

CBE 310 Molecular Concepts and Applications

Boltzmann Distribution and Partition Functions

2014 10 10

Reading Chapter 16 Atkins Physical Chemistry,
Supplementary reading assignments are in the handouts section

Monday will be a quick Review of Thermodynamics
(CBE 210 in a day)

Wednesday we will be deriving the molecular partition function

Defining statistical mechanics:

Statistical Mechanics provides the bridging connection between microscopic world governed by the laws of quantum mechanics and the macroscopically observable world that is described by thermodynamics.

The macroscopically observable quantities such as temperature, pressure, entropy, free energy, heat capacity, chemical potential, viscosity, spectra, reaction rates, etc. can be derived and /or explained as the average properties of large collection of individual molecules with particular quantum mechanically allowed behaviors.

The aspect of statistical mechanics that we will most be concerned with is how you go from a understanding of individual molecules to the bulk properties of matter.

Probability, definitions and some of its properties

We talked about simplistic system consisting of colored marbles of different diameters to introduce the idea of probabilities and explore the properties of probability as it relates to a collection of objects

$$P_i = \frac{n_i}{n_{total}} = \frac{n_i}{n}$$

$$P_{i \text{ or } j} = P_i + P_j$$

$$P_{\text{not } i} = 1 - P_i$$

$$\sum_i P_i = 1$$

These rules apply to independent observables

P_i is the probability of observing some quantity of the system "i",

n_i is the number of ensemble members with a given value of "i"

n is the total number of ensemble members

These are general equations that are valid for any property of the members of the ensemble,