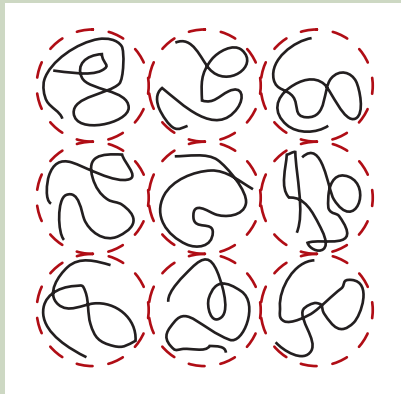# Semidilute and Concentrated Polymer Solutions

# Concentrated Polymer Solutions.

Up to now (except for the chapter on the viscosity of entangled polymer systems) we discussed mainly the dilute polymer solutions, where single chains do not interact with each other. Now we consider more systematically the equilibrium properties of concentrated polymer solutions of overlapping coils.
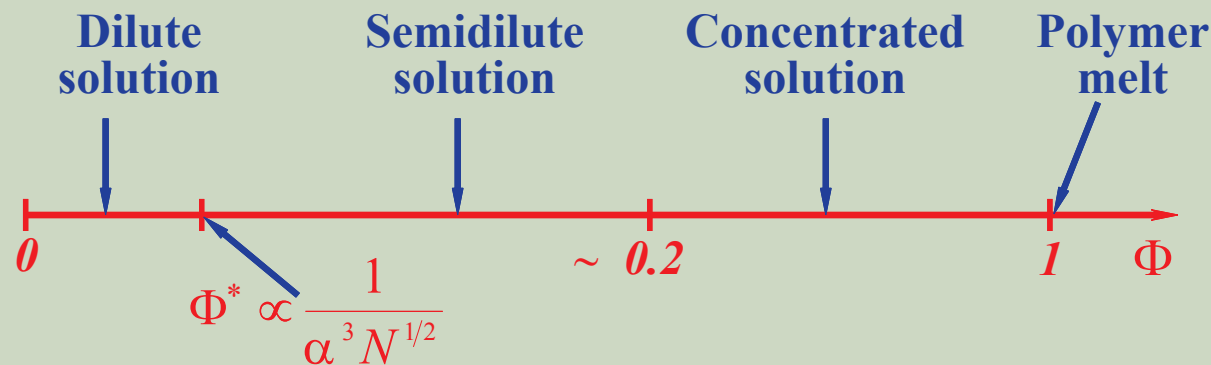


The overlap concentration of monomer units is

$$c^* \sim \frac{N}{4\pi R^3/3} \sim \frac{N}{\alpha^3 N^{3/2} a^3} \sim \frac{1}{\alpha^3 N^{1/2} a^3}$$

The corresponding volume fraction

$$\phi^* \sim c^* \upsilon \sim \frac{\upsilon}{\alpha^3 N^{1/2} a^3} \ll 1$$

# Semidilute Polymer Solutions.

Since $\phi^* \ll 1$, the overlap of the coils occurs already at a very low polymer concentration. Therefore, there is a wide concentration region where ($i$) coils are overlapping and strongly entangled; and ($ii$) $\phi \ll 1$. Such solutions are called semidilute.

**Dilute solution**     **Semidilute solution**     **Concentrated solution**     **Polymer melt**

$0$     $\sim 0.2$     $1$    $\Phi$

$$\Phi^* \propto \frac{1}{\alpha^3 N^{1/2}}$$

The semidilute regime existls only in polymer solutions, it is a specific polymer feature. The crossover volume fraction between the dilute and semidilute regimes is

$$\phi^* \sim N^{-1/2} \quad \text{for } \Theta\text{-solvents (ideal coils),}$$

$$\phi^* \sim \alpha N^{-1/2} \sim N^{-4/5} \quad \text{for good solvents (swollen coils).}$$

# Screening of the Excluded Volume Interactions.

Consider a chain swelling in a good solvent because of the excluded volume. If the concentration is above the overlap concentration $c^*$ an important phenomenon called the screening of excluded volume interactions takes places (Flory, Edwards): as the chain concentration increases in the region $c > c^*$, coils swelling gradually diminishes and finally it vanishes in the melt (i.e., in the melt the coils are ideal - the Flory theorem).

A qualitative explanation of this phenomenon is as follows.

Consider a square lattice, whose sites are filled with a melt of dimers (each molecule occupying two sites) with a small number of monomers dispersed in this melt.

