CHEM 117A/217A Fall 2008

Statistical Mechanics

"Statistical Mechanics is the discipline concerned with interpreting the measurable properties (T, p, V) of materials in terms of the properties and interactions of the constituent atoms and molecules."

Harold L. Friedman in "A Course in S. M."

"The premise of statistical mechanics is simple: the motion of the molecules in a material determines its macroscopic properties."

Horia Metiu in "Physical Chemistry: S. M."

"Statistical mechanics is the theory with which we analyze the behavior of natural or spontaneous fluctuations."

David Chandler in "Introduction to Modern Statistical Mechanics"

We will use all three of these definitions in our development of statistical mechanics.

We begin by considering the entropy (S) [the subject of the 2nd (and 3rd) Law of Thermodynamics] and its relationship to probability. Before connecting entropy and probability we need to cover some basic probability (and counting) theory.

Principles of Probability (Dill Chp. 1)

<u>probability</u>: If N is the total number of possible outcomes of an event and n_A of outcome fall into the category A, then p_A, the probability of outcome A is:

$$p_A = \frac{n_A}{N}$$

- outcomes A and B are independent if outcome A is not correlated with outcome B

ex. rolls of a die
flips of a coin

- if outcomes A, B and C are the only possible outcomes (i.e. are mutually exclusive and collectively exhaustive) then

$$p_A + p_B + p_C = 1 = \frac{(n_A + n_B + n_C)}{N}$$

- the quantities n_A, n_B and n_C are known as the statistical weights of outcomes A, B and C

<u>multiplicity</u>: the total number of ways in which different outcomes can possibly occur. For the example of outcomes A, B and C the multiplicity

$$W = n_A n_B n_C$$

- consider an event with possible outcomes A and B, the probability that both A and B occur (i.e. A then B or B then A) is called the joint probability $p(AB)$. If A and B are independent outcomes then

$$p(AB) = p(A)\,p(B)$$

note this is stated without proof (see Dill pgs. 89-99 for how this applies to S)

Combinatorics

permutations: Consider an ordered sequence of the letters ~~x~~, w, x, y and z

there are four possible choices for letter 1, three for letter 2, two for letter 3 and one for letter 4 (see Dill pg. 10 for all permutations)

$$W = (4)(3)(2)(1) = 4! = 24$$

in general

$$W = N! \quad \text{for distinguishable permutations}$$

What if we wanted ordered sequences of

w, x, w, z (i.e. switched y for another w)

note: the w's are <u>indistinguishable</u>

$$W = \frac{(4)(3)(2)(1)}{2!} = \frac{4!}{2!} = 12$$

generally, for a collection of N objects and t categories

$$W = \frac{N!}{n_1!\, n_2! \cdots n_t!}$$

where n_i = # of category i

Special case $t = 2$ (i.e. heads/tails or success/failure)
we write for n successes in N trials

$$W(n,N) = \binom{N}{n} = \frac{N!}{n!\,(N-n)!}$$

Ex: 10 flips of a fair coin the multiplicity for 4 heads ($\Rightarrow$ 6 tails) is

$$W(4,10) = \frac{10!}{4!\,6!} = \frac{(10)\overset{3}{\cancel{(9)}}\cancel{(8)}(7)}{\cancel{(4)}\cancel{(3)}\cancel{(2)}(1)} = 210$$

How about 10 flips, 5 heads?

$$W(5,10) = \frac{10!}{5!\,5!} = \frac{\overset{2}{\cancel{(10)}}(9)\overset{2}{\cancel{(8)}}(7)\cancel{(6)}}{\cancel{(5)}\cancel{(4)}\cancel{(3)}\cancel{(2)}(1)} = 252$$

How about 10 flips, 8 heads?

$$W(8,10) = \frac{10!}{8!\,2!} = \frac{(\cancel{10}^{5})(9)}{(\cancel{2})(1)} = 45$$

The highest multiplicity occurs for half heads/half tails! This is an important result, which will be generalized later.

Probability Distribution Function

For t mutually exclusive outcomes, $i = 1, 2, \cdots, t$ the distribution function is $p(i)$, the set of probabilities of all the outcomes

$$\sum_{i=1}^{t} p(i) = 1$$

Probability distribution functions can be continuous functions such that if outcome variable x ranges from $x = a \rightarrow x = b$ then

$$\int_a^b p(x)\,dx = 1$$

sometimes these distributions are characterized by a function $\psi(x)$ which is not normalized and can be normalized by integration such that

$$p(x) = \frac{\psi(x)}{\int_a^b \psi(x)\, dx}$$

Examples of distribution functions

1. Binomial Distribution

- this dist'n characterizes trials with only 2 outcomes (hence binary); one outcome with probability p [success] and the other with probability $(1-p)$ [failure]
- these are also called Bernoulli trials
- for N trials, the probability of n successes is given by:

$$p(n,N) = p^n (1-p)^{N-n}\, W(n,N)$$

$$= p^n (1-p)^{N-n} \frac{N!}{n!\,(N-n)!}$$

- it is easy to generalize this distribution to a multinomial distribution

2. Flat Distribution

- a uniform distribution

$$p(x) = \frac{1}{a} \qquad \text{for } 0 \le x \le a$$

- note:

$$\int_0^a p(x)\,dx = \frac{1}{a}\int_0^a dx = \underline{1}$$

3. Boltzmann Distribution (exponential)

- extremely important in statistical mechanics

$$p(x) = a\,e^{-ax} \qquad 0 \le x \le \infty$$

Average Value and Standard Deviations

discrete

$$\langle i \rangle = \sum_{i=1}^{t} i\,p(i)$$

continuous

$$\langle x \rangle = \int_a^b x\,p(x)\,dx$$