Physical Chemistry

Lecture 23

Maxwell-Boltzmann Distribution

Macroscopic and microscopic properties

- Relation between measured (macroscopic), Q, and theoretical (microscopic), q, properties of a system

$$Q = N < q >$$

- Angular brackets {<....>} indicate an average over the distribution of properties of particles in the sample

Average values from probability distributions

- Average energy found as a sum over all possible values for the ensemble
  - p_k = probability of finding u_k in the ensemble

$$< u > = \frac{1}{N}\sum_k n_k u_k = \sum_k p_k u_k$$

- Must find the form of p_k to evaluate averages
  - Depends on ensemble
  - Random distributions considered

Description of molecular systems in terms of energetics

- Every state described by energy and other characteristics
- Probability is a function of energy

$$p_k = p(u_k)$$

- Find average of other property by its dependence on energy

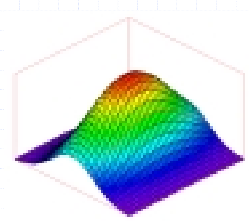
$$< q > = \sum_k q(u_k) p(u_k)$$

Finding the most probable equilibrium distribution

- Probability governed by two effects
  - Maximize entropy
  - Hold the average energy constant
- Find probability distribution that does both simultaneously
  - May not be the state of absolute maximal entropy
  - May not be the state of absolute minimal energy
- Like finding the maximum height of a mountain subject to the requirement that one stays on a road

Example of a constrained maximum

- The largest value of this function of x and y is in the red zone
- The largest value of this function, subject to the restriction that x has a certain value (indicated by the red line) is in the green zone
- To find the constrained maximum, one must determine how to satisfy two requirements simultaneously



Lagrange' method of finding a constrained maximum

- Object: find the probability distribution that
  - Maximizes the number of ways of achieving the distribution (maximizes entropy)
  - Simultaneously keeps the total energy at a constant value
  - Simultaneously keeps the sum of probabilities equal to 1
- Form the function that represents all three requirements

$$K = \frac{S}{Nk} + \alpha\left(1 - \sum_k p_k\right) + \beta\left(< u > - \sum_k p_k u_k\right)$$

  - α and β are undetermined multipliers
- Maximizing K satisfies all three requirements

$$\frac{\partial K}{\partial p_j} = 0$$

Finding the Maxwell-Boltzmann distribution

- The maximization condition on K gives

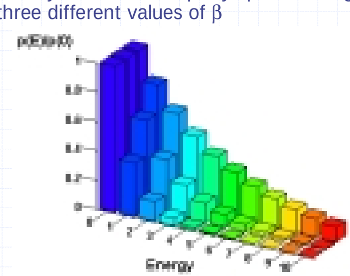
$$\frac{\partial K}{\partial p_j} = 0 = -\ln p_j - 1 - \alpha - \beta u_j$$

- Solution gives most probable distribution with constraints

$$p_j = \frac{1}{\sum_k e^{-\beta u_k}} e^{-\beta u_j}$$

Maxwell-Boltzmann distribution

- Probability function for equally spaced energy states for three different values of β



Average energy in the Maxwell-Boltzmann ensemble

- Definition

$$< u > = \sum_k p_k u_k = \frac{\sum_k e^{-\beta u_k} u_k}{\sum_j e^{-\beta u_j}}$$

- Observation about derivative

$$< u > = -\frac{\sum_k \frac{\partial e^{-\beta u_k}}{\partial \beta}}{\sum_j e^{-\beta u_j}} = -\frac{1}{\sum_j e^{-\beta u_j}} \frac{\partial \sum_k e^{-\beta u_k}}{\partial \beta}$$

$$= -\frac{1}{z}\frac{\partial z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln z$$

- Need only sum to determine average energy (and, therefore, macroscopic energy)

Summary

- W determines relative probability of configuration of molecules among single-molecule energy states
- Solution with Lagrange's method simultaneously
  - Maximizes entropy
  - Holds average energy fixed
  - Requires the sum of probabilities to be 1
- Maxwell-Boltzmann distribution
- Applies to a system of molecules at equilibrium
- Distribution depends on the undetermined multiplier β
- Need only the sum's dependence on β to calculate average energy