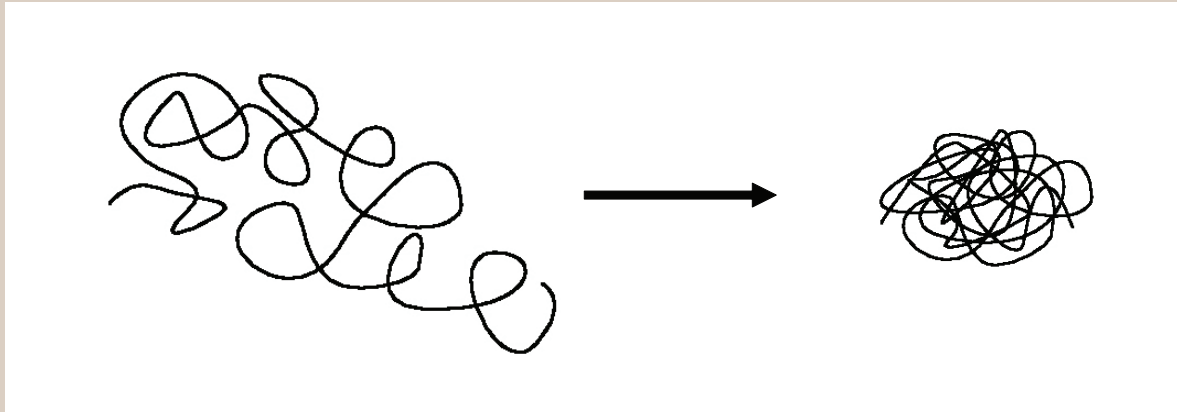


# Swelling and Collapse of Single Polymer Molecules and Gels.

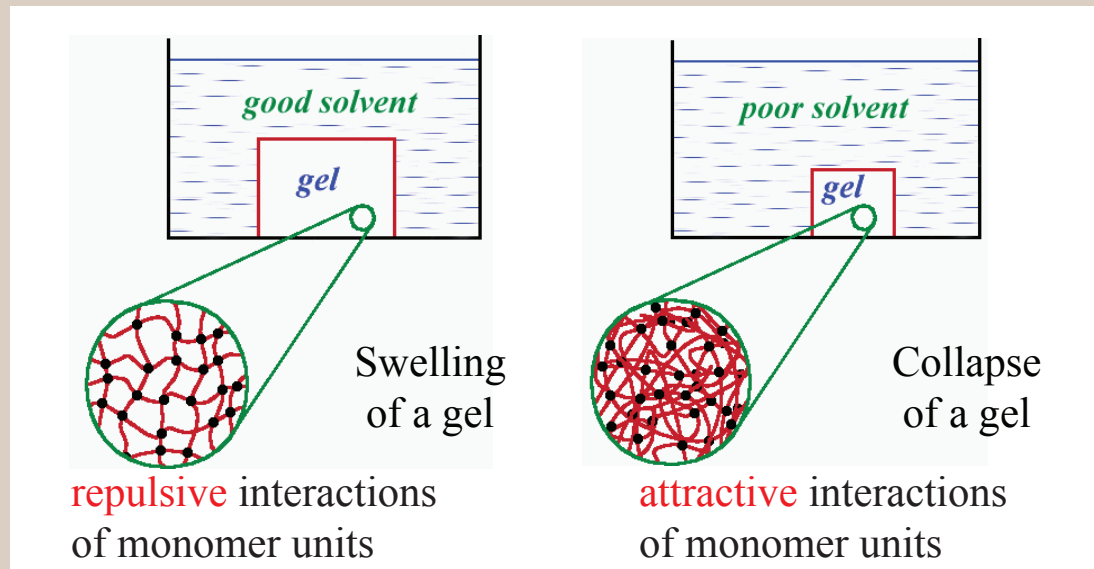
# Coil-Globule Transition in Single Polymer Molecules.



the coil-globule  
transition

If polymer chains are not ideal, interactions of non-neighboring monomer units (the so-called **volume interactions**) should be taken into account. If these interactions are **repulsive**, the coil **swells** with respect to its ideal dimensions. If monomer units **attract** each other, contraction leads to the “**condensation**” of polymer chain upon itself with the formation of a “dense droplet” conformation, which is called a **polymer globule**.

