Outline:

Electrostatics
• Coulombic forces
• multipoles

Intro to Stat Thermo

Three coins in a fountain

Note: Overall, I assume that all of you can read, so I am intentionally not going to use lecture to repeat what is in the text. I’m going to try to present some fraction of what is in the chapter in a slightly different way than the text, highlighting things I think are important.

Review:
$$\mathbf{F} = -\nabla U$$

Lennard-Jones potential – repulsive (Pauli), attractive (dispersion), no interaction

These interactions lead to more realistic equation of state... Van der Waals Equation

$$\left( P + \frac{a}{V^2} \right) \left( V - b \right) = RT$$
$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

Didn’t get to Electrostatics last time

Electrostatic Forces (important for polar molecules & ions)

**Coulomb’s law:** charges repel or attract

$$U = \frac{q_1 q_2}{4 \pi \varepsilon R_{12}}$$

**electric dipole:** consists of two electric charges $q$ and $-q$ separated by a distance $l$ and represented by a vector $m$ that points from the negative charge to the positive charge. The magnitude of the vector is $q*|l|$ and is called the electric dipole moment.
A molecule possesses a nonzero electric dipole moment if it has an asymmetric charge distribution:

- H-F  nonzero
- N-N  zero (symmetric)

Thus, we refer to HF as a polar molecule. What about CO$_2$, CCl$_4$, CH$_3$Cl

Larger molecules are more complicated sums of charges and positions. Usually reasonably correct to take vector sums of individual little dipoles. (show $\alpha$-helix with carbonyl and amine dipoles pointing in same direction)

Most molecules have complicated charge distributions that are not well described by a dipole moment alone.

What should we do? Expand. Another expansion to describe complicated charge distribution with fairly simple terms.

charge distribution = monopole (charge) + dipole moment + quadrupole moment + octupole moment + …

monopole (n=0): one point charge (Na$^+$)
dipole (n=1): two point charges that has no monopole ($^d$H — $^d$F)
quadrapole (n=2): four point charges that has no dipole ($^d$O = $^d$C = O$^d$)
octupole (n=3): eight point charges that has no dipole or quadrupole (CH$_4$)
and so on

Note that large molecules are rarely described by any 1 term, but usually a sum of many terms (an expansion!)

Distance Dependence of Electrostatic Forces
Interactions between these charge descriptions (using Coulomb’s law and some geometry) are
found by summing over the multipoles for each molecule (where m and n are the respective multipole indices for the interacting molecules):

\[ U(r) \propto \frac{1}{r^{n+1}} \]  
(can be positive or negative)

monopole-monopole: \( q_1 q_2 / r \)
dipole – dipole: \( \mu_1 \mu_2 / r^3 \)
quad-quad: \( \theta_1 \theta_2 / r^5 \)
dipole – quad?: \( \mu_1 \theta_2 / r^4 \)

(long range or short range??)

Note that electrostatic interactions have orientation dependence. They can be either attractive or repulsive. Draw aligned and anti-aligned and ask which is attractive?

This is a big difference between electrostatic and dispersion forces. Dispersion have no directionality (isotropic) and always are attractive.

Because of the shorter range of electrostatic forces, dispersion forces are much smaller than electrostatic forces in polar molecules such as \( \text{H}_2\text{O} \) (show ice structure). Therefore, dispersion forces are most often important in non polar systems such as benzene.

**Approximate Magnitudes of the Chemical Bonding for Representative Systems**

\( \text{H-H: } 500 \text{ kJ mol}^{-1} \) (chemical bond)
\( \text{H}_2\text{O} - \text{H}_2\text{O: } 20 \text{ kJ mol}^{-1} \) (intermolecular (electrostatic) bond)
\( \text{Ar - Ar: } 1 \text{ kJ mol}^{-1} \) (intermolecular (dispersion) bond) (can be larger in bigger molecules)

It is the magnitude of these energies that determines the condensed phase properties of materials. Ether is a low-boiling compound because it is held together in the liquid phase by weak dispersion interactions and water is a high boiling compound because it is held together by strong electrostatic interactions (hydrogen bonds).

**Now, we get back to the beginning – Chapter 1.**

- Classical thermodynamics
  - Predates the acceptance of atomic theory
  - **Empirical?** theory
  - Simple = Based on 3 fundamental laws, and very general
  - Combination of simplicity and generality make it extremely powerful!
    - A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore, the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown. – Albert Einstein: *Philosopher Scientist*
Clearly properties depend on materials, so should be able to reconcile the detail of atomic theory
with generality of thermodynamics

This is Statistical Thermodynamics - our text is a synthesis of classical and statistical
thermodynamics.