Screening means an appearance of some additional attraction which neutralizes the repulsion.
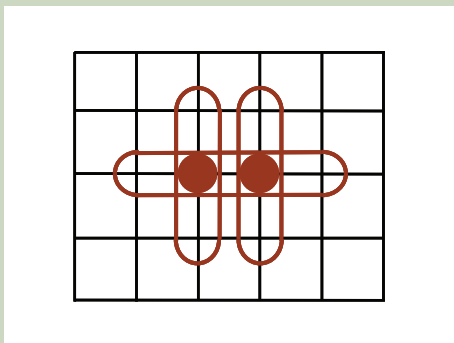
# Screening of the Excluded Volume Interactions.
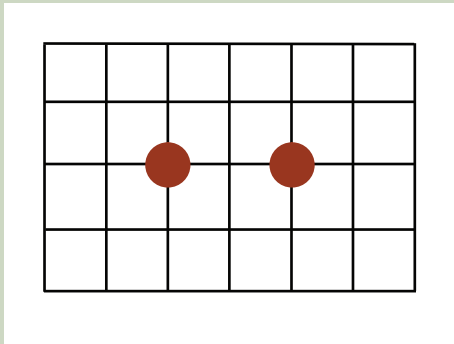
Two sites with excluded volume repel each other.
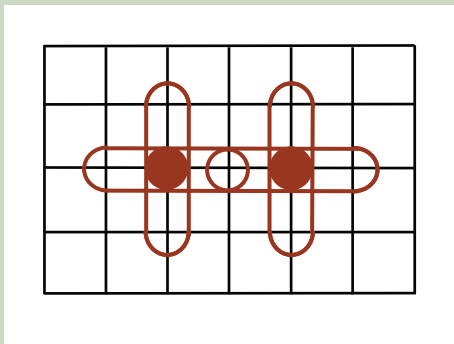
In the liquid of dimers two sites normally exclude 8 possible dimers positions.

If these sites are nearest neighbors, they exclude only 7 dimer positions thus leading to additional attraction.

In the liquid of polymers (multimers) this effect becomes even larger and leads to the complete screening of excluded volume.

# An Example of Scaling Arguments: Chain Size in a Semidilute Solution.

Thus, in the solution of flexible polymer chains far above the $\Theta$-point $R \sim aN^{3/5}$ at $\phi < \phi^*$ and $R \sim aN^{1/2}$ at $\phi = 1$.

To determine the value of $R$ in the intermediate region $\phi^* \ll \phi \ll 1$ (i.e, in the semidilute polymer solution) we use the so-called scaling method.

Scaling considerations are widely used in polymer science. We use this particular problem - that of concentration dependence of $R$ in the semidilute polymer solutions - as an example to illustrate how these considerations generally work. They usually include the following three steps.

**Step 1**. We assume that $\phi^*$ is the only characteristic polymer volume fraction in the range $0 < \phi < 1$. Thus, the desired $R$ should be a function of the form

$$R = aN^{3/5} f\left(\phi / \phi^*\right)$$

where $f(x)$ is some unknown function of a single argument.

# An Example of Scaling Arguments: Chain Size in a Semidilute Solution.

**Step 2**. Since for dilute solutions $R \sim a N^{3/5}$ the asymptotic form of $f(x)$ at low $x$ is

$$f(x)\big|_{x \ll 1} \approx 1$$

For large $x$ we assume

$$f(x)\big|_{x \gg 1} \approx x^n$$

i.e., a power law with some yet undefined exponent $n$. Thus, since $\phi^* \sim N^{-4/5}$ in a good solvent, one has for $\phi \gg \phi^*$

$$R = const \times a N^{3/5} \left(\phi / \phi^*\right)^n = const \times a N^{3/5} \left(\phi N^{4/5}\right)^n$$

**Step 3**. The exponent $n$ is chosen from some additional physical considerations. In this particular case we know that at $\phi = 1$ $R \sim a N^{1/2}$ (Flory theorem). Thus,

$$\frac{3}{5} + \frac{4}{5} n = \frac{1}{2}; \quad n = -\frac{1}{8}$$

# An Example of Scaling Arguments: Chain Size in a Semidilute Solution.

We get, thus, the final result: in semidilute solutions (i.e. in the for $\phi^* \ll \phi \ll 1$) the following relation holds

$$R \sim aN^{3/5}\left(\phi/\phi^*\right)^{-1/8} \sim aN^{3/5}\left(\phi N^{4/5}\right)^{-1/8} \sim aN^{1/2}\phi^{-1/8}$$

I.e., the size of polymer coil drops with the increase of $\phi$ in the semidilute solution range; at $\phi \sim 1$ all the swelling vanishes.

The scaling arguments of this type has been successfully used for a number of polymer problems. The scaling approach allows to obtain answers which are correct up to some numerical constants, while avoiding complicated calculations. Note, however, that to give correct scaling predictions one should have beforehand a rather deep physical insight into the problem under consideration (see the assumption of "one characteristic volume fraction" in this particular case).

# Polymer Solutions in Poor Solvents.

In a poor solvent (i.e., below the $\Theta$-point) the attraction between the monomer units prevails. Single chains (or chains in the dilute enough solutions) collapse and form a globule. However, in concentrated solutions the macroscopic phase separation takes place as well. One can consider it as a kind of intermolecular collapse.