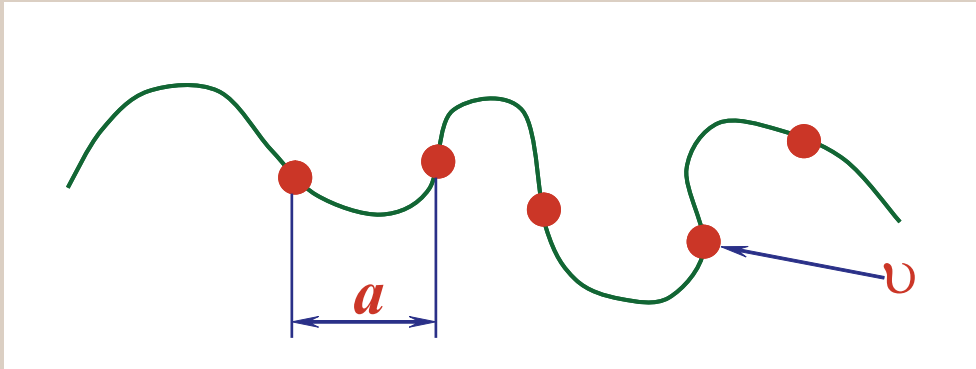
# Swelling and Collapse of Polymer Gels.



The gel as a whole is in fact just one **giant three-dimensional molecule**.

**Advantage** of studying gels vs. dilute polymer solutions: possibility of direct **visual observation** of conformational transitions. Main **disadvantage**: very **slow equilibration** in macroscopic gel. For the sample of 1 cm it takes several days. Equilibration time  $\tau$  can be diminished by using smaller size  $L$  of the sample, one can show that  $\tau \sim L^2$ .

# Models to Study Volume Interactions: Beads on a String.



The chain is considered as a sequence of beads of volume  $u$  connected by an immaterial filament. The connectivity of beads manifests itself in the fact that the probability distribution for a vector  $\vec{r}$  between neighboring beads is :

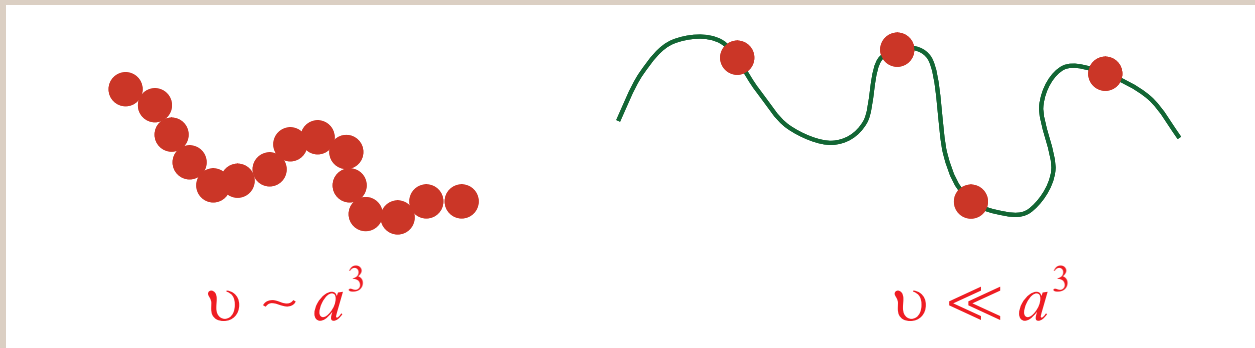
$$g(\vec{r}) = \left(2\pi a^2/3\right)^{-3/2} \exp\left(-3\vec{r}^2/2a^2\right)$$

(note, that this distribution is equivalent to assuming that the neighbouring beads are connected by an ideal string with zero equilibrium length).

For any real chain one can construct an equivalent model of beads by dividing it into segments of several persistent lengths and by assigning all the mass of each segment to the dividing points.

