

# Statistical Physics and Thermodynamics of Macromolecules

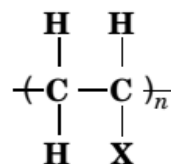
## Lecture Notes

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## Theme 1. Macromolecules Architecture:

*linear, branched and comb -- like chains; models of macromolecules in a continuous and discrete space; real and ideal chains*

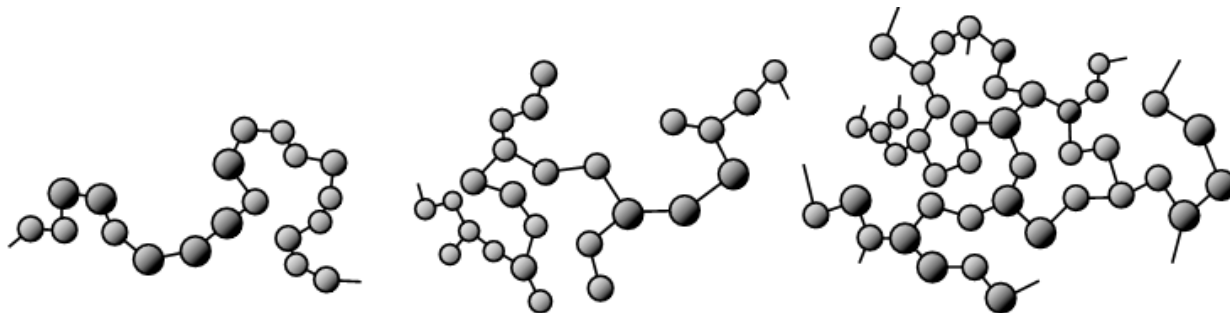
A polymer molecule consists of the same repeating units, called monomers, or of different but resembling units. Figure 1.1 shows an example of a vinyl polymer, an industrially important class of polymer. In the repeating unit,  $X$  is one of the mono-functional units such as  $H$ ,  $CH_3$ ,  $Cl$ , and  $C_6H_5$  (phenyl).



*Fig. 1.1. Vinyl polymer.*

The respective polymers would be called polyethylene, polypropylene, poly(vinyl chloride), and poly-styrene. A double bond in a vinyl monomer  $CH_2=CHX$  opens to form a covalent bond to the adjacent monomer. Repeating this polymerization step, a polymer molecule is formed that consists of  $n$  repeating units. We call  $n$  the **degree of polymerization** (DP). Usually,  $n$  is very large. It is not uncommon to find polymers with  $n$  in the range of  $10^4 - 10^5$ .

In the solid state, polymer molecules pack the space with little voids either in a regular array (crystalline) or at random (amorphous). The molecules are in close contact with other polymer molecules. In solutions, in contrast, each polymer molecule is surrounded by solvent molecules. The large  $n$  makes many of the properties common to all polymer molecules but not shared by small molecules. A difference in the chemical structure of the repeating unit plays a secondary role. The difference is usually represented by parameters in the expression of each physical property.



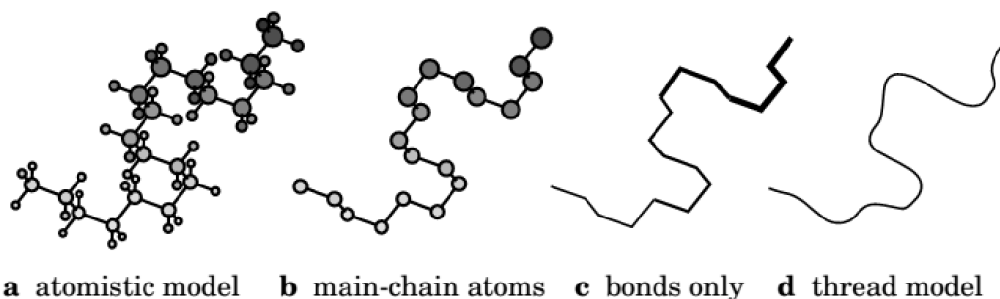
*Fig. 1.2. Architecture of polymer chain: a linear chain (a), a branched chain (b), and a cross-linked polymer (c).*

Figure 1.2 shows three architectures of a polymer molecule: a **linear chain** (a), a **branched chain** (b), and a **cross-linked polymer** (c).

A bead represents a monomer here. A vinyl polymer is a typical linear polymer. A branched chain has branches, long and short. A cross-linked polymer forms a network encompassing the entire system. In fact, there can be just one supermolecule in a container. In the branched chain, in contrast, the branching does not lead to a supermolecule. A cross-linked polymer can only be swollen in a solvent. It cannot be dissolved. We will learn linear chain polymers in detail and about branched polymers to a lesser extent.

Some polymer molecules consist of more than one kind of monomers. An A -- B **copolymer** has two constituent monomers, A and B. When the monomer sequence is random, i.e., the probability of a given monomer to be A does not depend on its neighbor, then the copolymer is called a **random copolymer**. There is a different class of linear copolymers. In an A -- B **diblock copolymer**, a whole chain consists of an A block, a B block, and a joint between them. In a triblock copolymer, the chain has three blocks, A, B, and C. The C block can be another A block. A polymer consisting of a single type of monomers is distinguished from the copolymers and is called a **homopolymer**.

A polymer chain in the solution is changing its shape incessantly. An instantaneous shape of a polymer chain in solution (Fig. 1.3a) is called a **conformation**. To represent the overall chain conformation, we strip all of the atoms except for those on the backbone (Fig. 1.3b). Then, we remove the atoms and represent the chain by connected bonds (Fig. 1.3c). In linear polyethylene, for instance, the chain is now represented by a link of carbon - carbon bonds only. We can further convert the conformation to a smoothed line of thread (Fig. 1.3d). In the last model, a polymer chain is a geometrical object of a thin flexible thread.



*Fig. 1.3. Simplification of chain conformation from an atomistic model (a) to main-chain atoms only (b), and then to bonds on the main chain only (c), and finally to a flexible thread model (d).*

Several coarse-grained geometrical models other than the skeletal chain model are being used to predict how various physical quantities depend on the chain length, the polymer concentration, and so forth, and to perform computer simulations. Figure 1.4 illustrates a **bead-stick model** (a), a **bead-spring model** (b), and a **pearl-necklace model** (c).

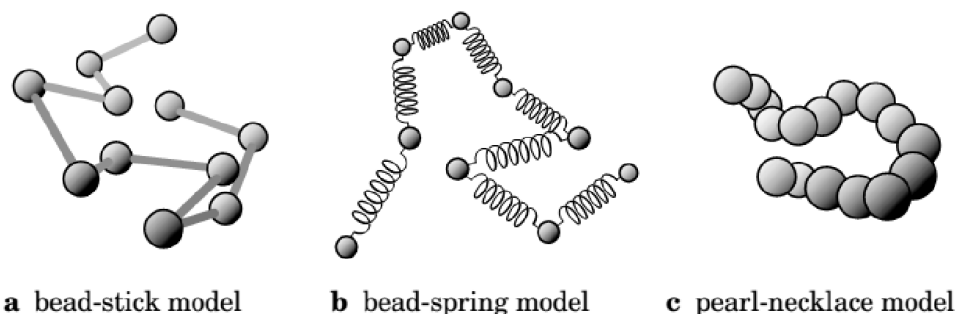


Fig. 1.4. Various models for a linear chain polymer in a continuous space: a bead-stick Model (a), a bead-spring model (b), and a pearl-necklace model (c).

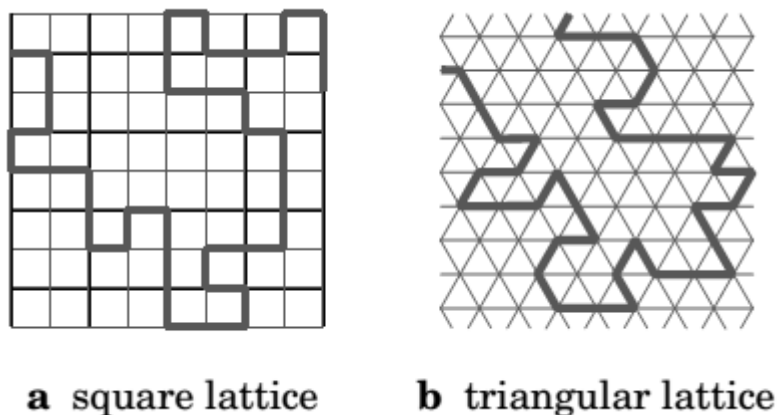
In the bead-spring model, the whole chain is represented by a series of beads connected by springs. The equilibrium length of each spring is zero. The bead-spring model conveniently describes the motion of different parts of the chain. The segment of this model is a spring and a bead on its end. In the pearl-necklace model, the beads (pearls) are always in contact with the two adjacent beads. This model is essentially a bead-stick model with the stick length equal to the bead diameter. The bead always has a positive diameter. As in the bead-stick model, we can restrict the bond angle and the dihedral angle.

