. Please be sure you can see a calculation through, beginning with Z and ending with a "response function" like specific heat.

- We have confidence that the *equipartition theorem* holds for sufficiently high T, and this gives us a guide to what $\bar{E}$ and C should be in the high temperature limit.

- *Magnetic systems* have a couple of observables that we care about in addition to $\bar{E}$ and C. These are the magnetization $m = -(\partial F/\partial B)_T$ and the susceptibility $\chi \propto \partial m/\partial B$. (It is the case that $\chi \propto m/B$ in the limit that $B \to 0$.) We will do more with paramagnets in a later week; for now just appreciate that we can find these things in the Canonical ensemble :-)

- **The Canonical ensemble for ideal gasses ...** Ch. 22 of B&B is all about the ideal gas; a review and extension of what we did last week. In particular it
  - reviews finding the density of states $g(k)$ and $g(E)$ with particle-in-a-box counting arguments.
  - emphasizes the importance of the thermal de Broglie wavelength, now called λ_{th}. The idea of *quantum concentration* was introduced in a problem last week, and is now called $n_Q = 1/\lambda_{th}^3$. When particles are much less concentrated than n_Q, they can be treated classically. An elegant way to write the single particle partition function for the ideal gas is:

    $$Z_1 = \frac{V}{n_Q}$$

  - extends what we already did, to find free energies like F, G and H for a Canonical treatment of the ideal gas. Please see Problem 8 ii) for a statement that *all ensembles* are supposed to give the same results for these in the thermodynamic limit!
  - calculates the Sackur-Tetrode entropy $S(T, V, N)$ and goes over the notion of *entropy of mixing* and the *Gibbs paradox.*
  - discusses as an example, the heat capacity of the diatomic ideal gas. B&B does quantitatively what we did qualitatively in G&T problem 6.47 last week, when we discussed equipartition for a diatomic molecule that could rotate (and vibrate).

- **The Canonical partition function: its uses and some useful facts ...** (some relevant items from last week's summary)

- One can not only find the expectation value of the energy: $\bar{E} = -\partial\ lnZ/\partial T$ but also the expected size of mean squared fluctuations in the energy:

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

- If we use a label α to signify a microstate, then

  $$Z = \Sigma_\alpha E^{-\beta E_\alpha} \qquad (1)$$

- 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. Now,

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

- $Z(T, V, N)$ is the partition function for N particles, but we read a lot about the *single particle partition function*. Why care about one particle? Because $Z(T, V, 1)$ is often much easier to calculate, and if we have N distinguishable particles, it is the case that *for noninteracting particles*

  $$Z(T, V, N) = Z(T, V, 1)^N \quad \textit{distinguishable particles}$$

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

  $$Z = Z_A \; Z_B \; Z_C$$

- 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 is essential to get the entropy of mixing correct:

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

    This approach is predicated on the idea that there are so many states, and so few particles (N is few? Yes, 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.

- **Simulation techniques ...**
- In our G&T reading, we learn
  - a tiny bit about *micro canonical simulations*, which will be more relevant when we do magnetic systems (because other things than energy are of interest)
  - *demon thermometer simulations*, which we have used with good results in previous weeks
  - *canonical simulations*, which could be done by solving $F = ma$ (molecular dynamics) but are easier to do via *Monte Carlo (MC)*. A description of the standard Metropolis algorithm is given, which involves the very useful accept/reject paradigm that will establish thermal equilibrium at temperature T.

Warmup Problem: *Due before seminar, Monday (best) or Tuesday (second best) or by seminar time (I'll take it ;-)*

1: High T limits of partition functions: B&B problem 20.1

Presentation: MC simulation: *Taking on this presentation presumes that you feel comfortable enough to write a straightforward MC simulation yourself. I think I recall from the warmup for Seminar 1 that all of you could do this. It could be a Matlab .m file, or a Python notebook, or Mathematica ... anything. If you do not feel comfortable with this assignment, talk to me early (like Monday) and we will figure something out?!*

i) Talk us through the standard steps of a Metropolis Monte Carlo simulation, as listed on G&T p. 227.

ii) Construct your own MC simulation and show us some results. Here is a suggested protocol that would simulate an Einstein solid:

1. Decide on a temperature. That is, let $1/kT = \beta$ and pick a value of β. I suggest a value not too different from $\beta = 1$, but you can try a couple of different values, and see what difference it makes.
2. Initialize: Create an array of N numbers representing the energies of a set of N particles. Let them each start with 0 energy.
3. Pick a random particle (That is, choose a random integer between 1 and N to determine your particle of interest.)

4. Trial move: Toss a "coin" (That is, choose another random integer, now either 0 or 1.) If heads, consider adding $\Delta E = +1$ to the energy of the particle. If tails, think about adding $\Delta E = -1$ to its energy.

5. Accept or reject the move:
   - Definitely accept the move if it would lower the particle's energy, but not below zero.
   - Definitely reject the move if it would lower the energy of the particle below 0.
   - Accept the move with probability $e^{-\beta\Delta E}$ if it would raise the energy. (To do this, you need to generate a real random number between 0 and 1, which G&T call r.)

6. Go back to step 3 and iterate a lot of times ... you want each of the N particles to experience many moves.

As the simulation proceeds, measure something interesting. Average energy? A histogram of energies? Other ...?

Regular problems:

1: Einstein solid + Magnetic system (a review of last week's methods)
G&T Problem 4.38
Note: My bad ... I really wanted folks to do 4.39 which matches this title. Whichever of these two you did ... it's all good.

2: Harmonic Oscillators (We did micro canonical as G&T 4.22 last week - now ... canonical!)
G&T Problem 4.28

3: More Harmonic Oscillators
G&T Problem 4.50
Hint: Much of this is done in B&B ... please fill in any gaps in math or logic for yourself.

4: Z and more for a 2-particle system:
G&T Problem 4.52

5: Hydrogen:
B&B Problem 20.8

6: A 2-state system with degeneracy:
B&B Problem 21.4
Also: Please compare and contrast your result for C, Eq. (21.46), with with Figure 20.4 part (a), which applies to a slightly different 2-state system.

7: Demonstrating an entropy-driven phase transition:
i) G&T Problem 4.34
ii) G&T Problem 4.56

8: Fluctuations in a mole of gas:
What is the probability that a mole of ideal gas at temperature T will have an energy that differs by a factor of 10^{-6} (i.e. one part in a million) from its mean energy?
Hint: Section 4.14.2 of G&T