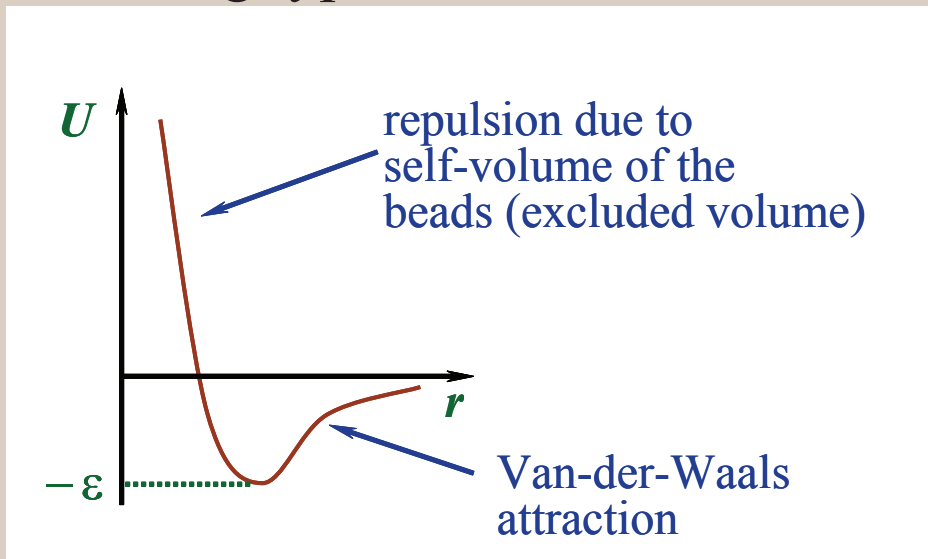
# Models to Study Volume Interactions: Beads on a String.

Both cases are possible:



( $a$  is the average distance between neighboring beads).

The beads interact with the interaction potential  $U(\vec{r})$  of the following typical form:



**Note:** in principle this potential is renormalized by the presence of the solvent, so its form can be much more complicated.



# The Concept of $\Theta$ -temperature.

It should be noted that for both models:

1. At high values of  $T$ , the ratio  $\epsilon/kT \ll 1$  and only repulsion matters. The coil should swell with respect to its ideal dimensions; this phenomenon is called the **excluded volume effect**. In this case the so-called **swelling coefficient** of the coil,  $\alpha$ , is larger than unity:

$$\alpha^2 = \frac{\langle R^2 \rangle}{\langle R^2 \rangle_0} > 1$$

2. At low values of  $T$ , the ratio  $\epsilon/kT \gg 1$ , and attraction dominates. The coil should shrink and form a **condensed globule** (the coil-globule transition).

3. There should be some **intermediate** value of  $T$ , when the effects of **repulsion and attraction compensate each other** and the coil adopts its ideal-chain (unperturbed) size. This temperature is called the  $\Theta$ -temperature.

# The Virial Expansion.

The **free energy of a coil** is a sum of energetic and entropic contributions:

$$F = E - TS$$

Contrary to the ideal case, the energy  $E$  does not equal zero.

Recall though that for the long chains the concentration of the monomer units inside the polymer coil is very small. This allows us to expand  $E$  in the powers of the monomer units concentration  $n$  (this is called **virial expansion**):

$$E = NkT (Bn + Cn^2 + \dots)$$

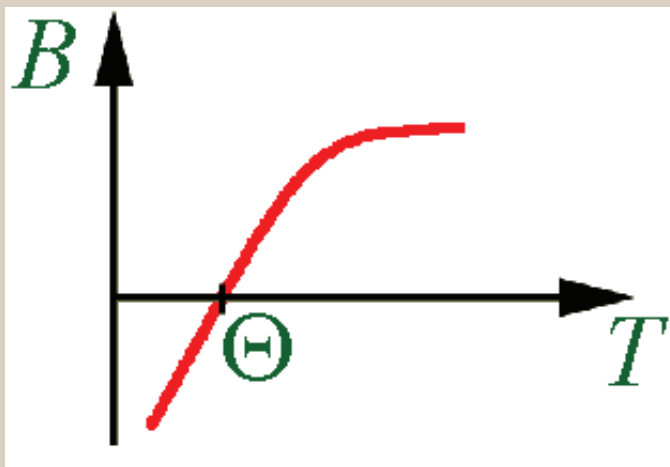
Here  $B$ ,  $C$ , ... are the second, third, ... **virial coefficients**; these coefficients are responsible for binary, ternary, etc. interactions of monomeric units, they depend only on the interaction potential between the units, e.g.

$$B(T) = \frac{1}{2} \int [1 - \exp(-U(r)/kT)] d^3r$$



# The Virial Expansion.

It is easy to see from the expression for  $B(T)$  that at high  $T$  ( $\epsilon/kT \ll 1$ )  $B \sim v$ , while with the decrease of  $T$  the value of  $B$  diminishes, and it reaches zero at some temperature  $\Theta$ .



A typical dependence of the second virial coefficient on temperature.