Table 1.1 compares two typical variations of the model: a **freely jointed chain** and a **freely rotating chain**. When the bond angle is fixed to the tetrahedral angle in the  $sp^3$  orbitals of a carbon atom and the dihedral angle is fixed to the one of the three angles corresponding to *trans*, *gauche*, and *gauche*, the model mimics the backbone of an actual linear vinyl polymer. The latter is given a special name, **rotational isometric state model** (RIMS). A more sophisticated model would allow the stick length and the bond

TABLE 1.1 Bead-Stick Models

Model	Bond Length	Bond Angle	Dihedral Angle
Freely jointed chain	Fixed	free	Free
Freely rotating chain	Fixed	fixed	free

The models described above are in a continuous space. The models on a discrete space are widely used in computer simulations and theories. The discrete space is called a **lattice**. In the lattice model, a polymer chain consists of monomers sitting on the grids and bonds connecting them. The grid point is called a **site**; Figure 1.5 illustrates a linear polymer chain on a square lattice



*Fig. 1.5. Linear chains on a square lattice (a) and a triangular lattice (b).*

The segment consists of a bond and a point on a site. In three dimensions, a cubic lattice is frequently used and also a diamond lattice to a lesser extent. There are other lattice spaces as well.

In any real polymer chain, two monomers cannot occupy the same space. Even a part of a monomer cannot overlap with a part of the other monomer. This effect is called an **excluded volume** and plays a far more important role in polymer solutions than it does in solutions of small molecules. We often idealize the chain to allow overlap of monomers. In the lattice model, two or more monomers of this **ideal chain** can occupy the same site. To distinguish a regular chain with an excluded volume from the ideal chain, we call the regular chain with an excluded volume a **real chain** or an **excluded-volume chain**. We can treat the effect of the excluded effect as a small difference from the ideal chains. More importantly, though, the real chain behaves like an ideal chain in some situations. One situation is concentrated solutions, melts, and glasses. The other situation is a dilute solution in a special solvent called a theta solvent.

## Theme 2. Random walks in two and three dimensions:

### *end-to-end distance and radius of gyration*

Here, we learn how to assess the dimension or the size of a polymer molecule. We consider a linear chain consisting of  $N$  bonds of length  $b$ . The positions of the joints are denoted by  $r_i$  ( $i = 1..N$ ).

The two ends of the  $i$ -th bond are at  $r_{i-1}$  and  $r_i$ . It is convenient to define the end-to-end vector  $R$  by

$$R = r_N - r_0 \quad (2.1)$$

$R$  is different for each configuration of the chain. Although the chain ends are not necessarily faced outward and therefore  $R$  does not always span the largest dimension of the chain, its average length is a good measure for the overall chain dimension. The *root-mean-square end-to-end distance*  $R_F$  (or simply *end-to-end distance*) of the chain is the root mean square of  $R$ :

$$R_F^2 = \langle (r_N - r_0)^2 \rangle \quad (2.2)$$

We can regard the whole chain as roughly being contained in a sphere of diameter  $R_F$ . Another often used measure of the chain dimension is the *root-mean-square radius of gyration*  $R_g$  (or simply *radius of gyration*). Its square,  $R_g^2$ , is the second moment around the center of mass of the chain. The latter is defined as the mean square of the distance between the beads and the center of mass. Roughly, the chain occupies a space of a sphere of radius  $R_g$ . The center of mass  $r_G$  of the chain is given as

$$r_G = \frac{1}{N+1} \sum_{i=0}^N r_i \quad (2.3)$$

Then,  $R_g$  is given by

$$R_g^2 = \left\langle \frac{1}{N+1} \sum_{i=0}^N (\mathbf{r}_i - \mathbf{r}_G)^2 \right\rangle = \frac{1}{N+1} \sum_{i=0}^N \langle (\mathbf{r}_i - \mathbf{r}_G)^2 \rangle \quad (2.4)$$

where the summation and averaging can be interchanged. As the name suggests,  $mR_g^2$  is the moment of inertia ( $m$  represents mass of the molecule) for rotational motion of this molecule around its center of mass.

Now we obtain  $R_F$  and  $R_g$  for ideal chains whose conformations are given as trajectories of random walkers. They include a random walk on a lattice, a freely jointed chain, a bead-spring model etc. It is easy to show that in that case

$$R_F^2 = b^2 N \quad (2.5)$$

and for any subchain between the  $i^{th}$  and  $j^{th}$  segments

$$\langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle = b^2 |i - j| \quad (2.6)$$

We can calculate the radius of gyration of the chain as

$$\begin{aligned} 2R_g^2 &= \frac{1}{(N+1)^2} \sum_{i,j=0}^N b^2 |i - j| = \frac{2b^2}{(N+1)^2} \sum_{i=0}^N \sum_{j=0}^i (i - j) \\ &= \frac{2b^2}{(N+1)^2} \sum_{i=0}^N \frac{1}{2} i(i+1) = b^2 \frac{N(N+2)}{3(N+1)} \end{aligned} \quad (2.7)$$

Thus, we find for large  $N$  ideal chains with no correlations between bonds have the dimensions of

$$R_F^2 = b^2 N, \quad R_g^2 = \frac{1}{6} b^2 N \quad (2.8)$$

### Theme 3. Basic models of macromolecules:

*Freely - jointed chain, chain of free rotations, worm – like chain; rotational isomers; Kuhn segment length and end-to-end distance.*

A polymer chain in the solution is changing its shape incessantly. An instantaneous shape of a polymer chain in solution is called a conformation. To represent the overall chain conformation, we strip all of the atoms except for those on the backbone. Then, we remove the atoms and represent the chain by connected bonds. In linear polyethylene, for instance, the chain is now represented by a link of carbon – carbon bonds only. We can further convert the conformation to a smoothed line of thread. In the last model, a polymer chain is a geometrical object of a thin flexible thread.

We now pull the two ends of the skeletal linear chain to its full extension (Fig. 3.1). In a vinyl polymer, the chain is in all-trans conformation. The distance between the ends is called the contour length. The contour length ( $L_c$ ) is proportional to DP or the molecular weight of the polymer. In solution, this fully stretched conformation is highly unlikely. The chain is rather crumpled and takes a conformation of a random coil.

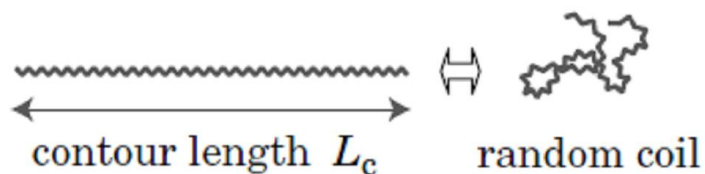


Fig. 3.1. A random-coil conformation is pulled to its full length  $L_c$

Several coarse-grained geometrical models other than the skeletal chain model are being used to predict how various physical quantities depend on the chain length, the polymer concentration, and so forth, and to perform computer simulations. Let us consider a bead-stick model, where the chain consists of beads and sticks that connect adjacent beads. If the angle between two adjacent sticks is free we have a freely jointed chain. If we restrict the angle between two adjacent sticks we have a freely rotating chain (see Table 3.1). When the bond angle is fixed to the tetrahedral angle in the  $sp^3$  orbitals of a carbon atom and the dihedral angle is fixed to the one of the three angles corresponding to *trans*, *gauche* +, and *gauche*—, the model mimics the backbone of an actual linear vinyl polymer. The latter is given a special name, rotational isometric state model (RIMS).



TABLE 3.1 Bead-Stick Models

Model	Bond Length	Bond Angle	Dihedral
Freely jointed	Fixed	Free	free
Freely rotating	Fixed	Fixed	free

As it was shown in the Section 2, the mean – square end – to – end distance for the freely – jointed chain is equal to

$$R^2_F = b^2 N \quad (3.1)$$

As it'll be shown below, any ideal chain could be approximated by freely – jointed chain with certain effective segment of the length  $b$  and the effective number of segments  $N$ . This segment is called *Kuhn segment*. More precise definition of the Kuhn segment will be introduced in the Section 5.