**Supernatant phase**

**Precipitant phase**
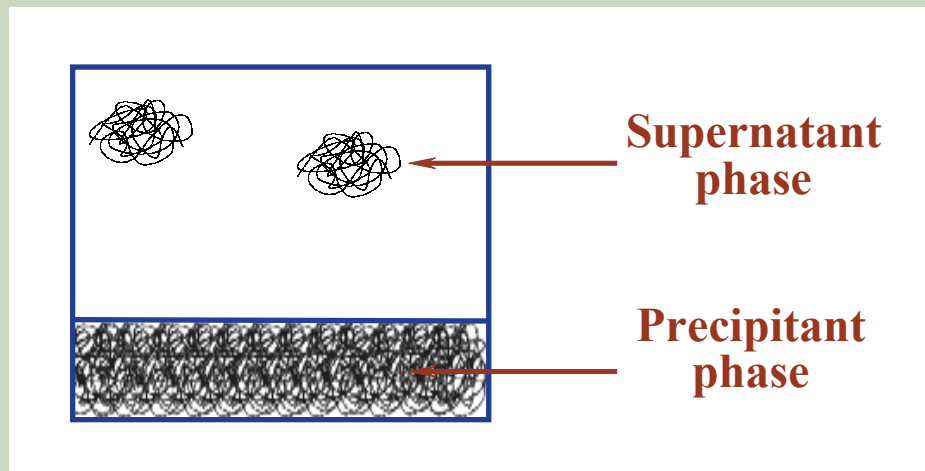
To find the conditions for macroscopic phase separation it is necessary to write down the free energy of a polymer solution. It was first proposed independently by Flory and Huggins in 1941-42 within a lattice model of polymer solutions.

# The Flory-Huggins Model.
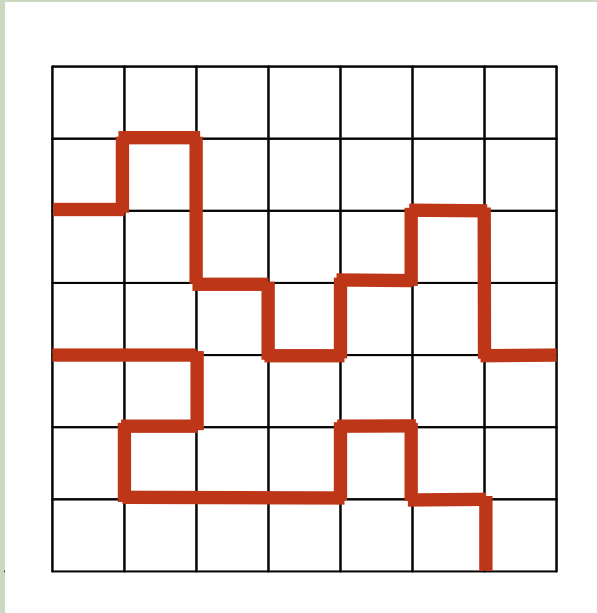
Polymer chains are represented by non-self-intersecting random walks on a lattice and energy $-\varepsilon$ is assigned to each close contact of two monomer units which are not neighbors along the chain. In the Flory-Huggins theory the number of conformations is counted and the entropy is derived as a logarithm of this number. The energy is calculated from the average number of close contacting monomer units, which is assumed to be proportional to $Nn\phi$, where $n$ is the total number of chains and $N$ is the number of units in each chain.

# The Flory-Huggins Model.
# The Entropy of Mixing.

Consider first the entropy $S$ due to the allocation of the polymer chains onto the lattice. As usual, we have

$$S(n, N, \Omega) = k \ln W(n, N, \Omega)$$

where $k$ is the Boltzmann constant, and $W$ is the number of possible ways to allocate all $n$ polymers chains, each of them consisting of $N$ units, while $\Omega \geq Nn$ is the total number of lattice sites.

To calculate $W$ let us put the chains on the lattice one by one. The number of possible ways to put the first chain on the lattice equals

$$W_1 = \frac{1}{2} \Omega z (z-1)^{N-2}$$

where $z$ is the lattice coordination number. Indeed, there are $\Omega$ ways to put the first link, then $z$ ways to put the second one on an adjacent site, and $(z-1)$ ways to put each of the rest $N-2$ links. The factor $1/2$ allows for the symmetry of the chain.

Note: we neglected the intrapolymer excluded volume interactions, a reasonable approximation in semidilute and concentrated regimes.

# The Flory-Huggins Model.
# The Entropy of Mixing.

Now, the number of possible ways to pu the *i*-th chain on the lattice can be estimated as follows

$$W_i = W_1 \left( 1 - \frac{(i-1)N}{\Omega} \right)^N$$

where the expression in brackets is a probability to find any particular latice site to be already occupied by the previously allocated chains.

The total desired number of possible allocations $W$ then equals

$$W = \frac{1}{n!} \prod_{i=1}^{n} W_i$$

where the factor $(n!)^{-1}$ allows for the indistinguishability of the chains. Putting it in other words

$$S(n, N, \Omega) = -kn \ln(n/e) + k \sum_{i=1}^{n} \ln W_i$$

where the Stirling formula is used:

$$\ln n! = n \ln n/e + O(\ln n)$$

# The Flory-Huggins Model.
# The Entropy of Mixing.

We get thus

$$S(n, N, \Omega)/k = -n \ln n + n + n \ln W_1 + N \sum_{i=1}^{n} \ln\left(1 - \frac{(i-1)N}{\Omega}\right) \approx$$

$$\approx -n \ln n + n + n \ln W_1 + (\Omega - nN)\ln\left(\frac{\Omega - nN}{\Omega e}\right)$$

where to calculate the sum we approximated it with an integral and used the formula

$$\int_0^x \ln(1 - kx')dx' = \frac{1}{k}(1 - kx)\ln\frac{1 - kx}{e}$$

We introduce now a new variable $\phi = nN/\Omega$, the volume fraction of the polymer, and rewrite the entropy per unit volume as follows:

$$S(n, N, \Omega)/k\Omega = \frac{\phi}{N}\ln\phi - \frac{\phi}{N}(\ln N - 1 + \ln W_1) +$$

$$+(1 - \phi)\ln(1 - \phi) - (1 - \phi)$$

# The Flory-Huggins Model.
# The Entropy of Mixing.

The result for the entropy of allocation we have obtained can be rewritten as follows:

$$S(n, N, \Omega)/k\Omega = \frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi) + \text{some terms linear in } \phi$$

and it turns out that the linear terms are, to the big extent, irrelevant. Indeed, these terms are proportional to the total number of particles in the system ($\phi\Omega = nN$) and thus they do not change in any process that does not change the number of particles. They are in fact indistinguishable from any possible contribution into the entropy due to the internal degrees of freedom the monomers units may have and lead just to a shift in the chemical potential of the monomers. The expression

$$S_{mix}(n, N, \Omega)/k\Omega = \frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi)$$

is called the entropy of mixing since it corresponds to the entropy change between the homogeneous state with volume fraction $\phi$ and the reference state in which polymer and solvent (represented by the empty sites) are fully separated.

# The Flory-Huggins Model.
# The Free Energy.

In turn, the energy $E$ due to the attraction between the monomer units of the polymer can be estimated as follows

$$E = -\varepsilon Nn(z-2)\phi/2 = -\frac{\varepsilon(z-2)}{2}\phi^2\Omega$$

Indeed, each of $Nn$ monomers has, on average $(z-2)\phi$ neighbors, apart from those two which are adjacent along the chain, and each contact gives the contribution to the energy equal to $-\varepsilon$; the factor one half allows for the fact that we have took each contact into account twice.

We have now all ingredients needed to constract the free energy $F = E - TS$. One has

$$F/kT\Omega = \frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi) - \chi\phi^2$$

where we have introduced the so-called Flory-Huggins parameter:

$$\chi = \frac{\varepsilon(z-2)}{2kT}$$

# The Flory-Huggins Model.
# The Free Energy.

$$\frac{F}{\Omega kT} = \frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi) - \chi\phi^2$$

The physical meaning of the terms in the Flory-Huggins free energy is as follows:

$\dfrac{\phi}{N}\ln\phi$ — This term describes the translational entropy of the coils (the free energy of an ideal gas of coils)

$(1-\phi)\ln(1-\phi)$ — This term, the "translational entropy" of the empty cites, effectively accounts for the excluded volume interactions: it provides the increase in the compressibility coefficient when $\phi$ approaches unity.

$-\chi\phi^2$ — This term is responsible for the attraction of the monomer units.

# The Flory-Huggins Model.

With the increase of $\chi$ the quality of the solvent becomes poorer. Which value of $\chi$ corresponds to the $\Theta$-point? To answer this question expand $F$ in the powers of $\phi$:

$$\frac{F}{\Omega kT} = \frac{\phi}{N}\ln\phi + \frac{1}{2}(1-2\chi)\phi^2 + \frac{1}{6}\phi^3 + \ldots$$

where

$\dfrac{\phi}{N}\ln\phi$       is the ideal gas term

$\dfrac{1}{2}(1-2\chi)\phi^2$       is the term describing the binary interactions (second virial coefficient $B$)

$\dfrac{1}{6}\phi^3$       corresponds to the ternary interactions and the third virial coefficient $C$
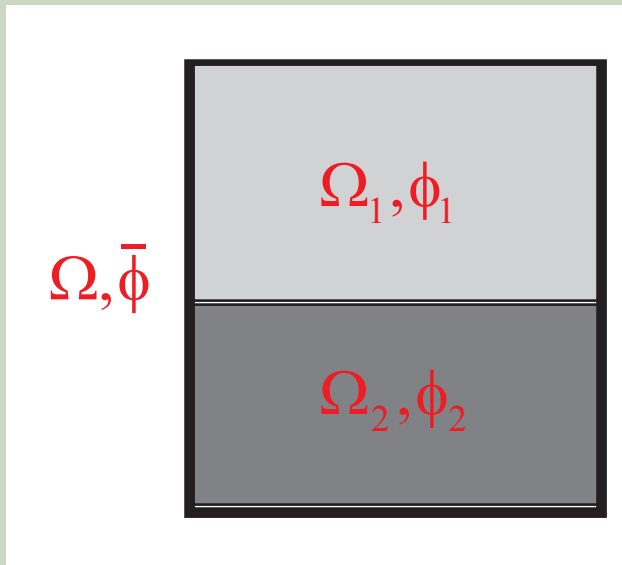
At $T = \Theta$   $B = 0$. Thus, the $\Theta$-point corresponds to $\chi = 1/2$:

$\chi < 1/2$    corresponds to good solvent

$\chi > 1/2$    corresponds to poor solvent

# Macroscopic Phase Separation.

Is the homogeneous solution with a given volume fraction $\overline{\phi}$ stable with respect to a decomposition into two different macroscopic phases? To answer this question, we proceed as follows.