Properties of Statistical Thermodynamics:
- Use a model for molecular behavior, average over an ensemble? of molecules to get the
  bulk properties of thermo, like temperature and pressure
- Molecular model of choice? is quantum mechanics
- All we need from quantum are the energy levels of the molecules - this is incredible from
  a chemists perspective because it means that detailed molecular properties like atomic
  masses, electron configurations, bond strengths/lengths etc. lead directly to bulk
  properties. This is like saying that if we just know how big and heavy a car is and how
  fast it goes, then we can understand exactly how traffic flows. (Of course the human
  drivers make this much more complicated, but you get the idea.)

So, all we need to know are values of energy levels. We’ll get to this later... be waiting for them.

In the meantime, we are going to develop some ways to deal with statistics. Clearly this is
important for statistical thermodynamics.

This is really great stuff; I am also doing things quite differently than the book so it would be good to
read these sections carefully to give you two different perspectives.

Everybody get a coin while I get spreadsheet up and running.

You are all going to flip 8 times and keep track on paper: e.g. HHTHTTHT.

Go through spreadsheet... hopefully gets close to 50 % heads as more trials are done

Go back and get exact order of first 4 tosses (using the book’s terminology 4 elementary events
combine to form 1 composite event). Point out that all 16 possible configurations are
equally likely

But if all we care about is total # heads, how does this change things? Each specific
configuration is equally likely, but since coins are indistinguishable, all of the 2-2
configurations are equivalent to us, that makes it more likely. Thus, for 4 coins, we don’t
have 16 configurations, there are really only 5 distinguishable configurations, weighted
1/16, 4/16, 6/16, 4/16, 1/16

Super, but what if we had a mole of coins, we need some kind of formula. We want something
like (weight of configuration) / (total # configurations)

Can anyone see what the denominator is? \(2^N\) == the total number of configurations
What about numerator? Let’s say we have 4 coins (A, B, C, and D): how many ways can we
arrange them? 4 choices for first, 3 for second, 2 for third, 1 for fourth, so \(4\times3\times2\times1 = 4!\)
= 24. This is total # arrangements, so we need to divide out the number of equivalent
ones. This is the same type of thing, so we get (# heads)! * (# tails!).

so the final formula is

\[
P(N,h) = \frac{M}{N!} \frac{h! (N-h)!}{2^N}
\]

Try it out ( 4! / 3! 1! ) / 2^4 = (24 / 6) / 16 = 4 / 16 –> perfect
This formula works when the probability of heads = tails. More generally the \( \frac{1}{2}^N \) needs to be divided up into the two different probabilities:

\[
P(N, k) = p^k(1-p)^{N-k} \frac{N!}{k!(N-k)!}
\]

So then, the above ‘general’ form further generalized for \( t \) different possible events (rather than 2 for coins or 6 for dice) is:

\[
P(N, k) = p_1^{n_1} p_2^{n_2} p_3^{n_3} ... p_t^{n_t} \left( \frac{N!}{n_1!n_2!n_3!...n_t!} \right)
\]

(remember this is for \( N \) dice of \( t \) sides each)

What if we were rolling five dice (like Yahtzee!)?

\[
P = \frac{5!}{n_1!n_2!n_3!n_4!n_5!} \frac{1}{6^5}
\]

OK, there are some important statistical things to notice. Let’s go back to all our flipping coins.

Let’s notice a couple more things about coins.

What if we flipped 2 coins –>

- probability of getting exactly half heads? = \( P(\text{half}) = 2 / 4 = .50 \)
- but notice ratio of \( P(\text{half heads}) : P(\text{zero heads})? = 2 : 1 = 2 \)

What if we flipped 4 coins:
probability of getting exactly half heads? = P(half) = 6 / 16 = .375
But again, ratio of P(half) : P(zero)? = 6 : 1 = 6

Go back to spreadsheet and show for # flips going up to 150. Probability of the dominant contribution falls off, but ratio of most likely to least likely increases dramatically.
For 100,000 flips, 49,000 - 51,000 heads contains 99.99999993 % of the distribution.

VERY IMPORTANT – as N becomes huge, the distribution gets very narrow.
So, if we have something like 10^{23} particles, then even though we can’t know the energy of any particular particle at all, we can know the most probable energy and the average energy very well.

OK, if we have time let’s look at how to calculate averages and std deviations and the like.

what if we have several discrete things like test scores?
67 83 95 100

what is the average? add them up and divide by n.
\[ \langle x \rangle = \frac{67 + 83 + 95 + 100}{4} = \frac{67}{4} + \frac{83}{4} + \frac{95}{4} + \frac{100}{4} = \sum x p(x) = \int x p(x) dx \]

other important property is the standard deviation, \( \sigma \), but we usually use the variance, \( \sigma^2 \)
\[ \sigma^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \]

Note from the text that the average is more formally known as the first moment, and the variance is the second moment.