#### Theme 4. Gaussian chain:

*central limit theorem and Gaussian distribution for the ideal linear macromolecule; monomers' density fluctuations and the length of correlations; entropic elasticity*

For the freely jointed chain, the vector  $\mathbf{R}$ , joining the ends of the chain equals the sum of  $N$  independent, randomly oriented contributions. According to the central limit theorem of probability theory, such a quantity has the Gaussian distribution

$$P_N(\mathbf{R}) = (2\pi Nl^2/3)^{-3/2} \exp[-3\mathbf{R}^2/(2Nl^2)], \quad (4.1)$$

where  $l$  is the length of the stick. The Gaussian function (4.1) decays at the distance of order  $R \sim N^{1/2}l$ , which agrees with the size of the freely jointed chain. Evidently, an accurate calculation of the mean square using the general formula  $\langle \mathbf{R}^2 \rangle = \int \mathbf{R}^2 P_N(\mathbf{R}) d^3R$  would yield precisely the result  $R \sim N^{1/2}l$ . Other ideal chain models with different flexibility mechanisms and without free joints are more complicated, because their consecutive elementary segments are not oriented independently. However, the orientational correlations decay with distance very rapidly, in fact, exponentially. One can expect, and this can be proved, that the central limit theorem also is valid for the exponential decay of correlations. Then, treating any ideal polymer as an effective freely jointed chain of Kuhn segments, we can obtain the correct result for the statistical distribution of the end-to-end vector

$$P_N(\mathbf{R}) = (2\pi \langle \mathbf{R}^2 \rangle / 3)^{-3/2} \exp[-3\mathbf{R}^2 / (2 \langle \mathbf{R}^2 \rangle)], \quad (4.2)$$

where  $\langle \mathbf{R}^2 \rangle$  is the mean – square end - to – end distance of the chain.

The mean value of the monomers' density is equal to

$$n \cong \frac{N}{R^3} \propto \frac{1}{\sqrt{N}} \quad (4.3)$$

Thus, the volume fraction of polymer inside the ideal polymer chain is very small and the most part of it is occupied by solvent. To calculate the local density of monomers, we need to assign the elementary volume  $\delta V$  inside the coil and estimate the mean number of monomers  $\delta N$  in it. Because of low mean density of monomers, the local density should be highly fluctuating quantity. The correlation length of fluctuations is comparable with the size of the coil, as it will be proved later.

The chain elasticity is the inherent feature of any polymer chain. The number of conformations, corresponding to the stretched conformation of an ideal (Gaussian) polymer chain is substantially less than in the absence of constraints. Thus, the stretched chain will work to

increase its entropy and to return into ideal state with the mean – square size  $R \sim N^{d/2} l$ .

## Theme 5. Chain rigidity:

*worm -- like chain and persistence length; persistence length and Kuhn segment.*

The flexibility of the freely jointed chain is caused by freely rotating connections between rigid segments. It can be said that flexibility is concentrated at the connection points. This so-called freely jointed flexibility mechanism is easy to describe but very difficult to realize in practice; it is observed in very few real substances. All sufficiently long polymer chains are quite flexible, however, the main reason being their great length.

Let us suppose that the straight-chain conformation corresponds to the absolute minimum of energy and that all links and bonds are so stiff that the thermal excitation energy  $\sim T$  produces only small deformations of their stereochemical structure. For small deformations, the atomic framework of a molecule can be regarded as a classical elastic construction, which in the case of the polymer is approximated by a thin, elastic, homogeneous filament obeying Hooke's law under deformation. Such a model of a polymer chain is called persistent or worm-like.

The conformation of a chain of the arc – length  $L$  is described by a continuous space curve  $\vec{r}(s)$ , where the arc – length  $s$  is satisfied by  $0 \leq s \leq L$ . To understand correlations in the worm – like chain let us introduce the unit tangent vector

$$\vec{u}(s) = \frac{d\vec{r}(s)}{ds} \quad (5.1)$$

Then, we introduce the correlation function  $\langle \vec{u}(s) \vec{u}(s') \rangle$ , the mean cosine of the angle between the chain segments separated by the length  $|s - s'|$ . This function of  $|s - s'|$  for many polymer chain models possesses the property of so-called multiplicativity: if the chain has two neighboring sections with lengths  $s_1$  and  $s_2$ , then

$$\langle \cos \theta(s_1 + s_2) \rangle \approx \langle \cos \theta(s_1) \rangle \langle \cos \theta(s_2) \rangle \quad (5.2)$$

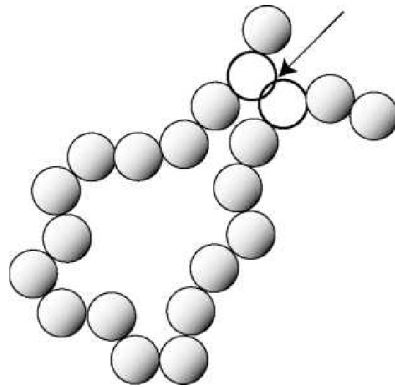
The function having this property is exponential  $\langle \cos \theta(s) \rangle \approx \exp(-s/\ell)$ , where the  $\ell$  is a constant for each given polymer. This constant is the basic characteristic of polymer flexibility and is called the persistent length of the polymer. The persistent length can roughly be considered as a maximum chain section that remains straight; at greater lengths, bending fluctuations destroy the memory of the chain direction. Because of the chain remain straight in two directions, Kuhn segment  $a$  is estimated as  $a \approx 2\ell$ .

## Theme 6. Real macromolecules:

*effect the short -- range interactions; excluded volume; self -- avoiding walks; Flory formula and Flory exponent; good and bad solvent regimes .*

In any real polymer chain, two monomers cannot occupy the same space. Even a part of a monomer cannot overlap with a part of the other monomer. This effect is called an excluded volume and plays a far more important role in polymer solutions than it does in solutions of small molecules. The excluded volume makes the real chains nonideal. The dimension of the real chain is different from that of the ideal chain of the same contour length, for instance.

In the polymer solution, the excluded volume does not disappear even in the low concentration limit. Suppose a polymer chain consisting of  $N$  spheres of diameter  $b$  (pearl-necklace model; see Fig. 6.1). We consider the dilute solution limit in which each chain is isolated from the other chains in the solution. When the chain dimension is  $R$ , these  $N$  spheres are contained in a cube of volume close to  $R^3$ , but no other spheres



*Fig. 6.1. Excluded volume in a chain molecule. The two white beads cannot overlap each other.*

will be found there. The free-energy change per chain due to the excluded volume is then,

$$\frac{\Delta U}{k_B T} \cong \frac{b^3 N^2}{R^3} \quad (6.1)$$

where the numerical coefficient is dropped. The interactions we are considering here are between monomers that may be widely apart along the chain contour. To distinguish these interactions from the short-range interactions such as the restriction on the bond angle and the dihedral angle we considered in Section 1.2.3, we call them long-range interactions. The “long” and “short” do not refer to the distance between the monomers in space. They refer to the distance along the backbone of the polymer chain.

The excluded volume is not limited to a pair of monomers on the same chain (intrachain

interaction). It exists equally for a pair of monomers on different chains (interchain interaction). At higher concentrations, the interchain interaction is the dominant part of the excluded volume effect. It is easy to expect that the excluded volume effect “swells” the chain compared with the dimension it would take were it not for the excluded volume effect. When we write the size of the real chain consisting of  $N$  monomers as  $R_F \cong bN^\nu$ , the exponent  $\nu$  is greater than 0.5, the exponent for the ideal chain. In fact,  $\nu$  was found to be about  $\nu = 3/5$ . The exponent  $\nu$  is called the Flory exponent.

Flory expressed the free energy of the real chain as a function of the overall dimension of  $R$ . Here,  $R$  is not the average dimension but is allowed to change as the shape of the chain changes. The free energy consists of three terms, one is the entropy due to the freedom for different chain conformations and two others are the interactions due both the excluded volume and attraction

$$\frac{F}{k_B T} \cong B \frac{N^2}{R^3} + C \frac{N^3}{R^6} + \frac{R^2}{Nb^2} , \quad (6.2)$$

where  $B$  and  $C$  are the second and third virial coefficients correspondingly. The free energy minima corresponds to the  $R_F \cong bN^{3/5}$  if  $B \cong b^3 > 0$ . Given scenario corresponds to solvents that dissolve the polymer well, which are commonly called “good solvents”. If  $B < 0$  and  $C > 0$ , the free energy (6.2) minimization yields  $R_F \cong bN^{1/3}$ , where solvent do not dissolve polymer (“bad solvent”).