Assume the new phases to have volume fractions $\phi_1$ and $\phi_2$, and volumes $\Omega_1$ and $\Omega_2$, respectively. Then the following relationships hold

$$\begin{cases} \Omega_1 + \Omega_2 = \Omega \\ \phi_1\Omega_1 + \phi_2\Omega_2 = \overline{\phi}\Omega \end{cases}$$

Solving this set of equations with resect to the phase volumes we get

$$\Omega_1 = \frac{\phi_2 - \overline{\phi}}{\phi_2 - \phi_1}\Omega; \quad \Omega_2 = \frac{\overline{\phi} - \phi_1}{\phi_2 - \phi_1}\Omega$$

# Macroscopic Phase Separation.

Now, the total free energy of the decomposed state $F_{dec}$ equals

$$F_{dec}\left(\phi_1, \phi_2, \bar{\phi}\right) = f\left(\phi_1\right)\Omega_1 + f\left(\phi_2\right)\Omega_2$$

where $f(\phi)$ is the free energy per unit volume. Therefore,

$$f_{dec}\left(\phi_1, \phi_2, \bar{\phi}\right) = \frac{F_{dec}\left(\phi_1, \phi_2, \bar{\phi}\right)}{\Omega} = \frac{\phi_2 - \bar{\phi}}{\phi_2 - \phi_1} f\left(\phi_1\right) + \frac{\bar{\phi} - \phi_1}{\phi_2 - \phi_1} f\left(\phi_2\right)$$

If the free energy of the decomposed state is less then the free energy of the initial homogeneous one: $f_{dec}\left(\phi_1, \phi_2, \bar{\phi}\right) < f\left(\bar{\phi}\right)$ then it is advantegeous for the system to separate into phases.

# Macroscopic Phase Separation.

$$f_{dec}(\phi_1, \phi_2, \overline{\phi}) = \frac{\phi_2 - \overline{\phi}}{\phi_2 - \phi_1} f(\phi_1) + \frac{\overline{\phi} - \phi_1}{\phi_2 - \phi_1} f(\phi_2)$$

It turns out that this formula has a very instructive geometrical meaning.
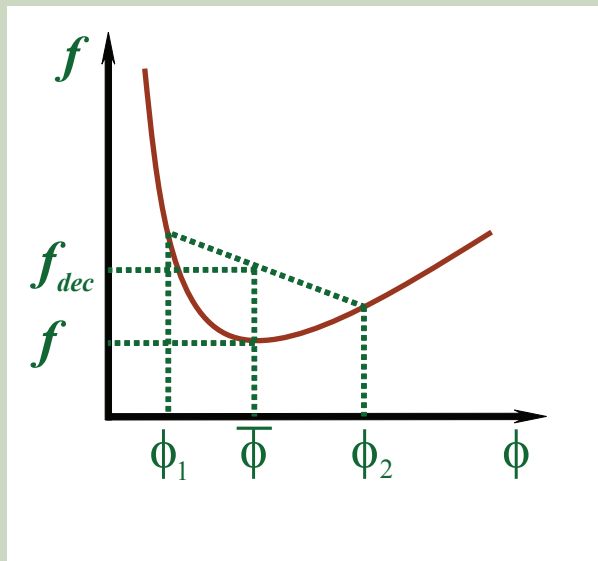


Indeed, if one plots the free energy as a function of $\phi$, then $f_{dec}$ is just the ordinate of the intersection of a secant line connecting the points of the plot with volume fractions $\phi_1$ and $\phi_2$, and the line $\phi = \overline{\phi}$.

We see thus that for the phase separation to be possible the free energy as a function of $\phi$ should have a concave part. If the free energy is convex for all $0 < \phi < 1$, the homogeneous state is always stable.

# Macroscopic Phase Separation.

The typical dependence of the Flory-Huggins free energy on the polymer volume fraction $\phi$ in poor solvents is as follows.
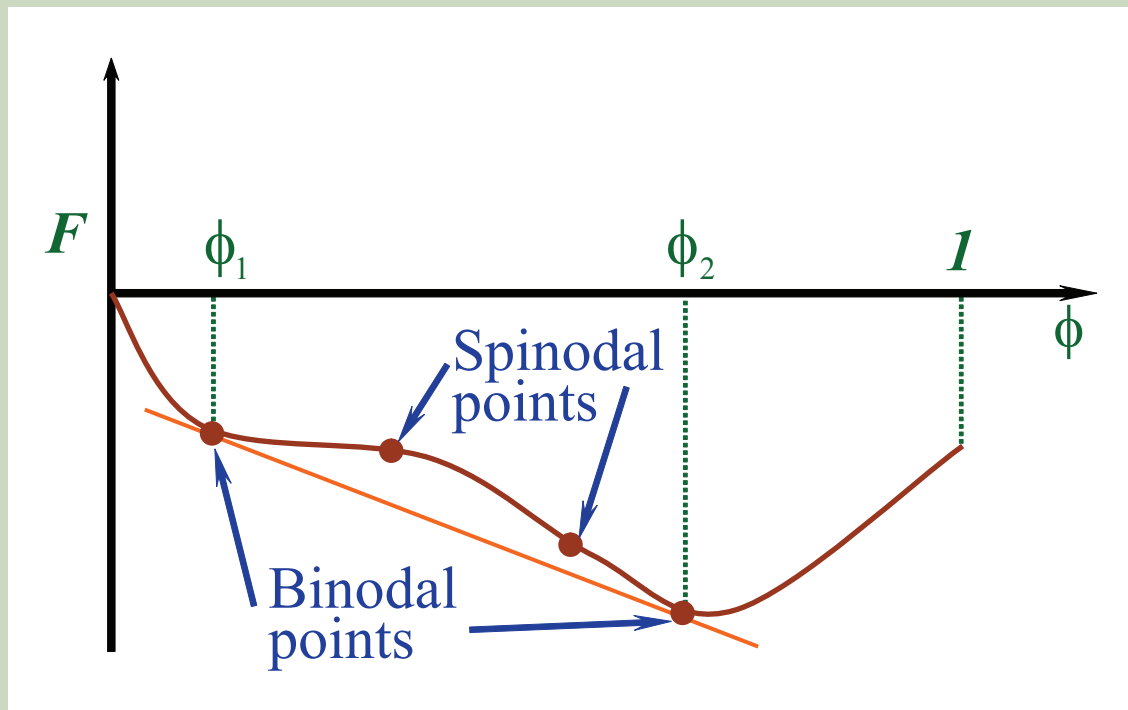