At  $T \sim \Theta$   $B \sim v\tau$  where  $\tau = \frac{T - \Theta}{T}$

At the  $\Theta$ -temperature  $B = 0$ , internal energy vanishes and chain adopts the ideal coil conformation. At  $T > \Theta$  repulsion dominates, coil swells due to the excluded volume effect, this is the region of **good solvent**. At  $T < \Theta$  attraction dominates, coil shrinks into globule, this is called the region of **poor solvent**.

# Remarks about $\Theta$ -temperature.

1. The complete compensation of the attractive and repulsive interactions at the  $\Theta$ -point is a specific polymer property (it never happens in gases, for example). This phenomenon is connected to the **low concentration** in polymer coils.
2. The fact that repulsion dominates for  $T > \Theta$  and attraction - for  $T < \Theta$  is valid for the usual form of the potential  $U(\vec{r})$ . For more involved forms of the potential the situation may be more complicated: the inverse temperature dependence may occur, or even several  $\Theta$ -points may arise.

# The Excluded Volume Problem.

Consider a polymer coil in the **good solvent** region far **above the  $\Theta$ -point**, and let us calculate the **swelling** of the coil due to the **excluded volume**.

$$F = E - TS = NkTBn - TS = NkTB \frac{3N}{4\pi R^3} + \frac{3kTR^2}{2Na^2} + const$$

In the second term we have used the expression for the entropy of a polymer coil **expanded** up to the size  $R$  (see the lecture about high elasticity of polymers).

The first term of this expression is the **excluded volume repulsion** which **induces** the coil swelling, while the second is **entropic elasticity** which **opposes** the swelling. The balance of these factors (as given by the minimization of  $F$  with respect to  $R$ ) gives the equilibrium coil size.

# The Excluded Volume Problem.

The free energy of a coil is

$$F = kT \left( \frac{3}{4\pi} \frac{N^2}{R^3} B + \frac{3}{2} \frac{R^2}{Na^2} \right)$$

Minimization of  $F$  with respect to  $R$  ( $\partial F / \partial R = 0$ ) gives

$$-\frac{BN^2}{R^4} + \frac{R}{Na^2} = 0$$

where we have omitted all numerical coefficients. Therefore,

$$R \sim (Ba^2)^{1/5} N^{3/5} \sim (\nu a^2)^{1/5} N^{3/5}$$

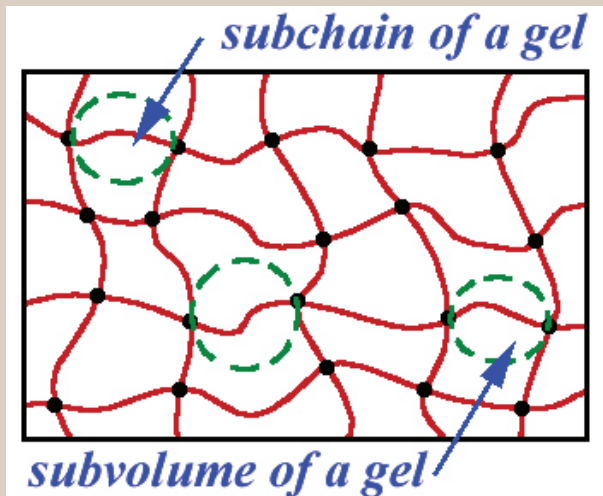
and for the swelling coefficient  $\alpha$

$$\alpha \sim \frac{R}{N^{1/2} a} \sim \left( \frac{\nu}{a^3} \right)^{1/5} N^{1/10} \gg 1$$

The polymer coil swells essentially due to the excluded volume. In spite of the low polymer concentration in the coil, the swelling is significant because of **high susceptibility of long polymer chains**.

# Swelling of Polymer Gels.

For simplicity, consider a gel synthesized in the presence of a large amount of solvent. For such gels **entanglements** between the gel chains are not important.