A polymer chain with an excluded volume can be modeled by a self-avoiding walk (SAW) on the lattice. Unlike the random walker for the ideal chain, this walker is not allowed to visit the sites it has already visited. Its trajectory is close to the conformation of a real chain with excluded volume on the lattice.

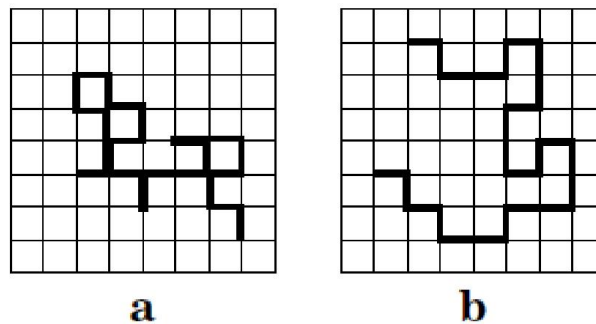


Fig. 6.2. Polymer chain on a square lattice. a: Random walk for an ideal chain. b: Self-avoiding

*walk for a real chain.*

## Theme 7. Ideal chain under external field:

*self-consistent field approximation; analogy with Schrödinger stationary and non-stationary equations; "wave" function and monomers' density; Schrödinger equation spectrum, free energy, correlation length and monomers' density fluctuations effect.*

For the simplest standard Gaussian model of a polymer chain, the microscopic state  $\Gamma$  (i.e., the chain conformation) is specified by the set of coordinates of "bead" links:  $\Gamma = (\vec{x}_0, \vec{x}_1, \dots, \vec{x}_N)$  (the total number of links in the chain equals  $N + 1$ ). The probability of a given microscopic state  $\Gamma$  is given by equation

$$\rho(\Gamma) = \exp(-\varphi(\mathbf{x}_0)/T) g(\mathbf{x}_0, \mathbf{x}_1) \exp(-\varphi(\mathbf{x}_1)/T) \times \\ \times g(\mathbf{x}_1, \mathbf{x}_2) \exp(-\varphi(\mathbf{x}_2)/T) \dots g(\mathbf{x}_{N-1}, \mathbf{x}_N) \exp(-\varphi(\mathbf{x}_N)/T) \quad (7.1)$$

where  $g(\vec{x}, \vec{x}') \propto \exp(-3(\vec{x} - \vec{x}')^2 / (2a^2))$  describe the bonds between neighboring links (i.e., the linear memory); the structure of the formula conforms to the one-dimensional linear connectivity of the ideal polymer chain.

The partition function is obtained by integrating the distribution  $\rho(\Gamma)$ . It is often convenient to consider a macromolecule whose both terminal links are fixed in space, that is, with the links indexed 0 and  $N$  fixed at the given points  $\vec{x}_0$  and  $\vec{x}_N$ , respectively. The partition function of such a macromolecule depends on  $\vec{x}_0$  and  $\vec{x}_N$  and is called the *Green function of the polymer chain*, or the *chain propagator*. According to (7.1) it yields

$$G\left(\begin{smallmatrix} 0 \\ \mathbf{x}_0 \end{smallmatrix} \middle| \begin{smallmatrix} N \\ \mathbf{x}_N \end{smallmatrix}\right) = \int \prod_{i=1}^N \left[ g(\mathbf{x}_{i-1}, \mathbf{x}_i) \exp\left(-\frac{\varphi(\mathbf{x}_i)}{T}\right) \right] d^3x_1 \dots d^3x_{N-1} \quad (7.2)$$

and satisfied by recurrence equation

$$G_{N+1}(\mathbf{x}_{N+1}) = \hat{Q} G_N(\mathbf{x}_N). \quad (7.3)$$

where  $Q(\vec{x}, \vec{x}') = g(\vec{x}, \vec{x}') \exp(-\varphi(\vec{x})/T)$ . Under the cyclic boundary conditions  $\vec{x}_0 = \vec{x}_N$ , the partition function of the  $N + 1$  links macromolecule in the limit  $N \gg 1$  is written as

$$G_N = \text{Tr}(\hat{Q}^N) \quad (7.4)$$

The transfer – operator  $\hat{Q}$  spectrum can be discrete or continuous. We consider both cases in turn. If a set of possible states for each link is limited, the transfer operator has a discrete spectrum and the correlations diminish exponentially along the chain; this proves in particular the law of exponential decay of orientational correlations along the chain. In the upper section of the spectrum of operator  $\hat{Q}$  is discrete, the free energy is written



$$F_N = -k_B T N \ln \Lambda_1, \quad (7.5)$$

where  $\Lambda_1$  is the maximal eigen value of the operator  $\hat{Q}$ . Generally speaking, the spectrum can be continouse.

The operator  $\hat{g}$  with Gaussian kernel  $g(\vec{x}, \vec{x}') \propto \exp(-3(\vec{x} - \vec{x}')^2 / (2a^2))$  is

$$\hat{g} = \exp\left(a^2 \frac{\Delta}{6}\right) \quad (7.6)$$

where  $\Delta$  is conventional Laplace operator. Expanding the transfer – operator  $\hat{Q}$  as

$$\hat{Q} = \exp(-\varphi/T) \hat{g} = \exp[-\varphi/T + (a^2/6) \Delta] \cong 1 - \varphi/T + (a^2/6) \Delta$$

and with taking into account  $G_{N+1} \approx G_N + \partial G_N / \partial N$ , obtaining

$$\frac{\partial G_N}{\partial N} = \left( \frac{a^2}{6} \Delta - \frac{\varphi(\vec{x})}{k_B T} \right) G_N \quad (7.7)$$

This equation coincides with the Schrodinger equation in imaginary time for a particle in the external field  $\varphi(\vec{x})$ .

At the same time, the transfer – operator  $\hat{Q}$  spectrum is defined by equation

$$\hat{Q}\psi = \Lambda\psi \quad (7.8)$$

According to (7.6) it can be rewritten as

$$\left( -\frac{a^2}{6} \Delta + \frac{\varphi(\vec{x})}{k_B T} \right) \psi(\vec{x}) = \varepsilon \psi(\vec{x}), \quad (7.9)$$

where  $\varepsilon = -\ln \Lambda$ . This equation coincides with the stationary Schrodinger equation for a particle in the external field  $\varphi(\vec{x})$ .

If  $\psi(\vec{x})$  and  $\psi^+(\vec{x})$  are the right and left – side eigengunctions of the transfer – operator  $\hat{Q}$  correspondingly, the partition function (7.2) is written

$$G\left(\begin{matrix} 0 \\ \vec{x}_0 \end{matrix} \middle| \begin{matrix} N \\ \vec{x}_N \end{matrix}\right) \cong \Lambda_1^N \psi^+(\vec{x}_0) \psi(\vec{x}_N) \quad (7.10)$$

Thus,  $\psi(\vec{x})$  and  $\psi^+(\vec{x})$  are the probability density functions of the chain ends. The monomers' density is satisfied by expression  $n(\vec{x}) = \psi^+(\vec{x})\psi(\vec{x})$ . The correlation length of the density fluctuations is written

$$\xi = \frac{1}{\ln\left(\Lambda_1 / \Lambda_2\right)} = \frac{1}{\varepsilon_2 - \varepsilon_1} \quad (7.11)$$

Thus, correlation length is finite in case of discrete spectrum, but has a macroscopic value if the spectrum is continuous.

