Introduction to Self Assembly of Macromolecules

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Outline

• Introduction to Statistical Mechanics
  ➢ Magnetic system with two states (up and down)
  ➢ Boltzman factor

• Polymers
  ➢ Polymer Conformation
  ➢ Polymer Solutions, Melts and Blends

• Copolymers
  ➢ Melts (SCMF)
  ➢ Micelles (Simulations)

• Polyelectrolytes
  ➢ bulk
  ➢ surface segregation
Introduction to Statistical Mechanics

- Relationship of number of accessible states to entropy
  \[ \sigma = \log g \] (1)

- Transfer of energy between two systems, increases entropy and achieves the same temperature
  \[ \frac{1}{\tau} \equiv \left( \frac{\partial \sigma}{\partial U} \right)_{N,V} \] (2)

- Probability of finding a system at energy \( \varepsilon \) over 0
  \[ \frac{P(\varepsilon)}{P(0)} = \frac{g(U_0 - \varepsilon)}{g(U_0)} = \frac{\exp[\sigma(U_0 - \varepsilon)]}{\exp[\sigma(U_0)\]]} \] (3)

- Thermal average energy at temperature \( \tau \)
  \[ <\varepsilon> = \sum_i \varepsilon_i P(\varepsilon_i) \] (4)

- Helmholtz free energy
  \[ F \equiv U - \tau \sigma \] (5)
Quantum States

- Fundamental assumption: equally likely to be found in any of the quantum states accessible to it
- Each quantum state has a definite energy
- Multiplicity or degeneracy: quantum states that have nearly the same energy
- Important: number of quantum states, not number of energy levels

Atomic hydrogen

0 ___________ (2)
2
4
6
8
10
12
14
(8) (32) (18) (50)
Binary Model System

- Magnetic system: $N$ non-interacting spins
- Spin value: $+m$ (↑) or $-m$ (↓)
- $2^N$ equally accessible arrangements
- Each arrangement specifies the configuration of the 1$^{st}$, 2$^{nd}$,…$N^{th}$ spin:

  ...↑↑↓↓↓↑↑↓↓↓↓↑↓...

- Total magnetization $M$: $Nm$, $(N-2)m$, $(N-4)m$,… $-Nm$
  - The same value of $M$ can occur with multiple arrangements
Enumeration of States

• Spin excess with $s$ being an integer having $N_\uparrow$ spins up and $N_\downarrow$ spins down:
  \[ N_\uparrow - N_\downarrow = 2s \]

• The multiplicity factor or the number of arrangements $[g(N,s)]$ for a system of $N$ magnets that have the same value of $s$:
  \[
  g(N,s) = \frac{N!}{\left(\frac{1}{2}N + s\right)! \left(\frac{1}{2}N - s\right)!} = \frac{N!}{N_\uparrow!N_\downarrow!}
  \]

• Application of magnetic field leads to a different energy for states with a different $s$

• Total number of arrangements:
  \[
  \sum_{s=-\frac{1}{2}N}^{1} g(N,s) = 2^N
  \]
Sharpness of the Multiplicity Function

- \( N! \) prevents calculation of multiplicity for large values of \( N \)
- Gaussian distribution (using the Stirling approximation) allows for the approximation of multiplicity when \( N \gg 1 \) and \( |s| \ll N \)
  - Sharp peak at \( s = 0 \)
  - System contains stable physical properties

\[
g(N, s) \approx g(N, 0) \exp\left(-\frac{2s^2}{N}\right)
\]
when
\[
g(N, 0) \approx 2^N \left(\frac{2}{\pi N}\right)^{1/2}
\]

- Average values are necessary – macroscopic measurements of a constantly changing system
Closed Systems

- Constant: energy, number of particles, volume, and external parameters affecting the system
- Probability ($P$) of a system being in an accessible state ($s$)

\[
P(s) = \frac{1}{g}
\]

- Two systems in thermal contact
  - Energy (only) is transferred freely between the two
  - Total energy is constant
  - Number of accessible states in the combined system:

\[
g(N,s) = \sum_{s_2} g_1(N_1,s_1)g_2(N_2,s-s_1)
\]

  - $N_1$, $N_2$, and $s$ are constant
  - Most probably conformation – when $g_1g_2$ is at a maximum; dictates most of the properties of the system
Entropy

- Using (1), relate entropy of two systems in thermal contact
  \[
  \left( \frac{\partial \sigma_1}{\partial U_1} \right)_{N_1} = \left( \frac{\partial \sigma_2}{\partial U_2} \right)_{N_2}
  \]

- (2) comes from: the equation above, the thermal contact of the two systems, and:
  \[
  \tau = k_B T
  \]

  - Boltzmann constant: \( k_B = 1.381 \times 10^{-23} \text{ joules/Kelvin} \)