A swollen polymer gel

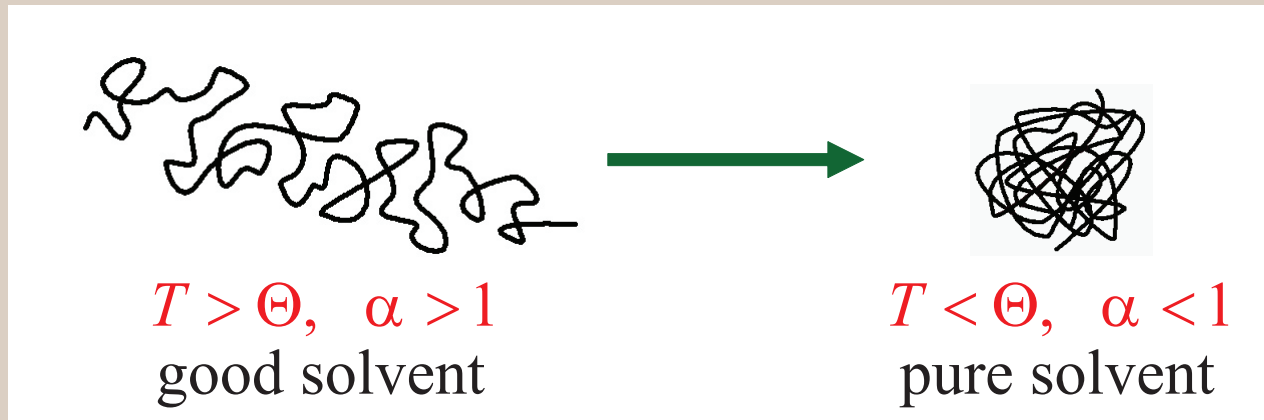
Since each **subchain of a gel swells independently** in its own subvolume:

1. The **swelling** degree of each subchain is equal to the swelling degree of the gel **as a whole**.
2. The **swelling** degree of each subchain is the same as the swelling degree of an **isolated chain in the good solvent**:

$$\alpha \sim \left( \nu a^{-3} \right)^{1/5} N^{1/10} \gg 1$$

# The coil-globule transition.

Consider now the whole range of temperatures. When the temperature is lowered below the  $\Theta$ -point, the **coil-globule transition** (i.e., polymer chain **collapse**) should take place.



The interest to the globular conformation of macromolecules is induced by molecular biophysics: the native conformations of proteins-enzymes correspond to globules. Denaturation of proteins is sometimes considered to be analogous to the transition from globule to coil.

# The Coil-Globule Transition.

To determine the characteristics of the coil-globule transition we once again study the free energy  $F = E - TS$  but now the expressions for both  $E$  and  $S$  should be modified.

**Energy.** For dense globules higher virial coefficients should be taken into account:

$$E = NkT (Bn + Cn^2 + \dots)$$

Indeed, below the  $\Theta$ -point the term  $Bn$  corresponds to attraction, and there should be some repulsive term to allow for the fact that the concentration of the globule cannot grow infinitely. This role is played by the repulsive  $Cn^2$  term, since normally  $C \sim v^2 > 0$  in the region of interest.

The higher-order virial coefficients, though relevant for very dense globules, can be neglected in the vicinity of the  $\Theta$ -point. Thus, omitting, as usual, all numerical coefficients, we have

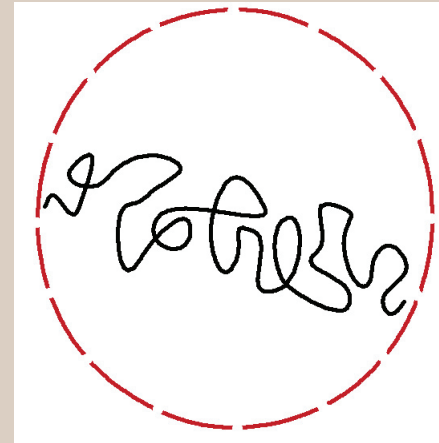
$$E = NkT \left( \frac{BN}{R^3} + \frac{CN^2}{R^6} \right)$$

# The Coil-Globule Transition.

**Entropy.** We are now to take into account the possibility of chain compression, not only extension.

For extended coil  $R \gg N^{1/2}a$

$$S = -\frac{3kR^2}{2Na^2} \sim -\frac{R^2}{Na^2}$$



For compressed globule  $R \ll N^{1/2}a$

$$S = -k \frac{N}{g} \sim -k \frac{Na^2}{R^2}$$



The subchain between two “collisions” with the globule surface (its length  $g$  satisfies  $ga^2 \sim R^2$ ,  $g \sim R^2/a^2$ ) is practically free. Each collision with the surface corresponds to the loss of entropy of order one.