### Theme 8. Semiflexible chains:

*worm-like chain, end -- to -- end distance, radius of gyration and persistence length.*

Let us consider a freely rotating chain with a fixed bond angle, but an unrestricted dihedral angle. When the bond angle  $\gamma = \pi - \theta$  is close to  $\pi$  and the bond length  $b$  is short, this model can represent a semirigid chain, as shown below. The orientation correlation of the  $i$ th stick and the  $j$ th stick was obtained (see Theme 5) as  $\langle \vec{u}_i \vec{u}_j \rangle = \exp\left(-|i-j|/\ell\right)$ , where  $\vec{u}_i$ , is the unit vector parallel to the  $i$ th stick. We now decrease  $\theta$ . When  $\theta \ll 1$ , the correlation between  $\vec{u}$  and  $\vec{u}'$  at two points separated by  $S = b |i-j|$  along the contour is  $\langle \vec{u} \vec{u}' \rangle = (1 - \theta^2/2)^{S/b}$ . We take the limit of  $b \rightarrow 0$  while holding  $2b/\theta^2$  unchanged. Then,

$$\langle \vec{u} \vec{u}' \rangle = \left[ (1 - b/\ell)^{S/b} \right]^S \rightarrow e^{-S/\ell} \quad (8.1)$$

where  $\ell = 2b/\theta^2$ .

In the limit, the conformation of the chain is not zigzag but rather a smooth curve in a three-dimensional space. This model is called a wormlike chain or a Kratky-Porod model (see Theme 5). We now calculate the end-to-end distance  $R_F$ . The end-to-end vector  $\vec{R}$  is written

$$\vec{R} = \vec{r}(L) - \vec{r}(0) = \int_0^L ds \vec{u}(s), \quad (8.2)$$

where the conformation of a chain of the arc-length  $L$  is described by a continuous space curve

$\vec{r}(s)$ , ( $0 \leq s \leq L$ ) and  $\vec{u}(s) = \frac{d\vec{r}(s)}{ds}$ . Therefore,

$$\langle R^2 \rangle = 2 \int_0^L ds \int_0^s ds' \langle \vec{u}(s) \vec{u}(s') \rangle \quad (8.3)$$

With (V.5.3), we obtain

$$R_F^2 = 2\ell \left[ L + \ell \left( e^{-L/\ell} - 1 \right) \right] \quad (8.4)$$

The radius of gyration of the wormlike chain is written

$$R_g^2 = \frac{1}{2L^2} \int_0^L ds \int_0^L ds' \langle |\vec{r}(s) - \vec{r}(s')|^2 \rangle \quad (8.5)$$

With taking into account  $\langle |\vec{r}(s) - \vec{r}(s')|^2 \rangle = 2\ell \left[ |s - s'| + \ell \left( e^{-\frac{|s-s'|}{\ell}} - 1 \right) \right]$  (see (8.4)), it is easily to calculate

$$R_g^2 = \frac{L\ell}{3} - \ell^2 + 2\frac{\ell^3}{L} \left[ 1 + \frac{\ell}{L} \left( e^{-\frac{L}{\ell}} - 1 \right) \right] \quad (8.6)$$

## Theme 9. Semiflexible chains under constraints:

*worm-like chain and energy density; worm - like chain puling; Marko and Siggia equation; worm - like chain in confined geometries.*

Theoretical understanding of a polymer under constraints, such as confined between parallel plates or inside a cylindrical or spherical pore or stretched by external force, is a topic that has generated much interest because of its relevance in practical systems. The configuration of a polymer is described by a continuous space curve  $\vec{r}(t)$ , for which the statistical weight depends on energy density expressed in terms of the local curvature variation and an external potential

$$P \propto \exp \left[ - \int_0^L dt \left\{ \frac{\ell}{2} \left| \frac{d\vec{u}(t)}{dt} \right|^2 + \beta V[\vec{r}(t), \vec{u}(t)] \right\} \right], \quad (9.1)$$

where  $\vec{u}(t) = d\vec{r}(t)/dt$  is the unit tangent vector,  $\beta = \frac{1}{k_B T}$ ,  $V(\vec{r}, \vec{u})$  is the external potential energy acting on a unit segment and  $\ell$  is the persistent length.

Perhaps the most elementary notion in polymer statistical mechanics is that to extend the ends of a long, linear flexible polymer, a force must be applied. The work done by this stretching goes into reduction of the conformational entropy of the chain. Thanks to huge technical advances in manipulation of the structure of double-helix DNA, it has become feasible to measure the force vs extension of single 10-100 pm long DNAs. In recent experiments by Smith et al. (1992) one end of a DNA was attached to a surface, while the other end was attached to a 3-pm-diameter magnetic bead which was then used to put the polymer under uniform tension. Rather different experiments of Schurr et al. (1990) and Perkins et al. (1995) anchored one end of a DNA and then stretched the polymer using either an electric field or the drag force exerted by hydrodynamic flow past the coil.

The effective energy of a stretched WLC is

$$\beta E = \frac{\ell}{2} \int_0^L dt \left| \frac{d\vec{u}(t)}{dt} \right|^2 - fz, \quad (9.2)$$

where the force  $f$  appears as a Lagrange multiplier to fix the end-to-end extension  $z = \hat{z}[\vec{r}(L) - \vec{r}(0)]$ .

When large forces are applied to a WLC, the extension approaches the total length  $L$ , and the tangent vector fluctuates only slightly around  $\hat{z}$ . From the constraint  $|\vec{u}| = 1$ , we see that if  $u_x$ , and  $u_y$  are taken as independent components, the  $u_z$  fluctuations are quadratic in the two-dimensional vector  $\vec{u}_\perp = (u_x, u_y)$  as

$$u_z = 1 - \frac{\vec{u}_\perp^2}{2} + O(\vec{u}_\perp^4)$$

In the Gaussian approximation we have

$$\beta E = \frac{1}{2} \int_0^L dt \left[ \ell \left( \frac{d\vec{u}_\perp(t)}{dt} \right)^2 + f \vec{u}_\perp^2(t) \right] - fL \quad (9.3)$$

Fourier transforms of the vector  $\vec{u}_\perp$  decouple the energy into normal modes and its average is written

$$\langle \vec{u}_\perp^2 \rangle = \int \frac{dq}{2\pi} \langle |\vec{u}_\perp|^2 \rangle = 2 \int \frac{dq}{2\pi} \frac{1}{\ell q^2 + f} = \frac{1}{\sqrt{f\ell}} \quad (9.4)$$

The extension is

$$\frac{z}{L} = \vec{u} \hat{z} = 1 - \frac{\langle u_\perp^2 \rangle}{2} = 1 - \frac{1}{\sqrt{4f\ell}} \quad (9.5)$$

and we see that for large forces,  $z$  approaches  $L$  with a distinctive  $1/\sqrt{f}$  behavior.

In case of the small forces (or extensions) separation of the ends of a WLC by an amount

$z \ll L$  like any flexible polymer costs free energy  $F = \frac{3k_B T}{2R_0^2}$  and therefore requires a force

$$f = \frac{\partial F}{\partial z} = \frac{3k_B T z}{2\ell L}. \quad (9.6)$$

Below the characteristic force of  $k_B T A$ , the extension  $z$  is small compared to  $L$  and this linear force law is valid.

The large – and low – force limits are summarized in an approximate interpolation formula for the WLC force versus extension

$$\frac{f\ell}{k_B T} = \frac{z}{L} + \frac{1}{\left(1 - z/L\right)^2} - \frac{1}{4} \quad (9.7)$$

This is asymptotically exact in the large- and small-force limits and has the scaling property that

$f\ell/k_B T$  is a function only of  $z/L$ .

To address the WLC in confined geometries let us consider the conditional probability,  $\Psi(\vec{r}, \vec{u}; t)$ , that a polymer portion of length  $t$  has an end located at  $\vec{r}$  and whose tangent vector points in the direction  $\vec{u}$ . One can show that  $\Psi(\vec{r}, \vec{u}; t)$  satisfies the partial differential equation

$$-\frac{\partial}{\partial t} \Psi(\vec{r}, \vec{u}; t) = -[\nabla_u^2 - 2\ell(\vec{u}, \nabla) - \beta V(\vec{r}, \vec{u})] \Psi(\vec{r}, \vec{u}; t) \quad (9.8)$$

with the “initial” condition  $\Psi(\vec{r}, \vec{u}; 0) = 1$ . Then, we need to obtain the groundstate solution to the eigenproblem

$$\beta\mu\Psi(\vec{r},\vec{u})=-\left[\nabla_u^2-2\ell(\vec{u},\nabla)-\beta V(\vec{r},\vec{u})\right]\Psi(\vec{r},\vec{u}) \quad (9.10)$$

After obtaining the ground – state eigenfunction  $\Psi_0(\vec{r},\vec{u})$  and eigenvalue  $\beta\mu$ , we have asymptotically for large  $t$

$$\Psi(\vec{r},\vec{u};t)\cong\Psi_0(\vec{r},\vec{u})\exp(-\beta\mu t) \quad (9.11)$$

To be specific let us consider the WLC inside the confinement gap of the width  $W$ . The solution to this eigenproblem leads to  $\beta\mu=\left(\pi^2/6\right)\left(a/W\right)^2$ . One of the most important features of the above formalism for  $\Psi_0(\vec{r},\vec{u})$  is that for a “wide” confinement gap,  $W \gg a$ , it recovers the well-known formalism for a flexible-chain confined in a slit.

