Physics 114 Statistical Mechanics Spring 2021
Week 1 Conceptual Overview

Concept checklist from Readings:

- Time has a direction for a large system ... "things fall apart"
- Energy naturally goes from a useful (able to do work) to a less useful (thermal energy) form.
- We might be tempted to say that energy goes from the form of work to the form of heat. But that's wrong ... why?
- How is heat, Q different from energy, E? How is it different from temperature, T?
- *Notation alert*: B&B uses U for energy, whereas G&T uses E. Look for other such notational differences as we read. Sigh.
- *System* and its surroundings: System can be open or closed; walls insulating or conducting.
- *Microstates* and *macrostates*: Their definition depends on what we are modeling (gas? magnet? black body?) For a classical, monatomic gas of N atoms, the macrostate for a closed system is characterized by three variables: P, V and T while a microstate has 6N variables, the positions and momenta of the atoms. N is large (on the computer, 10^6 and in real life, 10^{23}).
- Thermodynamic variables can be *intensive* or *extensive.*
- *Entropy* (whose rigorous definition is postponed for a future week) is something that increases in all real-world processes. It is also something that labels a macrostate. It is larger for macrostates that correspond to larger numbers of microstates.
- Simulations: A *molecular dynamics* simulation solves $\vec{F} = d\vec{p}_i/dt$ numerically, to find $\vec{r}_i(t)$ and $\vec{v}_i(t)$ for $i = 1, 2, ..., N$ particles.
- Systems *spontaneously approach equilibrium.* In equilibrium we observe a mean, or average, value of a macroscopic quantity. Yes, this definition is somewhat circular ... the system is in equilibrium when its macroscopic properties don't change and are described by the laws of (equilibrium) thermodynamics.

- Macroscopic properties include variables of state (also known as thermodynamic parameters) and functions of them ... so called *functions of state.* Functions of state change if we change *parameters* of the system, and their change is always described as an exact differential. Thus, they are independent of the path in parameter space, depending only on the starting and ending values of the parameters.

- Equilibrium is not the same thing as being static. There are *equilibrium fluctuations* in equilibrium mean values. E.g. the simulation `ApproachToEquilibriumParticlesInBox` will show us a mean number on the left side, $\bar{n}$, but also a variance, $\sigma^2 = \overline{(n - \bar{n})^2}$.

  This week, I just want you to get a flavor for means and variances (which measure fluctuations around the mean). In later weeks, we will calculate these theoretically, and estimate them with simulations. We will also see how means and variances scale with system size, temperature, ...

- The postulates of *history independence* and *equal a priori probabilities.*

- Pressure arises from microscopic collisions of particles with walls.

  $$P = F/A = \frac{1}{A}\frac{dp_x}{dt}$$

  where just for argument's sake, we consider collisions with the area A of a wall in the $y - z$ plane, so the x component of momentum p_x is what changes during the collision.

- *The 0th law of thermodynamics*: One statement is that when two bodies are in thermal equilibrium with a third body, they are in thermal equilibrium with each other. "Thermal equilibrium" means same temperature. Two systems come to the same temperature when they are allowed to exchange energy. Of course, this might not be the original temperature of either system. A thermometer subtracts only a tiny amount of energy from a system. It thus does not change the system's original temperature, but merely reports on it.

- The *ensemble* concept : Many different systems, each one in equilibrium. On the other hand, simulations and experiments often involve just one system advancing in time. The *ergodic hypothesis* lets us equate the two pictures. Thus an ensemble of many equilibrium systems, and one system in equilibrium measured over time will show us the same physics.

- *Sensitivity to initial conditions* suggests that history independence and the ergodic hypothesis apply. As a system evolves, it eventually "forgets" the details of how it began.

- How long does the system take to forget its starting configuration? There will be some *relaxation time* - a time scale for reaching equilibrium. This time depends on the size of the system, the type of contact with its surroundings, etc. You can run G&T programs like `ApproachToEquilibrium...` or `SensitivityToInitialConditions` to get a sense of this for specific cases. G&T section 1.13.1 gives you the case of N particles in a box with two sides, and allows you in Problems 1.2 and Problem 1.10 to calculate the time scale, τ over which the system equilibrates. Here, $\tau = N/2$.

- Models of matter:
  - ideal gas particle
  - particles that interact via a pure repulsion as in G&T Eq. (1.5)
  - the LJ interaction
  - lattice models

- Important constants and their values: k, N_A and R.

- The Kelvin temperature scale. The ideal gas temperature scale is a related idea. We will talk about the "triple point later".

- A *pressure equation of state* is sometimes written $P = f(T, \rho)$ where $\rho = N/V$; though more casually we just write a function relating P, T, N and V. The ideal gas one is $PV = NkT$ (physicist-preferred) or $PV = nRT$. (chemist-preferred). The van der Waals equation of state corrects some assumptions about idealized gasses.