# The Coil-Globule Transition.

One can write down an **interpolation formula** for the entropy which is valid by the order of magnitude in the whole region of intermediate  $\alpha$ :

$$S = -k \left( \frac{R^2}{Na^2} + \frac{Na^2}{R^2} \right)$$

Thus, for the free energy one has

$$F = E - TS = NkT \left( \frac{BN}{R^3} + \frac{CN^2}{R^6} \right) + kT \left( \frac{R^2}{Na^2} + \frac{Na^2}{R^2} \right)$$

Minimization of  $F$  with respect to  $R$  ( $\partial F / \partial R = 0$ ) gives

$$\frac{R^5}{Na^2} - RN a^2 - \frac{CN^3}{R^3} = BN^2$$

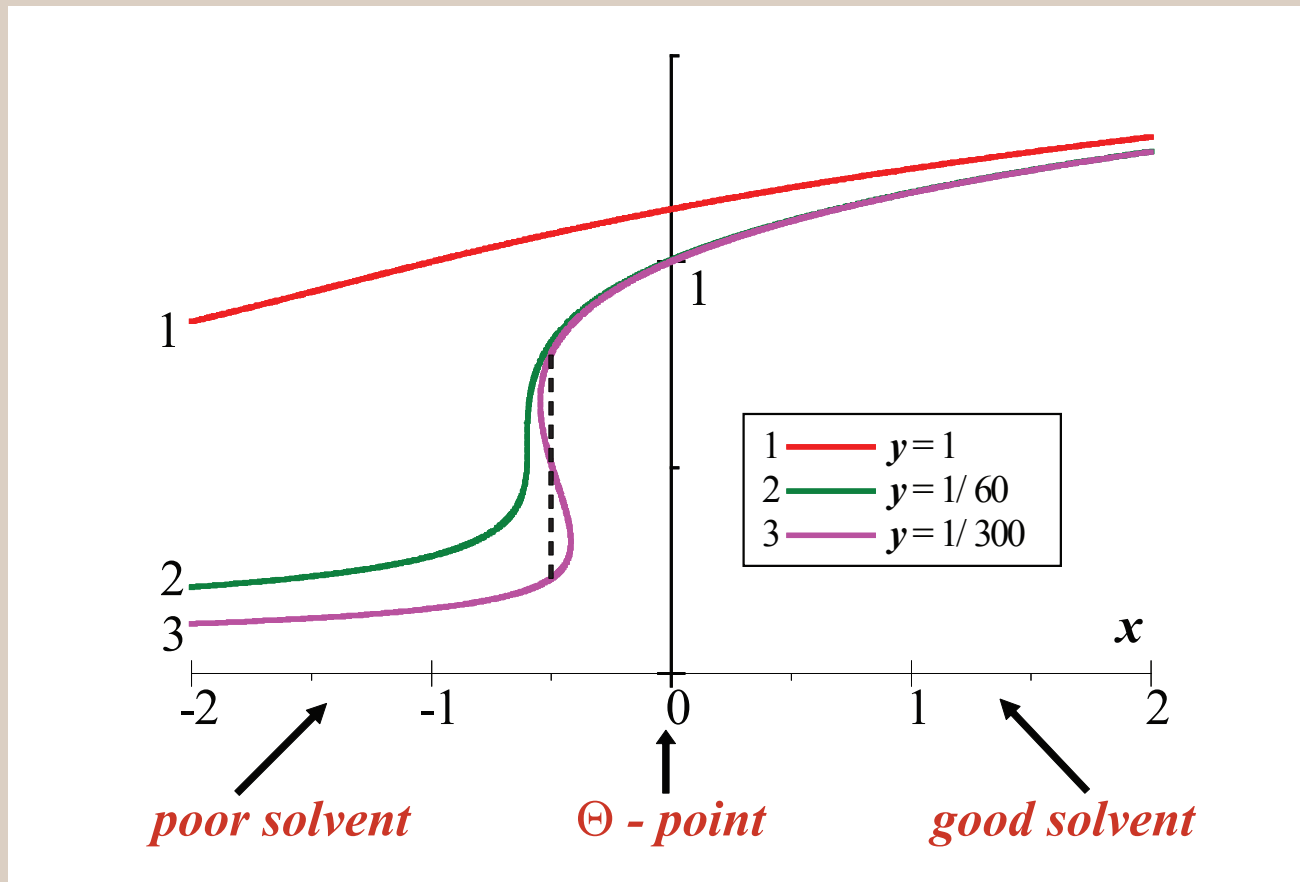
# The Coil-Globule Transition.