## Theme 10. Directed polymers:

*models; generating function formalism and exact results; rod – to – coil transition.*

Linear polymers are probably the simplest physical systems that can be studied in the framework of random walk models. They are long, chain-like molecules formed by repetitions of a basic unit or segment. More importantly, a long polymer chain is flexible, i.e., it can assume different geometric configurations. In order to study the average geometrical features of polymers (their sizes, shapes, etc.), a chain of  $N$  monomers is represented by a broken line consisting of  $N$  segments. For mathematical convenience, the configurations of such a line or *walk* are considered on a regular  $d$ -dimensional lattice. Thus, in its simplest form, this approach models polymer configurations by ordinary *random walks*, i.e., a succession of  $N$  steps, starting from some origin and reaching an arbitrary end-point. Depending on the physical situation, one may impose additional restrictions such as self-avoidance, directedness, etc.

During the past several decades a number of methods, both numerical and analytical, have been developed for the solution of the random walk problems. Among the numerical methods, we already mentioned the direct counting and Monte Carlo simulations. The analytical techniques include field theoretical methods, the transfer matrix approach, and various versions of the generating function method. The generating function technique is frequently used for the solution of random walk problems and lattice statistics problems in general. The approach is based on the following observation: Instead of calculating the quantities of interest, e.g.,  $\langle R^2 \rangle$ , directly, it is often easier to calculate the *function*, which generates these quantities. Once the generating function is known, various characteristic quantities are easily obtained by, e.g., taking the appropriate derivatives. In order to illustrate the technique, let us consider the fully directed SAW on the two-dimensional square lattice (Fig. 10.1). The fully directed SAW (FDSA) on the square lattice consists of steps which start at the origin and are allowed to proceed only in the  $+X$  or  $+Y$  directions, see Fig. 10.1. Here we take the  $X$  and  $Y$  axes to coincide with principal directions on the square lattice. We will carry out the calculation in the fixed fugacity,  $z$ , grand-canonical type ensemble. For each  $N$ -step SAW we assign statistical weight  $z^N$ . To make the model slightly more general we also introduce statistical weight  $w$  for



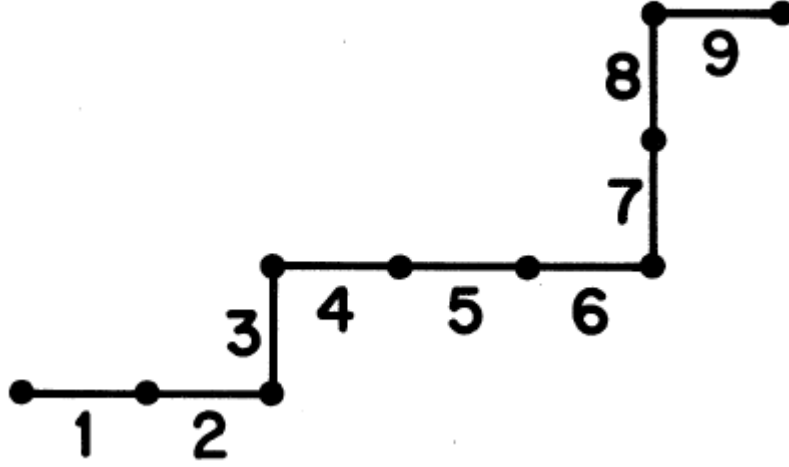


Fig. 10-1. Fully directed SAW (+X, +Y steps only).

every turn (of  $90^\circ$ ) in the walk. These turn-weighted models are used to describe single-chain rod-to-coil transition, which will be considered below. Note also that ordinary FDSA W is obtained by setting  $w = 1$ . The partition function for the N-step T-turn walk is then

$$Z(z; w) = \sum_{\text{walks}} z^N w^T \quad (10.1)$$

To calculate the appropriate generating function we assign statistical weights:  $x$  per each  $+aX$  step and  $y$  per each  $+aY$  step. Let  $n_x$  and  $n_y$  denote the number of  $+X$  and  $+Y$  steps in a given walk, so that  $N = n_x + n_y$ . It is convenient to introduce three generating functions,

$$G(x, y; w) = \sum_{\text{walks}} x^{n_x} y^{n_y} w^T = G_x + G_y \quad (10.2)$$

$$G_x = \sum^{(x)} x^{n_x} y^{n_y} w^T \quad (10.3)$$

$$G_y = \sum^{(y)} x^{n_x} y^{n_y} w^T, \quad (10.4)$$

The sum in (10.2) is over all possible walks. The sum in (10.3) is over all walks that start with the  $+aX$  step, while the sum in (10.4) is over walks that start with the  $+aY$  step. We are actually interested in the total generating function  $G(x, y; w)$  since the partition function of the FDSA W is equal to  $Z(z; w) = G(z, z; w)$ . The restricted generating functions satisfy the recursion relations

$$G_x = x + xG_x + wxG_y \quad (10.5)$$

$$G_y = y + yG_y + wyG_x \quad (10.6)$$

With taking into account eqs. (10.2, 10.5, 10.6) obtaining the required partition function as

$$Z(z; w) = G(z, z; w) = \frac{2z}{1 - z(w+1)} \quad (10.7)$$

Below we will address the rod-to-coil transition of polymer chains. Rod-to-coil transitions in general exhibit an interesting property of scaling function nonuniversality which, in the case of directed models, can be demonstrated explicitly. In the fixed fugacity ensemble, the average number of steps,  $N(z; w)$  is written as

$$N(z; w) = \frac{\sum N z^N w^T}{\sum z^N w^T} = z \frac{\partial}{\partial z} \ln Z(z; w) \quad (10.8)$$

The summation in (10.6) is over “all walks”. For *fixed*  $w$ , the quantity  $N(z; w)$  has a simple pole singularity at  $z_c(w)$ . Since  $Z(z; w)$  has a power law singularity with the critical exponent  $\gamma$ , one can further conclude that in the limit  $z \rightarrow z_c(w)$ , with  $w$  fixed,

$$N(z; w) \approx \frac{\gamma z_c(w)}{z_c(w) - z} \quad (10.9)$$

$\gamma = 1$  for DSAW. Let us now consider scaling in the rod-to-coil transition regime. This regime is defined by  $w \rightarrow 0$ ,  $N \rightarrow \infty$ , with the scaling combination

$$\omega = wN(z; 0) = w\bar{N} \quad (10.10)$$

where  $\bar{N}$  is defined by (10.9), which takes a particularly simple form for  $w = 0$  since  $z_c(0) = 1$

$$N(z; 0) \equiv \bar{N}(z) = \frac{1}{1 - z}$$

In the scaling limit  $\omega$  takes values  $O(1)$ . Physically, this means that for fixed  $w$ , long chains will be coiled provided  $N \gg 1/w$ . For fixed length  $N$ , stiff chains ( $w \ll 1/N$ ) will be rodlike. Thus, the transition occurs when  $w$  and  $1/N$  are comparable.

**Theme 11. Relationships between macromolecules and critical phenomena:**  
*phase transition of the second order, magnetic susceptibility and correlation function; the n-vector model;  $\epsilon \rightarrow 0$  limit and single chain problem..*

There is a strong analogy between the statistics of linear, flexible polymers and various features of critical phenomena. To make it clear, we first describe some essential aspects of ferromagnetic transition points – ferromagnets are the best example for our purpose. From a macroscopic point of view, ferromagnets are characterized by a magnetization  $M$ . This is a vector with a number  $n$  of independent components.