- An *energy equation of state* looks like $E = f(N, V, T)$. The ideal gas and van der Waals equations are found in G&T section 2.9. Note that energy of an ideal gas does not care about its density, $\rho = N/V$, but for the more realistic gas, energy changes - in the case of Eq. (2.24) it is lower - when density is higher.

- The monatomic ideal gas energy of state $E = \frac{3}{2}NkT$ will be derived later (though you may know it if you've already studied kinetic theory of gasses or the equipartition theorem).

- *Processes* take us from one thermodynamic macrostate to another. *Quasi static* means that the system passes through a set of equilibrium states at every stage. *Reversible* means that one can find a practical way to run the process in reverse. For example, any process where friction acts is irreversible. An irreversible process can be quasistatic in principle. But non-quasistatic processes are irreversible. Subtle? Hell yes. (It will also be subtle when we distinguish isentropic from adiabatic.)

- The *work done on a gas* undergoing a quasi static process from state 1 to 2 is

  $$W_{1\to 2} = -\int_{V_1}^{V_2} P dV$$

  We can use this equation plus the equation of state for an ideal gas to find the work done on processes that are

  - isothermal
  - isochoric
  - isobaric

- Schroeder (Phys 13) called this kind of work "compression work" which is smart - it reminds you that there are other kinds, though this is the one we most often think of ... gas in cylinder acted upon by piston.

- An *adiabatic* process takes place when the system is insulated from its surroundings, so no heating or cooling happens. For an adiabatic process, $Q = 0$. Careful: this is not saying that the temperature of the system is constant on an adiabat. Rather, work done on the system, W, will change its thermal energy: $W = \Delta E$, and hence its temperature will change. (Exception: The system is undergoing a phase transition.)

- The net work *on* a gas is the negative of area of a cycle like Fig. 2.4 in G&T. If arrows would reversed, sign of work changes. For the work done *by* the gas, again the sign changes.

- *The 1st law of thermo:* $\Delta E = W + Q$.

- For an ideal gas, with the help of the 1st law, we can calculate Q, ΔE, and W for a process as shown on a PV diagram. In particular, know how to do this for the four fundamental kinds of processes: isochores, isobars, isotherms and adiabats.

- For adiabats and ideal gasses, we derive that $PV^\gamma = const$. Equivalently, $TV^{\gamma-1} = const$. (Early in Phys 13, in Ch. 1 of Schroeder, we learn the definition $\gamma = (f+2)/f$, where f is the number of "degrees of freedom" a molecule has. For a monatomic ideal gas, $f = 3$. Both G&T and B&B stick with that case for now, using $\gamma = 5/3$.) The symbol γ is called the "adiabatic index" or "adiabatic constant".

- We will talk more about *enthalpy*, H, later. For now, note that the definition of this function of state is $H = U + PV$. Schroeder (Phys 13) gave us this memorable way to think about the difference between H and U:

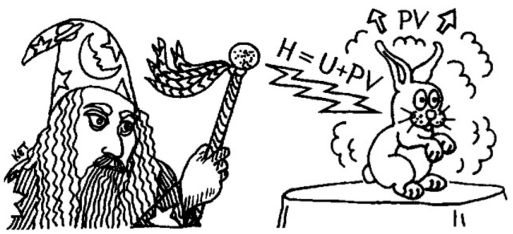

Figure 1.15. To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV, to push the atmosphere out of the way to make room. The *total* energy required is the **enthalpy**, $H = U + PV$.

- *Heat capacity* is $C = \frac{Q}{\Delta T}$. Different processes might be involved as T changes, yielding different values of C. Two popular cases are isochoric and isobaric changes:

  $$C_V \equiv (\partial E/\partial T)_V \quad ; \quad C_P \equiv (\partial H/\partial T)_P$$

  The heat capacity for isobaric processes is higher because some of Q goes into work, not solely into increasing T as for an isochoric process. For an ideal gas, it can be shown that $\gamma = \frac{C_p}{C_v}$. Similarly, $C_P - C_V = R$.

- The *specific heat capacity* is the heat capacity per unit mass of the substance. We often note specific heat as c. Sometimes people want the heat capacity of exactly one mole: this is called the *molar heat capacity.* (It can be a tiny bit confusing to read C_V in B&B and not know if it is for one mole or n moles, but the units give it away.)

Checklist: Math concepts (some from Week 0 "gathering our tools"):

- easy-to-evaluate integrals as in G&T 1.13.2
- given $f(x, y)$, how to take a partial derivative like $(\partial f(x, y)/\partial x)_y$.
- writing a Taylor series for a function
- the definition of an exact differential - for example that the integral of $f(x, y)$ is independent of the path between its endpoints, and that partial differentiation can occur in any order, so $(\partial^2 f/\partial x \partial y) = (\partial^2 f/\partial y \partial x)$