Rewrite this equation in terms of new variables

$$\alpha^2 = R^2 / Na^2; \quad y = C/a^6 \sim v^2/a^6; \quad x = BN^{1/2}/a^3 \sim v\tau N^{1/2}/a^3$$

The final equation reads

$$\alpha^5 - \alpha - y/\alpha^3 = x$$



# Conclusions.

1. Coil-globule transition occurs at  $x \sim 1$ , i.e. at  $N^{1/2}v|\tau|/a^3 \sim 1$  or  $|\tau| \sim a^3/(vN^{1/2}) \ll 1$ , only slightly lower the  $\Theta$ -point. Putting it in our words, it is enough to have a **very weak attraction** to induce the transition into globule (this is not the case for condensation of gases). Reason: due to the chain connectivity the **independent motion of monomer units is impossible**, polymer coil is **poor in entropy**.
2. For  $y \ll 1$  the chain collapse is discrete, while for  $y \sim 1$  it is continuous. The value of  $y$  depends on  $v/a$  ( $y \sim v^2/a^6$ ).  $v \ll a^3$  corresponds to  $y \ll 1$ , while  $v \sim a^3$  corresponds to  $y \sim 1$ . For realistic chain models  $y \ll 1$  corresponds to stiff chains, and  $y \sim 1$  to flexible chains. Indeed, it can be shown that  $C \sim d^3l^3$ ,  $a \sim l$  and therefore  $y = C/a^6 \sim d^3/l^3$ . Thus, for stiff polymer chains the collapse is discrete, while for flexible chains it is continuous.

# Conclusions.

3. In the limit of small  $\alpha$ ,  $B < 0$  (i.e., in the globular region) the size of the globule is defined by the balance of the following two terms:

$$-\frac{CN^3}{R^3} = BN^2$$

Thus, the size of the globule is

$$R^3 = -\frac{CN}{B} \quad \text{or} \quad R = \left(C/|B|\right)^{1/3} N^{1/3}$$

The volume fraction of monomer units within the globule is

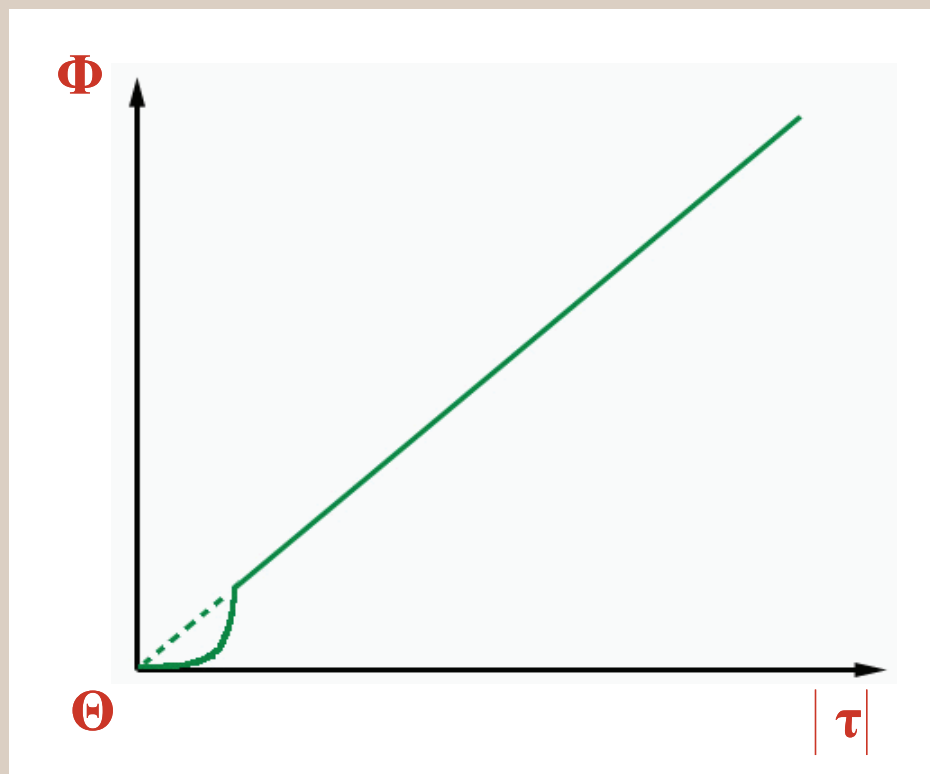
$$\Phi = \rho = \frac{N}{R^3} \nu = \frac{|B|}{C} \sim \frac{\nu \nu |\tau|}{\nu^2} \sim |\tau|$$

For a globule  $R \sim N^{1/3}$  (compare with  $R \sim N^{1/2}$  for an ideal coil, and  $R \sim N^{3/5}$  for a coil with excluded volume).