This dependence contains both convex and concave parts. Thus, the macroscopic phase separation is possible in this case. It indeed occurs in the region of volume fractions between the two so-called binodal points.
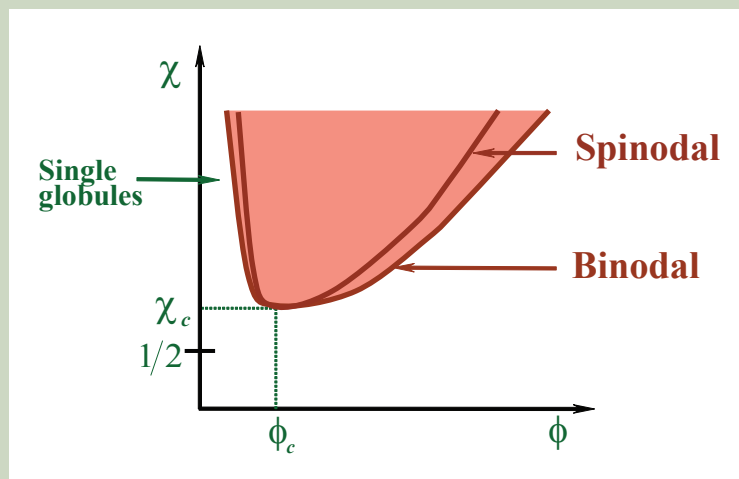
# Macroscopic Phase Separation.

The region corresponding to the macroscopic phase separation is bound by the common tangent straight line giving rise to the so-called binodal curve. The condition of the absolute instability of the homogeneous phase at a given concentration is determined from the positions of inflexion points ($\partial^2 F/\partial\phi^2 = 0$) which gives rise to the so-called spinodal curve.

The spinodal condition reads

$$\frac{1}{N\phi} + \frac{1}{1-\phi} - 2\chi = 0 \quad \text{or} \quad \chi = \frac{1}{2}\left(\frac{1}{N\phi} + \frac{1}{1-\phi}\right)$$

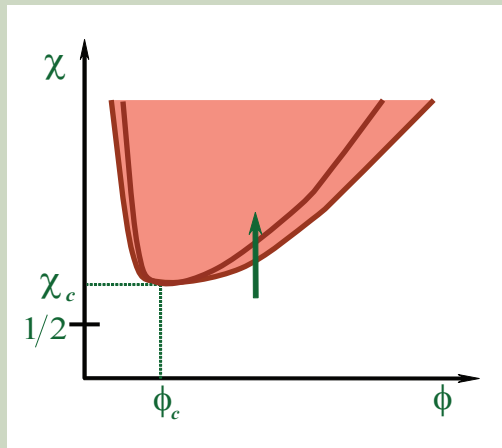This dependence together with the binodal is shown in the figure:



$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{N}}$$

$$\phi_c = \frac{1}{\sqrt{N}}$$

# Macroscopic Phase Separation. The spinodal decomposition.

Let us now adress the question of how the phase separation actually occurs. Consider a homogeneous system out of its region of stability (prepared, for example by rapid cooling of a stable system as shown by the green arrow on the figure), and consider an infinitesimal concentration fluctuation $\delta\phi$ in this homogeneous system. According to the general formula derived above, the change of the free energy per unit volume due to such a fluctuation equals

$$\delta F = \frac{1}{2}\left[F(\phi + \delta\phi) + F(\phi - \delta\phi)\right] - F(\phi) = \frac{(\delta\phi)^2}{2}\frac{\partial^2 F}{\partial\phi^2}$$

Thus, the homogeneous system beyond the spinodal curve, i.e., one with $\partial^2 F/\partial\phi^2 < 0$, is unstable with respect to any infinitesimal concentration fluctuation, and any such fluctuation grows with time leading to the process of the so-called spinodal decomposition.

# Macroscopic Phase Separation. The spinodal decomposition.

One can imagine the process of the spinodal decomposition as follows. In any thermodynamic system there is always a pattern of concentrational fluctuations, usually each of them decays rapidly with time: if there happens to be a region reach in some component, the component diffuses out of this region returning the system back to the homogeneous state. In the spinodal decomposition just the opposite process takes place. If there happens to be a region rich in polymer, the polymer starts diffusing into this region, thus increasing the fluctuation until the equilibrium volume fraction of a new phase is reached.

