An overview of Physical Chemistry

Microscopic

QM: wavefunctions
CM: classical positions & velocities

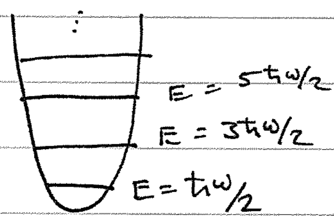
→ **"Glue"** Statistical Mechanics → **Macroscopic** Thermodynamics, Kinetics

Spectroscopies

← Chem 30321 | Chem 30322 →

This semester is about emergent behavior of collections of microscopic systems.

We'll start with a simple quantum view of the world. States are quantized, but not all states are equally likely. Consider the Harmonic oscillator:



These are the first 3 energy levels of the quantum mechanical harmonic oscillator.

How do we get physical properties from an ensemble or collection of molecules where each one might be in a different state?

$$\langle X \rangle = \sum_{\text{molecules}} X_{\text{molecule}}$$

average of property X

Altenatively,

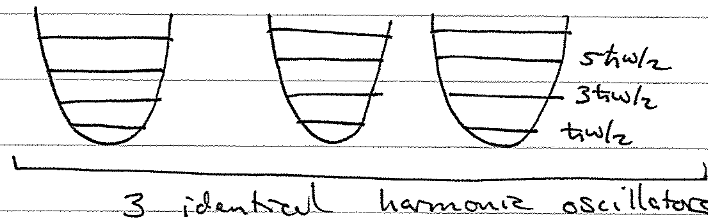
$$\langle X \rangle = \sum_{\text{states}} X_{\text{state}} \, P_{\text{state}}$$

property X for all molecules in a particular state

probability of being found in that state

The main trick is figuring out what the state probabilities are!

Consider:



Suppose our 3 oscillator system has a total of $9\frac{\hbar\omega}{2}$ to distribute. Since the ground state energy is $3 \times \frac{\hbar\omega}{2}$, this leaves 3 quanta of energy to distribute. Let's map out all possible ways of doing this:

System State	state of HO #1	state of HO #2	state of HO #3
a	3	0	0
b	0	3	0
c	0	0	3
d	2	1	0
e	2	0	1
f	1	2	0
g	0	2	1
h	1	0	2
i	0	1	2
j	1	1	1

There are 10 ways of dividing up the energy between these identical oscillators.

$$C(N, n_0, n_1, n_2, n_3) = \frac{N!}{n_0!\, n_1!\, n_2!\, n_3!} = \text{count of configurations}$$

N: # of quanta to distribute
n_0: # of oscillators in ground state
n_3: # of oscillators in state 3

$C(3,2,0,0,1)$ = States with 1 oscillator in $n=3$ and 2 oscillators in $n=0$ (system states a, b, and c)

$$= \frac{3!}{2!\,0!\,0!\,1!} = 3$$

$C(3,1,1,1,0)$ = States with 1 oscillator in each of $\begin{cases} n=0 \\ n=1 \\ n=2 \end{cases}$

= system states d, e, f, g, h, i

$$= \frac{3!}{1!\,1!\,1!\,0!} = 6$$

$C(3,0,3,0,0)$ = states with 3 oscillators with $n=1$

= system state j

$$= \frac{3!}{0!\,3!\,0!\,0!} = 1$$

C is the number of ways of distributing objects between boxes.

$$W = \frac{N!}{\prod_{i=1}^{3} n_i!} = \text{permutations}$$

The number of permutations turns out to be directly related to the entropy.

$$S = \underbrace{k_B}\ \ln W$$

entropy of a macrostate

Boltzmann's constant

indistinguishable permutations or microstates that contribute to that macro-state

Which arrangement above has the largest entropy?

A rough overview of what's coming next:

- Stat Mech basics
- Gas theory
- Boltzmann & Partition Functions
- 1st law of Thermodynamics
- 2nd, 3rd & 0th laws
- Equilibria (phase & chemical)
- Kinetic theory of gases
- Kinetics
- Better kinetics using Statistical Mechanics