The plot of free energy  $F$  as a function of  $M$  has two equivalent minima (Fig. 11.1), and the system will reach one of them. Then we measure a finite average magnetization  $M_0(T)$ . A critical temperature  $T_c$  separates the two

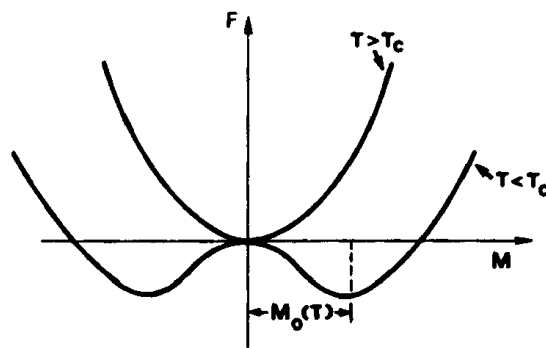


Fig. 11-1. Free energy vs. magnetization.

regimes. The following discussion is concerned with the immediate vicinity of  $T_c$  for the following reason. Consider a temperature  $T = T_c(1 + \epsilon)$  with  $\epsilon$  small and positive. Since we are above  $T_c$ , the average  $M$  is zero. However, if we look at the local distribution of  $M(r)$ , (as is possible by neutron scattering techniques) we find that for small  $\epsilon$ , there are regions where  $M$  does not average to zero. The characteristic size of these regions is called the correlation length  $\xi$ , and it obeys a scaling law of the form

$$\xi \cong a |\epsilon|^{-\nu} \quad (11.1)$$

if  $\epsilon \rightarrow 0$ , where  $a$  is the distance between neighboring atoms, and  $\nu$  is a certain "critical exponent." The essential feature is that when  $\epsilon$  is small,  $\xi \gg a$ . In solids we can typically achieve values of  $\xi$  of a few hundred Angstroms. The correlated regions are much larger than a lattice unit, and all details of the lattice structure, of the couplings, and so forth, become

irrelevant. We reach a very universal regime, where only two essential parameters remain; one is the dimensionality ( $d$ ), the other is the number of equivalent components ( $n$ ). It turns out that all critical exponents such as  $\nu$  depend only on  $d$  and  $n$ .

Let us address the so called “ $n$ -vector” model. We assume that the magnetic atoms are located on a periodic lattice. Each magnetic atom ( $i$ ) carries a spin  $\vec{S}_i$ ; this is a vector, with  $n$  components  $S_{i1}, S_{i2}, \dots, S_{in}$ . In our considerations, we ignore all quantum effects; the components  $S_{ia}$  are just numbers. There is one constraint—i.e., the total length of each spin is fixed

$$\sum_{\alpha=1}^n S_{i\alpha}^2 = n$$

The Hamiltonian is written

$$H = -\sum_{i<j} K_{ij} \vec{S}_i \vec{S}_j - \sum_i \vec{h} \vec{S}_i, \quad (11.2)$$

where  $K_{ij} = K > 0$  for the nearest neighbour pairs ( $ij$ ) and  $K_{ij} = 0$  otherwise. The partition

function of the spin system is  $Z = \prod_i \int d\Omega_i e^{-H/T}$ , where integration is performed over the solid angles of the spins. In case of the zero field  $h = 0$ , we can rewrite the partition function as

$$Z = \Omega \left\langle \prod_{i<j} \left[ 1 + \frac{K_{ij}}{T} \sum_{\alpha} S_{i\alpha} S_{j\alpha} + \frac{1}{2} \left( \frac{K_{ij}}{T} \sum_{\beta} S_{i\beta} S_{j\beta} \right)^2 \right] \right\rangle_0, \quad (11.3)$$

where  $\langle \dots \rangle_0$  means the average over all equally weighted orientations and  $\Omega$  is the total volume of the phase space for the spins.

Successive terms of  $Z/\Omega$  may be represented by graphs on the lattice. To each nearest neighbor link  $K_{ij}$  is associated a continuous line. To each site  $i$  must be associated two spin components  $S_{i\alpha} S_{i\alpha}$  (to obtain a nonzero average). These rules mean that the only allowed graphs are *closed loops*. The loop can never intersect itself. If it did, at one site  $i$ , this would imply the vanishing average  $\langle S_i^4 \rangle_0$ . At this point we begin to see the connection between magnetism and self-avoiding chains.

First let us settle some technical points concerning the partition function. The quadratic terms  $\left( \frac{K_{ij}}{T} \right)^2$  in the expansion simply correspond to the smallest loop, and could be drawn as



Note that each loop has a single value of the component index  $\alpha$  occurring at all its sites, because of the two factors  $\vec{S}_i$  at one point involve the same component. When we sum over the component index  $\alpha$  for one loop, we get

$$\left(\frac{K}{T}\right)^N n,$$

where  $N$  is the number of bonds in the loop, and  $n$  is the component index. Because  $n = 0$  in our case, the contribution of all loops ultimately vanishes, and we can write

$$Z = \Omega \quad (n \rightarrow 0)$$

Consider now the one-component ( $\alpha$ ) spin-spin correlation function in zero field:

$$\langle \vec{S}_{i\alpha} \vec{S}_{j\alpha} \rangle = \frac{\langle \exp(-H/T) \vec{S}_{i\alpha} \vec{S}_{j\alpha} \rangle_0}{\langle \exp(-H/T) \rangle_0} \quad (11.4)$$

Again, for  $n = 0$ , the only graphs which contribute are self-avoiding paths, but here they are not closed loops because eq. (11.4) contains two extra spin factors  $\vec{S}_i \vec{S}_j$ . In fact what we have is a sum over all self-avoiding walks linking sites  $i$  and  $j$  (Fig. 11.2).

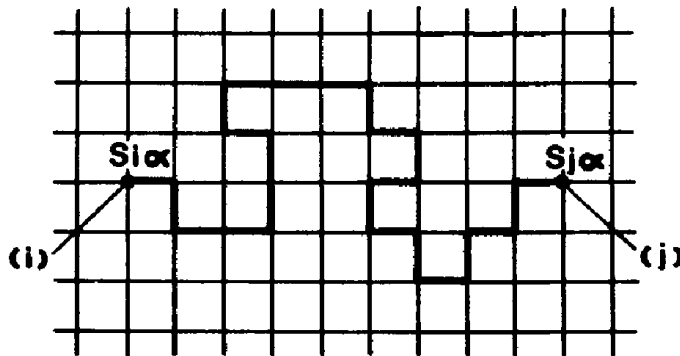


Fig. 11-2. Free energy vs. magnetization.

If the walk involves  $N$  steps,

$$\left\langle \vec{S}_{i\alpha} \vec{S}_{i\alpha} \right\rangle \Big|_{n=0} = \sum_N \Pi_N(i, j) \left( K/T \right)^N \quad (11.5)$$

where  $\Pi_N(i, j)$  is the number of self-avoiding walks of  $N$  steps linking points

(i) and (j) on the lattice. Eq. (11.5) is the basic link between chains and magnets. If we consider temperatures  $T$  slightly above  $T_c$ , we can write  $T = T_c(1 + \varepsilon)$ , where  $\varepsilon$  is small parameter. The total number of SAWs of  $N$  steps, starting from point (i) is:

$$\Pi_N = \sum_j \Pi_N(i, j) \cong \tilde{z}^N N^{\nu-1} \quad (N \gg 1), \quad (11.6)$$

where  $\tilde{z}$  is the effective coordination number of the lattice. Using the Eq. (11.6) it can be shown that the critical temperature is defined by condition

$$T_c = K\tilde{z} \quad (11.7)$$

With taking into account Eqs. (11.5-7) we rewrite correlation as

$$\left\langle \vec{S}_{i\alpha} \vec{S}_{i\alpha} \right\rangle \Big|_{n=0} = \sum_N \Pi_N(i, j) \exp(-\varepsilon N)$$

Thus the relationship between number of paths  $\Pi_N(i, j)$  and magnetic correlations is of the Laplace transform type. We can say that  $\varepsilon$  and  $N$  are conjugate variables and a small  $\varepsilon$  corresponds to a large  $N$ . The correlation (11.5) decays on the scale of the correlation length  $\xi$  which is a single scale describing behavior of the spin system in the vicinity of the critical point ( $\varepsilon \rightarrow 0$ ). Thus, the analog of  $\xi$  is the range of the self-avoiding walk, or the Flory radius  $R_F \cong aN^\nu$ .

To summarize, all properties of one self-avoiding walk on a lattice can be related to the spin correlation of a ferromagnet with an  $n$ -component magnetization when we formally set  $n = 0$ . This introduces a link between the exponents for self-avoiding walks and critical exponents. The temperature of the polymer system is not related to the temperature  $T$  of the magnetic system, but

$\varepsilon = (T - T_c)/T_c$  is the conjugate variable of the degree of polymerization,  $N$ .