# Conclusions.

3. In the globule far from  $\Theta$ -point ( $|\tau| \sim 1$ ) the volume fraction of monomer units is generally not small. This is a **dense liquid droplet**.

The globule **swells** as the  $\Theta$ -point (and the coil-globule transition point) is approached, so the description in terms of  $B$  and  $C$  only in the vicinity of transition point is valid.

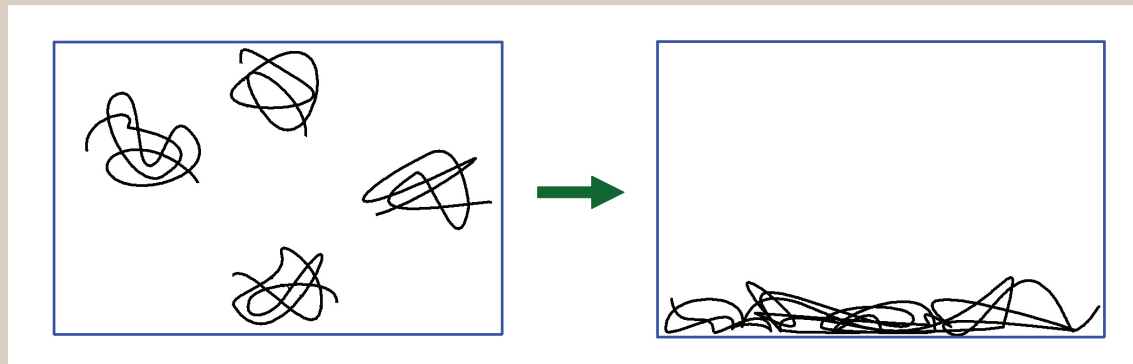


The volume fraction of monomer units within a globule as a function of reduced temperature.

# Conclusions.

4. Experimentally the coil-globule transition was observed for many polymer-solvent systems. A very convenient system for its observation is polystyrene in cyclohexane, since the  $\Theta$ -temperature in this case equals  $\Theta = 35^\circ\text{C}$ .

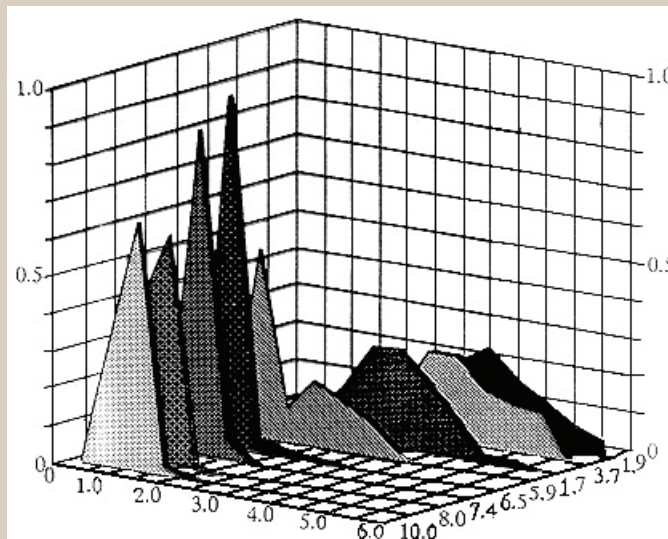
The main difficulty in experimental observations of the coil-globule transition is the possibility of intermolecular aggregation and formation of a **precipitate**, instead of coil-globule transition in single molecules. To avoid this difficulty the concentration of polymer in the solution should be extremely small (e.g., the convenient concentrations to observe the coil-globule transition in the polystyrene-cyclohexane system are of order  $10^{-4}\text{g/l}$ ).



Formation of the precipitate in polymer systems.

# Conclusions.

5. One of the most interesting possibilities to study the coil-globule transition (in particular, for the case of DNA molecules) is to use direct visualization via the fluorescence optical microscopy. In this case it is possible to work at very low polymer concentrations (up to  $10^{-5}$ g/l) thus solving the problem of chain aggregation. One may observe the bimodality of the histogram of observed sizes which is the indication of the first order of the coil-globule transition. This is in full agreement with the theory outlined above, since DNA is a stiff-chain polymer.



Histogram of the DNA sizes as a function of concentration of added poly(ethylene oxide) - an agent which makes the solvent quality poorer.