Statistical Mechanics

CHEM 361A: Introduction to Physical Chemistry

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Lecture 6

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Learning Objective: Develop statistical mechanical concepts and use them to derive the internal energy and heat capacity.

References:

- Chang Chapter 23

Macrostates and Microstates

In thermodynamics

- A **macrostate** is described by properties such as pressure, temperature, volume, internal energy and enthalpy.
- A **microstate** is described by quantifying the variables associated with the states of the individual atoms or molecules in a system.

We are typically not interested in individual microstates so we examine their average properties to get the macrostates of a system.

- The number of different microstates that leads to the same macrostate determines the probability of the macrostate occuring.

This is due to a major assumption of statistical mechanics, **the principle of equal a priori probability** which states that all microstates are equally probable.

Throwing Dice

The key thing is that as the number of total microstates increases, the number of probable/observable macrostates decreases.
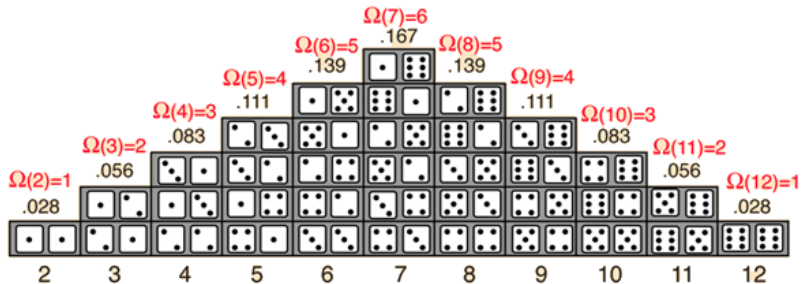

Total number of microstates: 36   Total number of macrostates: 11

This idea allows us to average over moles of particles ($\approx 10^{23}$ molecules) to get predictable observable quantities.

Molecular Systems

Suppose we have three identical, non-interacting molecules distributed over energy levels, where the total energy of the system is 3. How many different ways can we distribute the molecules (Assume that molecules can be distinguished from one another by their locations)?
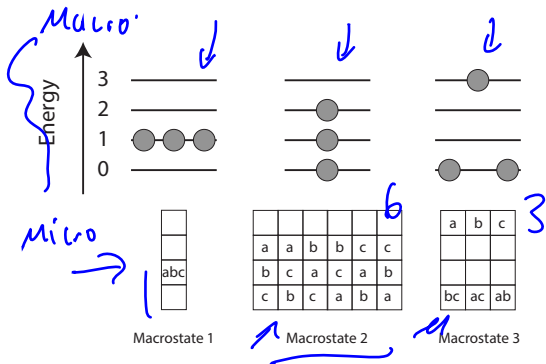
There are 10 ways (**10 microstates**) to distribute the molecules into three distinct distributions (**3 macrostates**). The microstates are all equally probably, however, the macrostates are not ($P(W_1) = \frac{1}{10}$, $P(W_2) = \frac{6}{10}$, and $P(W_3) = \frac{3}{10}$)

Counting Microstates

The general formula for calculating the number of microstates in a distribution (W) is

$$W = \frac{N!}{\prod_i n_i!}$$

where

- N is the total number of particles
- n_i is the number of particles in the nth energy level
- the symbol ! is called 'factorial' where $N!$ (or anything factorial) is given by

$$N! = N(N-1)(N-2)\cdots 1$$

- $\prod_i n_i!$ is the product of all $n_i!$. Written a different way:

$$\prod_i n_i! = n_1!n_2!\cdots n_{i-1}!n_i!$$

Three Particle System Example

Using the general formula for calculating the number of microstates in a distribution, calculate the number of microstates in each macrostate for three identical, non-interacting molecules distributed over energy levels, where the total energy of the system is 3. How many different ways can we distribute the molecules (Assume that molecules can be distinguished from one another by their locations).

Boltzmann Distribution Law

We have already seen one form of the Boltzmann Distribution Law

$$\frac{n_2}{n_1} = e^{-\frac{\Delta E}{k_B T}}$$

Which looks at the relative populations of two energy levels. The population of a single energy level, n_i is

$$n_i = n_0 e^{-\frac{\epsilon_i}{k_B T}}$$

where the total population can be determined by

$$N = \sum_i n_i = n_0 \sum_i e^{-\frac{\epsilon_i}{k_B T}}$$

n_i/N gives the fraction of the population in energy level i:

$$\frac{n_i}{N} = \frac{e^{-\frac{\epsilon_i}{k_B T}}}{\sum_i e^{-\frac{\epsilon_i}{k_B T}}}$$

Partition Functions

The summation term in the Boltzmann Distribution Law has great theoretical importance and is call the **partition function**, q:

$$q = \sum_i e^{-\frac{\epsilon_i}{k_B T}} \qquad P = \frac{q_1}{q}$$

where ϵ_i is the energy of state i, and the summation extends over all states.

- q has no units; it is just a number
- q tells us the number of accessible states to a particle at a given temperature. For example, at $T = 0$ only the ground state n_0 is accessible (we set $\epsilon_0 = 0$)
- It can be used to calculate various thermodynamic properties

Partition Function Example

A certain system has three energy levels at 0, 2.00×10^{-21} J and 8.00×10^{-21} J. Calculate the partition function, q, of the system at 300 K.