Thus, there rapidly arises a pattern of interpenetrating domains with concentrations $\phi_1$ and $\phi_2$, known as Cahn-Hilliard concentration waves. Then the wavelength of these waves (i.e., the typical domain size) starts growing with time, finally leading to a macroscopically separated state.

# Macroscopic Phase Separation. Nucleation and Growth.

Consider now the case when the homogeneous phase is unstable but $\partial^2 F/\partial\phi^2 > 0$. This indeed happens if the state in question lies between the binodal and spinodal curves (see figure).
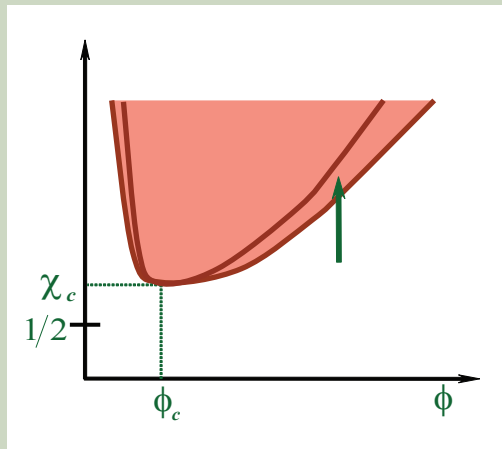


In this case the small concentration fluctuations are still suppressed similary to the stable case. To initiate the phase separation a fluctuation exceeding some critical size (both in terms of the concentration difference and in terms of the spatial extent) is needed (Lifshitz, Slezov, Wagner).

These extremely large fluctuations act as nuclei for the new phase which starts to grow around them.

Note that this process is much slower then the spinodal decomposition, since large fluctuations are extremely rear. The presense of some external nucleation centers in the system (like dust or irregularities on the surface of the reaction vessel) can speed up the process. However, the homogeneous state is said to be metastable in this case.

# Macroscopic Phase Separation. Conclusions.

Phase diagram with both the binodal and the spinodal:
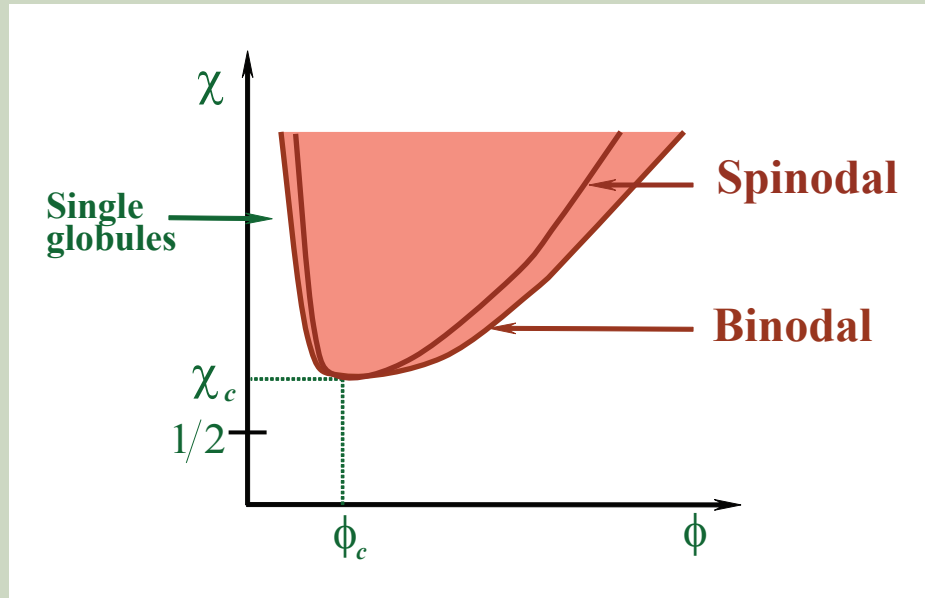


1. Macroscopic phase separation takes place at the quality of the solvent only slightly poorer than the $\Theta$-solvent:

$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{N}}$$

2. The critical point for macroscopic phase separation corresponds to the dilute enough solution: $\phi_c = \frac{1}{\sqrt{N}}$

# Macroscopic Phase Separation. Conclusions.

**3.** The region of isolated globules in solution corresponds to very low polymer concentrations, especially at the values of $\chi$ significantly larger than 1/2.

