Physics 114 Statistical Mechanics Spring 2021
Week 6 Conceptual Overview

Concept checklist from Readings:

- *About entropy of mixing*: G&T section 6.1 show us by explicitly using $S(T, V, N)$, that mixing identical gas particles results in $\Delta S = 0$, as it should be :-)
- *Applications of the Boltzmann distribution:* It 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 and speeds.
- A second application of the Boltzmann distribution is the beautiful *equipartition theorem.* This is done in G&T section 6.2.1 and B&B Ch. 19. The theorem can be summarized by saying that if a particle has f independent, quadratic terms in its Hamiltonian, then its expected equilibrium energy is $< E >= \frac{f}{2}kT$.
- A natural consequence for gasses is that $C_v = \frac{f}{2}R$ per mole. Similarly, $C_p = (\frac{f}{2} + 1)R$ and the adiabatic constant is $\gamma = 1 + \frac{2}{f}$.
- Equipartition is derived assuming a continuous distribution of energies. Thus, if $kT >> \Delta E_q$, where ΔE_q is a typical separation between quantum levels, equipartition applies. On the other hand, if $kT << E_1 - E_0$, that mode will be "stuck" in its ground state whose energy is E_0.
- B&B have several examples of equipartition: a harmonic oscillator, a solid (modeled as a set of N harmonic oscillators in $3d$, monatomic and diatomic gasses). Be sure that you can use equipartition to find their average energies and their specific heats.
- $Z(T, V, N)$ 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

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

- In a related way, if we have several 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:

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

    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.

- 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.

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

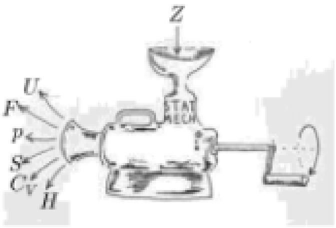
  $$S/k = \beta \bar{E} + ln\ Z$$

  (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:

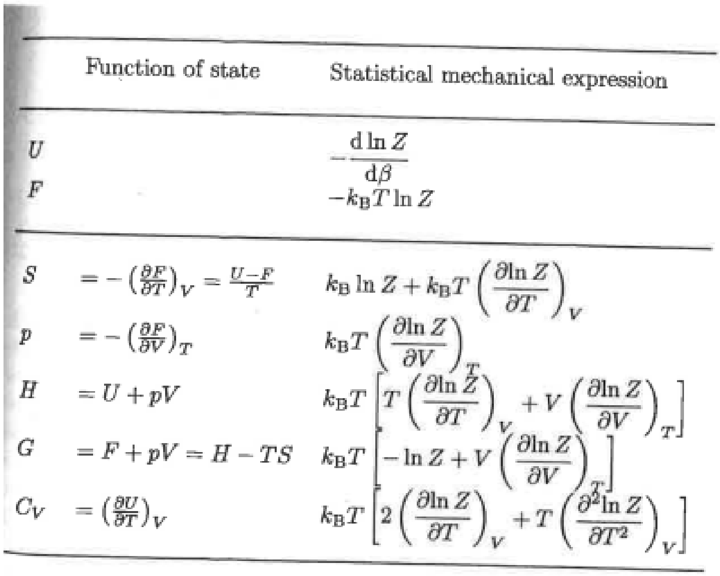
  $$F(T,V,N) = -kT\ ln\ Z(T,V,N) \quad or\ equivalently \quad Z = e^{-\beta F}$$

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

- The partition function as a sausage-making machine:



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



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

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:*** 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 *quantum concentration* is $n_Q = 1/\lambda_{th}^3$. 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. *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 are asked to doin G&T Problem 6.46 this week ... find $Z = Z_{trans}Z_{rot}$ for a diatomic molecule that can rotate. (Not assigned, but G&T Problem 6.47 talks about the specific heat of molecules that can vibrate too ... so we'd begin with $Z = Z_{trans}Z_{rot}Z_{vib}$ where Z_{vib} is derived as G&T Eq. (4.128) and B&B Eq. (20.28).

- ***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*

- *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.