Molecular Partition Functions

To calculate any thermodynamical quantity, we need the partition functions for molecular systems. The energy of a single molecule in the ith state with energy ϵ_i is the sum of its various motions:

$$\epsilon_i = (\epsilon_i)_{trans} + (\epsilon_i)_{rot} + (\epsilon_i)_{vib}$$

- This sum is a good approximation since the energies of these motions are not independent

Substituting this sum into the definition of the partition function

$$q = \sum_i e^{-\frac{(\epsilon_i)_{trans} + (\epsilon_i)_{rot} + (\epsilon_i)_{vib}}{k_B T}}$$

$$= \sum_i e^{-\frac{(\epsilon_i)_{trans}}{k_B T}} \sum_i e^{-\frac{(\epsilon_i)_{rot}}{k_B T}} \sum_i e^{-\frac{(\epsilon_i)_{vib}}{k_B T}}$$

$$= q_{trans} q_{rot} q_{vib}$$

Molecular Partition Functions - Translation

The energies of a given state for the molecular partition functions are based on quantum mechanical results. For translation

- QM Model: Particle in a box

$$\epsilon_{trans} = \frac{n^2 h^2}{8mL^2} \quad \text{and} \quad q_{trans} = \frac{(2\pi m k_B T)^{\frac{3}{2}} V}{h^3}$$

where the volume of the container, V, is in m^3

Molecular Partition Functions - Rotation

The energies of a given state for the molecular partition functions are based on quantum mechanical results. For rotation

- QM Model: Rigid Rotator

$$\epsilon_{rot} = \frac{J(J+1)h^2}{8\pi I^2} \quad \text{and} \quad q_{rot} = \frac{8\pi^2 I k_B T}{\sigma h^2}$$

where σ is the symmetry number, which is the number of indistinguishable orientations that can be produced by rotations less than or equal to $360°$. For example

Homonuclear diatomic molecule
(H-H)

- Two indistinguishable orientations ($180°$ and $360°$)

- $\sigma = 2$

Heteronuclear diatomic molecule
(H-F)

- One indistinguishable orientation ($360°$)

- $\sigma = 1$

Molecular Partition Functions - Vibration

The energies of a given state for the molecular partition functions are based on quantum mechanical results. For vibration

- QM Model: Harmonic Potential

$$\epsilon_{vib} = \left(n + \frac{1}{2}\right) h\nu \quad \text{and} \quad q_{vib} = \frac{1}{1 - e^{-\frac{h\nu}{k_B T}}}$$

- If there are several vibrational modes, as for polyatomic molecules, then take the product of all the q_{vib} values each with their own frequency, ν.

- $q_{vib} \approx 1$ at room temperature indicates that only the ground state is thermally accessible.

Molecular Partition Functions Example

Determine the three molecular partition functions for carbon monoxide at 300 K. Assume that the CO molecule is in a box with a volume of 1 m^3, it has a moment of inertia, $I = 1.45 \times 10^{-46}$ kg m^2, and the fundamental frequency of vibration is 6.40×10^{13} s^{-1}.

Calculating Internal Energy using Partition Functions

Partition functions can be used to find state functions. For example, to find the internal energy we begin with the energy per molecule

$$\frac{E}{N} = \frac{\sum_i n_i \epsilon_i}{\sum_i n_i}$$

Substituting $n_i = n_0 e^{-\frac{\epsilon_i}{k_B T}}$ gives

$$E = \frac{N \sum_i n_0 \epsilon_i e^{-\frac{\epsilon_i}{k_B T}}}{\sum_i n_0 e^{-\frac{\epsilon_i}{k_B T}}} = \frac{N \sum_i \epsilon_i e^{-\frac{\epsilon_i}{k_B T}}}{q}$$

Calculating Internal Energy using Partition Functions (cont.)

To simplify this expression further, we must first return to the definition of a partition function and take the derivative as a function of temperature at constant volume

$$\left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial \left(\sum_i e^{-\frac{\epsilon_i}{k_B T}}\right)}{\partial T}\right)_V = \frac{1}{k_B T^2} \sum_i \epsilon_i e^{-\frac{\epsilon_i}{k_B T}}$$

Rearranging gives

$$\sum_i \epsilon_i e^{-\frac{\epsilon_i}{k_B T}} = k_B T^2 \left(\frac{\partial q}{\partial T}\right)_V$$

which is in the numerator in the expression for Energy

Calculating Internal Energy using Partition Functions (cont.)

Putting these two terms together

$$E = \frac{Nk_B T^2 \left(\frac{\partial q}{\partial T}\right)_V}{q}$$

since

$$\frac{\left(\frac{\partial q}{\partial T}\right)_V}{q} = \left(\frac{\partial \ln q}{\partial T}\right)_V$$

Substituting this and assuming one mole of gas ($Nk_B = R$) gives

$$E_m = RT^2 \left(\frac{\partial \ln q}{\partial T}\right)_V$$

Adding heat to the system at constant volume means that

$$U_m - U_{0,m} = RT^2 \left(\frac{\partial \ln q}{\partial T}\right)_V$$

Internal Energy from Partition Function Example

Determine an expression for the internal energy and $C_{V,m}$ for one mole of a monatomic gas using partition functions.

Summary

- A microstate quantifies the state of individual molecules while a macrostate groups together microstates with similar properties
- As the number of atoms increases, the number of likely observable macrostates decreases
- The number of microstates in a distribution is found by

$$W = \frac{N!}{\prod_i n_i!}$$

- The partition function, quantifies the number of accessible states at a given temperature and is determined by

$$q = \sum_i e^{-\frac{\epsilon_i}{k_B T}}$$

- Partition functions are used to determine thermodynamic state functions such as internal energy.