Course 565/665 Lecture Number ____ Date 3/27/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Correction (from Last Lecture)

$$p(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}$$

Last Time

Q at low T $(T \to 0)$

$$\frac{E_j}{kT} \longrightarrow \infty \quad \text{for } j \neq 1$$

$$\frac{E_1}{kT} = 0 \quad \text{for all } T.$$

$$Q = e^{-E_1/kT} + e^{-E_2/kT} + e^{E_3/kT} + \dots$$

(Energy levels go to infinity (∞).)

Low T Limit

$$p_j = \frac{e^{-E_j/kT}}{Q} = \begin{cases} 1 & j=1 \\ 0 & j \neq 1 \end{cases} \qquad Q = 1$$

Thus, all molecules are in the ground state. This is also the same as having energy levels that are infinitely spaced from each other.

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In the High T Limit $(T \to \infty)$

$\frac{E_j}{kT} = 0$; $e^{-E_j/kT} = 1$.

If a system has t energy levels, then

$Q = t$. This implies that at this infinitely high T limit, each energy level is equally likely to be populated.

This is the same as having energy levels that are ~~infinitely~~ infintesimally spaces (very close).

$$P_j = \frac{e^{-E_j/kT}}{Q} = \frac{1}{t}$$ for t energy levels.

In real life, people evaluate $\frac{E_j}{kT}$. "kT" is the thermal energy. When energy level spacings are much smaller than kT, many levels are populated (rotational energy levels). When energy level spacings are much larger than kT, most molecules are in the ground state (vibrational or electronic levels).

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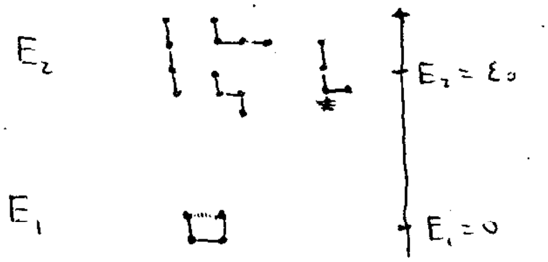
The Polymer Example Revisited



Sometimes different microstates are degenerate, or having the same energy.

In real life, you can often measure "compact" (c) vs "open" (o) conformations but not distinguish the number of microstates in o.

Density of States / Degeneracy W(E)

W(E) = # of microstates in a given energy level E.

l = number of energy levels.

$$Q = \sum_{E_j=1}^{l} W(E_j)\, e^{-E_j/kT} \qquad P_j = \frac{W(E_j)\, e^{-E_j/kT}}{Q}$$

Sum over energies.

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Example | Collapse of a 4-beaded polymer chain.

Q?: How do populations of "c" and "o" depend on T.

$$Q = 1 + 4e^{-\varepsilon_0/kT}$$

Low T: $T \to 0$, $Q = 1$

$$p_c = \frac{1}{Q} = 1 \; ; \quad p_o = \frac{4e^{-\varepsilon_0/kT}}{Q} = \frac{0}{1} = 0$$

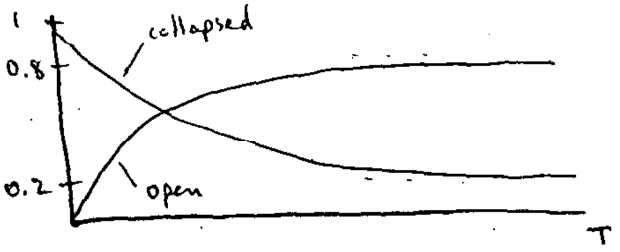
All are in the collapsed state.

High T: $T \to \infty \Rightarrow Q = 5$

$$p_c = \frac{1}{Q} = \frac{1}{5} = 0.2$$

$$p_o = \frac{4}{5} = 0.8$$

Most of the polymer is unfolded (in the "o" state.



Factoring Q

Dealing with subsystems, extending results to entire systems.