

140a Lecture 1, 1/8/19

★ Week 1 reading: Blundell+Blundell, chapters 1,2,3,4,5,6. Then skip to chapter 11.

- Thermodynamics is remarkable. It grew out of a practical desire to build efficient engines and machines. It ended up leading to the understanding of some of the most important principles of Nature, such as the conservation of energy and aspects of the arrow of time (first and second laws). Let's write the first law as an appetizer, we'll explain it more later:  $dE = \delta Q + \delta W$ . Here we see energy  $E$  (often also called  $U$ ), heat change  $\delta Q$ , and work done  $\delta W$ . An early goal was to convert heat energy into mechanical work, e.g. in a steam engine. A wonderful thing about thermodynamics is how little goes into the theory, and how much comes out of it – perhaps best theories ever in output/input ratio.

- Statistical mechanics explains thermodynamics, and goes beyond it, in terms of the likely configurations of the particles that make up matter. (There is also statistical mechanics for fields, and indeed the particles are actually quanta of fields.) There are two options for how to teach 140a: the historical approach where we first develop thermodynamics, deferring stat mech for later in the quarter, or starting with stat mech and deriving thermodynamics later as a consequence. We will follow the presentation of the textbook, with a hybrid, integrated approach.

- Some large numbers: estimated age of the universe since the big bang, in seconds:  $4.32 \times 10^{17}$ . Estimated number of stars in the universe: about  $10^{10}$  galaxies and  $10^{11}$  stars per galaxy, so about  $\approx 10^{21}$  stars. Estimated number of grains of sand on Earth  $\approx 10^{19}$ . Estimated total number of nucleons (protons + neutrons) in the universe  $\sim 10^{80}$ . Number of distinct configurations of 52 cards in a shuffled deck  $52! \approx 8.07 \times 10^{67}$ . (Recall Stirling's approximation  $N! \approx (N/e)^N$ , which for  $N = 52$  gives  $(52/e)^{52} \approx 4.45 \times 10^{66}$  - pretty good, and gets better for larger  $N$ .) Recall that 1g of stuff has about  $N = 6.02 \times 10^{23}$  nucleons. If we put those nucleons on a line, can get  $N!$  configurations for this large  $N$ , so  $\approx (10^{24})^{10^{24}}$ . Wow. It's hopeless to try to track them in detail. Fortunately, laws of large numbers come to the rescue – average properties can *simplify* for large  $N$ .

- For example, often get approximately a Gaussian normal distribution, which fully specified by the mean  $\bar{x}$  and the standard deviation  $\sigma$ . Recall  $P_G(x)dx = Ce^{-\lambda(x-\bar{x})^2}$ , gives  $\langle f(x) \rangle = \int dx P_G(x) dx f(x)$ . Determine  $C$  such that  $\langle 1 \rangle = 1$ . Show that  $\langle x \rangle = \bar{x}$ . Determine  $\lambda$  such that  $\langle (x - \bar{x})^2 \rangle = \langle x^2 \rangle - \bar{x}^2 = \sigma^2$ . Gives  $C = 1/\sigma\sqrt{2\pi}$  and  $\lambda = 1/2\sigma^2$  (note that the units work, whatever the units of  $x$  are).

- Example: consider a coin which has probability  $p$  to land heads and  $q = 1 - p$  to land tails - usually  $p = 1/2$  but let's be more general. Suppose the coin is flipped  $N$

times. The probability of getting  $r$  heads and  $N - r$  tails is then  $P_r = \binom{N}{r} p^r q^{N-r}$ , where  $\binom{N}{r} \equiv N!/r!(N-r)!$  is called “ $N$  choose  $r$ ” and is the number of distinct ways of grouping  $N$  objects into a group with  $r$  of them and another group with  $N - r$  of them. As a check,  $\sum_{n=0}^N P_n = (p+q)^N = 1$ . The average number of heads is  $\langle H \rangle = \sum_{n=0}^N n P_n = Np$ . The standard deviation is  $\sqrt{\langle H^2 \rangle - \langle H \rangle^2} = \sqrt{Np(1-p)}$ . Note that  $\sigma \sim \sqrt{N}$ , and  $\sigma/\langle H \rangle \sim 1/\sqrt{N}$ , so the distribution relative to the mean becomes sharply peaked as  $N$  increases.

Trick to evaluate the sums here: use the identity  $(p+q)^N = \sum_{r=0}^N \binom{N}{r} p^r q^{N-r}$  and take  $p \frac{d}{dp}$  of both sides to bring down powers of  $r$ , so  $N(p+q)^{N-1} p = \sum_{r=0}^N \binom{N}{r} r p^r q^{N-r}$

and  $N(N-1)(p+q)^{N-2} p^2 + N(p+q)^{N-1} p = \sum_{r=0}^N \binom{N}{r} r^2 p^r q^{N-r}$ , and then set  $p+q=1$  at the end.

Related example: random walk on a line, with probability  $p$  to go a distance  $L$  forward and  $1-p$  to go  $L$  backwards. Then after  $N$  steps we can use again  $P_n$  to give the probability of  $n$  forward and  $N-n$  backwards, so the average distance travelled is  $\langle x \rangle = \sum_{n=0}^N P_n (n - (N-n)L) = LN(p - (1-p))$ , e.g. for  $p = 1/2$  then  $\langle x \rangle = 0$ , as expected. The standard deviation is  $\sqrt{\langle x^2 \rangle - \langle x \rangle^2}$ , which for  $p = q = \frac{1}{2}$  gives  $\sqrt{NL}$ .

- Some thermodynamic variables: pressure  $p$ , volume  $V$ , temperature  $T$ . The 0-th law of thermodynamics is that one can define temperature as a property of a system: bring systems into thermal contact with each other and wait until they are in equilibrium. Prior to that, heat is transferred from subsystem  $A$  to subsystem  $B$ , in which case we say that  $T_A^i > T_B^i$ . Once equilibrium is achieved, the two subsystems have  $T_A^f = T_B^f$ . If we bring in another subsystem, the equilibrium or heat transfer properties are consistent with heat flowing from hotter to colder and if  $A$  is in equilibrium with  $B$  (so  $T_A = T_B$ ), and  $B$  with  $C$  (so  $T_B = T_C$ ), then  $A$  and  $C$  are in equilibrium ( $T_A = T_C$ ). Equilibrium requires  $\phi_A(P_A, V_A) = \phi_B(P_B, V_B) = \phi_C(P_C, V_C)$  and we can define  $\phi(p, V)$  to be the temperature.

- Example: the ideal gas law,  $PV = nRT = nk_B T$ . Next time: units and intensive vs extensive variables.