- Positive change in entropy when the two systems come into contact:
  \[
  \Delta \sigma = \left( \frac{\partial \sigma_1}{\partial U_1} \right)_{N_1} (-\Delta U) + \left( \frac{\partial \sigma_2}{\partial U_2} \right)_{N_2} (\Delta U) = \left( -\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) \Delta U
  \]
Entropy Flow Between Systems

- Energy flow: from the system with higher temperature ($U_1$) to system with lower temperature ($U_2$)
- The entropy increases until the system reaches the most probable configuration

\[ U_2 = U - U_1 \]
Ways to Increase the Entropy of a System

1. Add particles
2. Add energy
3. Increase the volume
4. Decompose molecules
5. Let a linear polymer curl up
Laws of Thermodynamics

- **Zeroth law**: if two systems are in thermal equilibrium with a third system, they must be in thermal equilibrium with each other.
- **First law**: heat is a form of energy (conservation of energy).
- **Second law**: if a closed system is in a configuration that is not the equilibrium configuration, the most probably consequence will be that the entropy of the system will increase (law of increase of entropy).
  \[
  \sigma_{\text{final}} \approx \log \left( \frac{g_1 g_2}{g_1 g_2} \right)_{\text{max}} \geq \sigma_{\text{initial}} = \log \left( \frac{g_1 g_2}{g_1 g_2} \right)_0
  \]
- **Third law**: the entropy of a system approaches a constant value as the temperature approaches zero.
Boltzmann Factor

- Closed system: small system in thermal contact with a very large system (reservoir)

<table>
<thead>
<tr>
<th>Reservoir $\mathcal{R}$</th>
<th>Energy $U_0 - \varepsilon_1$</th>
<th>$g_{\mathcal{R}}(U_0 - \varepsilon_1)$ states</th>
</tr>
</thead>
<tbody>
<tr>
<td>System $S$</td>
<td>State 1</td>
<td>Energy $\varepsilon_1$</td>
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</table>

<table>
<thead>
<tr>
<th>Reservoir $\mathcal{R}$</th>
<th>Energy $U_0 - \varepsilon_2$</th>
<th>$g_{\mathcal{R}}(U_0 - \varepsilon_2)$ states</th>
</tr>
</thead>
<tbody>
<tr>
<td>System $S$</td>
<td>State 2</td>
<td>Energy $\varepsilon_2$</td>
</tr>
</tbody>
</table>

- When $S$ is in a specific state the total number of accessible states = $g_{\mathcal{R}}$

- A Taylor series expansion on (3) altered for the two states above gives:
  \[
  \frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp(-\varepsilon_1/\tau)}{\exp(-\varepsilon_2/\tau)}
  \]
  - Boltzmann factor: term in the form of $\exp(-\varepsilon/\tau)$
  - Probability of finding the system in quantum state 1 versus 2
Partition Function and Helmholtz Free Energy

- **Partition function:**
  \[ Z(\tau) = \sum_s \exp\left(-\frac{\varepsilon_s}{\tau}\right) \]

- Proportionality between the probability and the Boltzmann factor
  \[ P(\varepsilon_s) = \frac{\exp\left(-\frac{\varepsilon_s}{\tau}\right)}{Z} \]

- The average energy for \( S \) given in (4) is \( U \) or \( \langle \varepsilon \rangle \)

- Helmholtz free energy (5) shows the balance of a system with minimum energy and maximum entropy

- Relation of the Helmholtz and the partition function:
  \[ Z = \exp\left(-\frac{F}{\tau}\right) \]

- Relation of probability to the Helmholtz and the energy
  \[ P(\varepsilon_s) = \frac{\exp\left(-\frac{\varepsilon_s}{\tau}\right)}{\exp\left(-\frac{F}{\tau}\right)} = \exp\left(\frac{F - \varepsilon_s}{\tau}\right) \]
Thermodynamics

The entropy

\[ s/K_B = \sigma = \log g(N,U) \]

Entropy increases if we add particles (N increases).

Polymer conformation is dominated by entropy: without interactions it is a random walk. In different environments (in solutions or in blends or if monomers are charged, etc) the conformation is affected.

Charged flexible chains high a) to low c) salt concentration (screened Coulomb interactions)

Netz + Andelman 2002
Entropy

\[ g(N,m) \sim g(N,0) \exp(-2m^2/N) \]

so \[ \sigma = \sigma(N,0) - 2m^2/N, \]

\[ F = U - TS \quad \text{or} \quad F/KT = U/KT - \sigma \]

In polymers \( m=R \) is in one dimension the end to end distance of the chain.

Get \( F(R) \) in units of \( KT \)

\[ F^\text{en}(R) = \frac{R^2}{2Na^2} \]
• Real flexible polymer molecules change *conformations* by rotation about single bonds (typically C-C bonds) in the backbone.

• Steric repulsions cause the rotation to be hindered, with three staggered rotational states (gauche (G), trans (T) and gauche' (G')) energetically favored. Calculation of the average shape of a flexible polymer chain, including all bonding details, is demanding.