**4.** The precipitant phase close enough to the $\Theta$-point is very diluted.

**5.** For different values of $N$ the binodal curves (boundaries of the phase separation region) have the form:



$$N_1 > N_2 > N_3$$
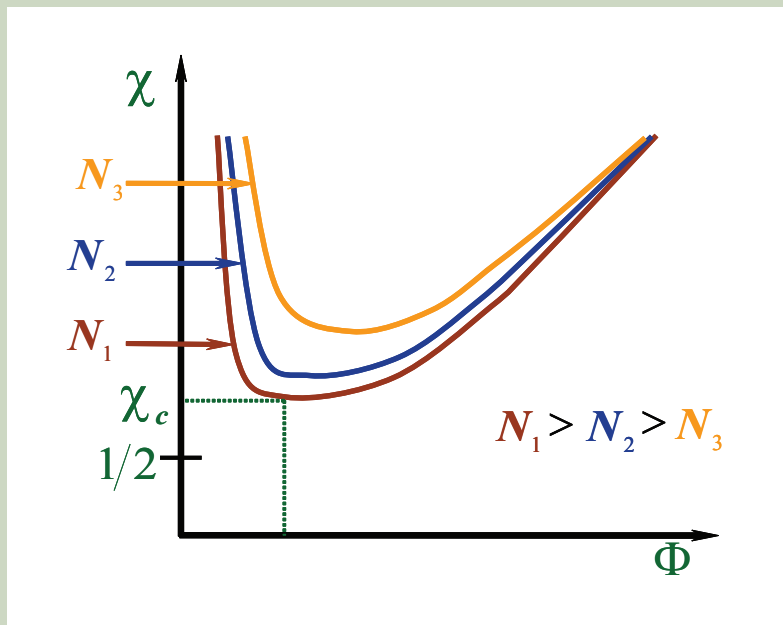
With the increase of $N$ the critical temperature becomes closer to the $\Theta$-point, and the critical concentration becomes lower.

# Method of Fractional Precipitation.

Method of fractional precipitation for the polydisperse polymer solutions: when the quality of solvent is becoming poorer or polymer concentration increases in the dilute enough range at first the most high-molecular fraction precipitates, then the next fraction, etc., ...; polymers with lower molecular weights require more significant increase in $\chi$ and $\phi$ to precipitate. In this way polymer fractionation is achieved.

Reverse method is called the method of fractional dissolution: when one moves from the region of insolubility to the region of partial solubility at first the fractions with the lowest values of $M$ are dissolved.

# Temperature dependence of $\chi$.

What is the connection between the Flory-Huggins parameter $\chi$ and the temperature $T$? Within the framework of the lattice model $\chi \sim \varepsilon/kT$, and in the experimental variables $T, c$ the phase diagram has the form shown in the figure, i.e. the poor solvent region corresponds to $T < \Theta$
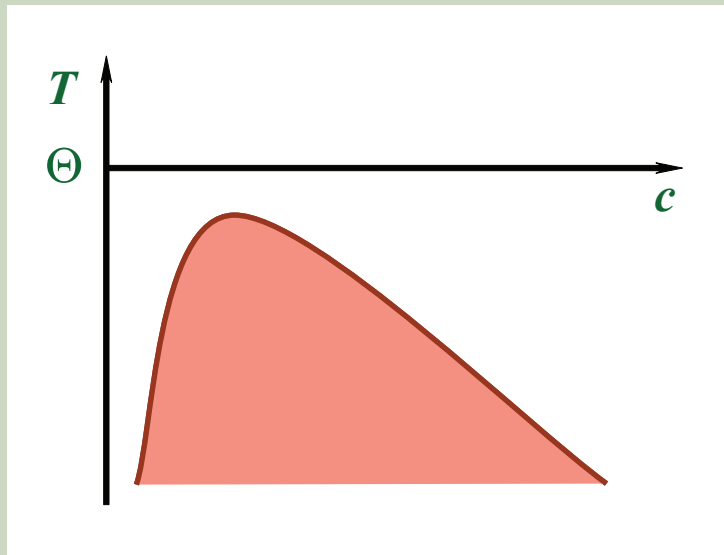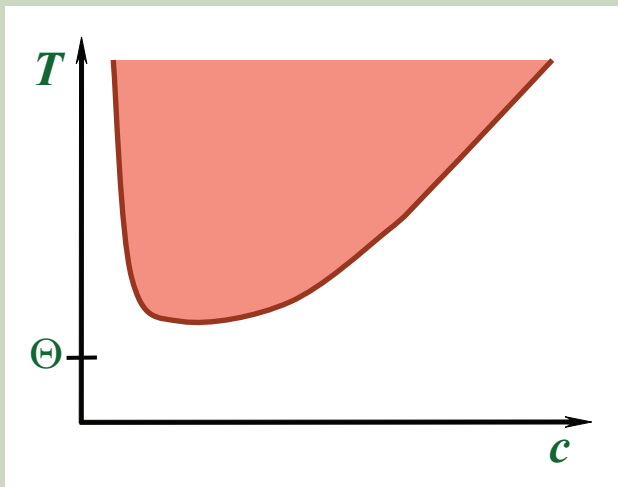


Such situation is called upper critical solution temperature (UCST) - critical point is "on the top" of the phase separation region.

Examples: poly(styrene) in cyclohexane (around $35^{o}$C), poly(isobutylene) in benzene, acetylcellulose in chlorophorm.

# Temperature dependence of χ.

However, due to the complicated renormalization of polymer-polymer interactions due to the solvent, sometimes effective $\chi$ increases with the increase of $T$. Then the $T, c$ phase diagram has the form shown in the figure below, i.e. the poor solvent region corresponds to $T > \Theta$.



This situation is called lower critical solution temperature (LCST) - critical point is "on the bottom" of the phase separation region.

Examples: poly(oxyethylene) in water, methylcellulose in water, in general - most of the water-based solutions.

The reason: increase of the so-called hydrophobic interactions with the temperature (organic polymers contaminate the network of hydrogen bonds in water reducing the network entropy).