• The oversimplified model can be modified to describe in statistical terms the shape of real polymer molecules.
Random Walk

- The freely jointed chain \( \mathbf{r} = \sum_{i=1}^{n} l_i \)
- The average value of the end-to-end vector \( \mathbf{r} \) is \( \langle \mathbf{r} \rangle = 0 \).
- The average of square of the end-to-end distance \( r^2 = \mathbf{r} \cdot \mathbf{r} \)

\[
= nl^2 + 0 \quad \langle \mathbf{r} \cdot \mathbf{r} \rangle = \left\langle \sum_{i=1}^{n} l_i \right \rangle \cdot \left\langle \sum_{k=1}^{n} l_k \right \rangle
\]

Hence \( \langle r^2 \rangle = nl^2 \)

- Diffusion eq. with \( t=n \) and \( D=l^2/6 \)

\[
\frac{\partial P}{\partial t} = D \nabla^2 P
\]
Interactions: SAW using Flory argument

\[ F = F^{en} + F^{ex} \]

\[ F^{ex} \sim \nu \frac{(N / R^3)^2}{2} R^3 \sim \nu \frac{(N)^2}{2 R^3} \]

\[ F^{en}(R) = \frac{3R^2}{2Na^2} \]

\( \nu \) is the excluded volume
\( \nu > 0 \) is good solvent or SAW
the solvent wants to be homogeneously mixed causing swelling of the chains.
Minimize \( F \) with respect to \( R \) to get Flory exponent in good solvent, which is close
the numerical value

\[ R \approx \nu^{1/5} N^{3/5} \]
Collapsed Chains in solvents

- When $v < 0$ the chain is in a bad solvent: it collapses

\[ R \approx N^{1/3} \]

(Add three body term in free energy)

- When $v = 0$ the chain is a random walk

\[ R \approx N^{1/2} \]
Polymer Solution: what is $v$ in solutions?

Flory-Huggins interaction parameter $\chi$

$$\chi = \frac{Z}{k_B T} \left( E_{AB} - \frac{E_{AA} + E_{BB}}{2} \right)$$

- $\chi = 0$  Ideal
  - No interaction

- $\chi > 0$  Repulsive, immiscible
  - Van der Waals

Degree of incompatibility: $v = 1 - 2\chi$

- $\chi \rightarrow$ energetic
- $N \rightarrow$ entropic

Free energy of mixing

$$\frac{F}{k_B T} = \frac{\phi}{N} \ln(\phi) + (1 - \phi) \ln(1 - \phi) + \chi \phi (1 - \phi)$$

Expand when solvent concentration is small

$$\frac{F}{k_B T} = \frac{\phi}{N} \ln(\phi) + \frac{1}{2} (1 - 2\chi) \phi \phi$$

volume fraction $\phi$
semi-dilute: overlapping of blobs:

Inside the blobs chains are SAW or swollen

For lengths larger than blobs chains are RW of blobs
Polymer melt state: Mean Field

Free energy of mixing

\[ \frac{F}{k_B T} = \frac{\phi}{N} \ln(\phi) + \frac{1-\phi}{N_1} \ln(1-\phi) \]

Expand when solvent concentration is small (virial expansion)

\[ \frac{F}{k_B T} = \frac{\phi}{N} \ln(\phi) + \frac{1}{N_1} \phi^2 \]

Degree of incompatibility: \( v \) is reduced by \( N \) then ideal chains if \( N_1 = N \)

Expansion of \( F(R) \) for \( R \sim R_0 \) \( (1 + 4z/3 + \ldots) \)  \( z \sim v N^{1/2}/b^3 \)

(from Flory at \( R = R_0 \)) then if \( v \sim 1/N_1 \) then \( z \sim N^{1/2}/N_1 \)
Polymer blend phase diagram

Flory-Huggins interaction parameter $\chi$

$$\chi = \frac{Z}{k_B T} \left( E_{AB} - \frac{E_{AA} + E_{BB}}{2} \right)$$

<table>
<thead>
<tr>
<th>$\chi$</th>
<th>Ideal mixing</th>
<th>No interaction</th>
</tr>
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<tbody>
<tr>
<td>$\chi = 0$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\chi &lt; 0$</td>
<td>Attractive, miscible</td>
<td>Hydrogen bonding</td>
</tr>
<tr>
<td>$\chi &gt; 0$</td>
<td>Repulsive, immiscible</td>
<td>Van der Waals</td>
</tr>
</tbody>
</table>

Degree of incompatibility: $\chi N$

$\chi \rightarrow$ energetic

$N \rightarrow$ entropic

Free energy of mixing

$$\frac{F}{k_B T} = \frac{\phi_A}{N_A} \ln(\phi_A) + \frac{\phi_B}{N_B} \ln(\phi_B) + \chi \phi_A \phi_B$$

Graph: 2 phase

Critical point

1 phase