## Theme 12. Polymer solutions of linear chains:

*concentration regimes, self -- consistent field approximation; fluctuation theory of polymer solutions: osmotic pressure, blob concept, correlation length, single chain dimensions.*

A fundamental distinction exists between dilute polymer solutions where the coils are separate (Fig. 12.1a) and more concentrated solutions where the coils overlap (Fig. 12.1b). At the overlap threshold ( $c = c^*$ ) the coils begin to be densely packed. Clearly this threshold is not sharp; it is more properly defined as a region of crossover between regimes (a) and (c), but the scaling properties of  $c^*$  are essential.

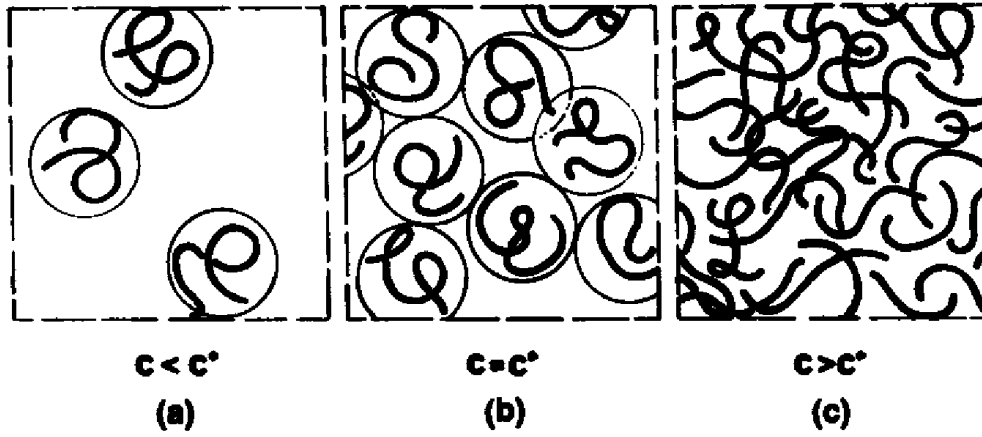


Fig. 12.1. Crossover between dilute and semi-dilute solutions: (a) dilute, (b) onset of overlap, and (c) semi-dilute.

We expect  $c^*$  to be comparable with the local concentration inside a single coil. In a very good (athermal) solvent this implies:

$$c^* \cong \frac{N}{R_F^3} = a^{-3} N^{-4/5} \quad (12.1)$$

In terms of the polymer fraction  $\Phi$  we may define the corresponding threshold  $\Phi^* \cong N^{-4/5}$ .

When  $c < c^*$ , we have a dilute system of coils. In the zeroth approximation, we can treat these as a perfect gas, with a number of coils per unit volume equal to  $c/N$  and an osmotic pressure of

$$\pi \cong \frac{c}{N} T \quad (12.2)$$

We now consider solutions where the coils do overlap but where the polymer fraction  $\Phi$  is still low

$$\Phi^* \ll \Phi \ll 1 \quad (12.3)$$

The two inequalities are compatible at  $N \gg 1$  because  $\Phi^* \ll 1$ . How do we predict the thermodynamic properties of semi-dilute solutions? The basic notion is a scaling law for the osmotic pressure, written as

$$\frac{\pi}{T} = \frac{c}{N} f_{\pi} \left( \frac{c}{c^*} \right), \quad (12.4)$$

where the function  $f_{\pi}(x)$  is dimensionless and satisfied by conditions

(i)  $f_{\pi} \cong 1 + O(x)$  at  $x \ll 1$  and

(ii) At large  $x$  (semi-dilute solutions) all thermodynamic properties must reach a limit which depends on  $c$  but which becomes independent of the degree of polymerization  $N$ . Physically this means that local energies, entropies, etc. are controlled entirely by the concentration  $c$ ; the local properties are not different for a solution of chains of  $N$  monomers each or a single chain that fills the whole vessel. In terms of  $\Phi$ , this gives

$$\frac{\pi}{T} = \frac{\Phi}{a^3 N} \left( \frac{\Phi}{\Phi^*} \right)^m,$$

where the power  $m$  is defined by condition (ii) and gives

$$\frac{\pi a^3}{T} \cong \Phi^{\frac{9}{4}} \quad (\text{semi-dilute}) \quad (12.5)$$

Let us address now spatial properties of the semi-dilute polymer solution. When photographed at a certain time, this looks very much like a network with a certain *average mesh size*  $\xi$ . Let us now construct the scaling form of  $\xi$  in the semi-dilute regime for a good solvent. This is based on two requirements:

- (i) For  $\Phi^* < \Phi$  the network structure on the scale  $\xi$  will depend only on concentration and not on the degree of polymerization  $N$  (the chains being much longer than the mesh size).
- (ii) For  $\Phi \sim \Phi^*$  where we have coils in contact (but not yet interpenetrating) the mesh size must be comparable with the size of one coil  $R_F$ .

These two requirements lead to the form



$$\xi(\Phi) = R_F \left( \frac{\Phi}{\Phi^*} \right)^m \quad (12.6)$$

if  $\Phi^* < \Phi$ . Here the exponent  $m$  must be such that the length  $\xi$  will be independent on  $N$ . This means that  $m = 3/4$  and

$$\xi(\Phi) \cong a\Phi^{-3/4} \quad (12.7)$$

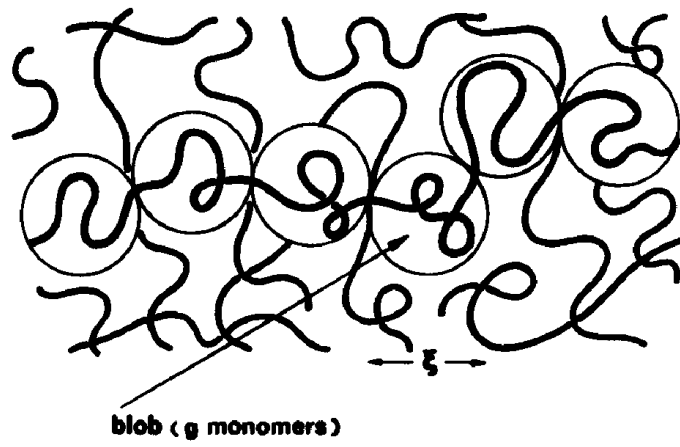
Thus, the mesh size decreases rapidly with concentration. Note an important scaling relationship between the osmotic pressure and the correlation length

$$\pi \cong \frac{T}{\xi^3}, \quad (12.8)$$

if  $\Phi^* \ll \Phi \ll 1$ .

Let us consider one particular chain in the semi-dilute solution. We may visualize it as a succession of units or “blobs” of size  $\xi$  (Fig. 12.2). Inside one blob, (from the definition of the mesh size) the chain does not interact with other chains. Thus, inside one blob we must still have correlations of the excluded volume type. This implies that the number of monomers per blob ( $g$ ) is related to  $\xi$  by the law of swollen coils  $\xi \sim g^{3/5}$ . Thus,  $g \cong \Phi^{-5/4}$ . With taking into account equation (12.7),  $g = c\xi^3$  that says that the solution is essentially a *closely packed system of blobs*. If we take the blobs as the basic units, we are led back to the molten chain, which is ideal on the large scales because of screening effect. Their mean square end-to-end size can be estimated from the ideal chain formula for  $N/g$  blobs of size  $\xi$  ( $\Phi^* \ll \Phi \ll 1$ )

$$R^2(\Phi) = \frac{N}{g} \xi^2 \cong Na^2 \Phi^{-1/4} \quad (12.9)$$



*Fig. 12.2. Single chain as a blobs sequence.*

### Theme 13. Thermodynamics of dilute polymer solutions:

*Flory - Huggins mean - field theory; free energy, chemical potentials and osmotic pressure; spinodal line; phase separation.*

It is convenient to represent the polymer chains as random walks on a lattice, each lattice site being either occupied by one (and only one) chain monomer or by a "solvent molecule". We denote the fraction of sites occupied by monomers as  $\Phi$ . This term is related to the concentration  $c$  (number of monomers per  $\text{cm}^3$ ) by  $\Phi = ca^3$ . A fundamental distinction exists between dilute polymer solutions where the where  $a^3$  is the volume of the unit cell in the cubic lattice.

The free energy  $F$  for this model has two components: an entropy term describing how many arrangements of chains can exist on the lattice for a given  $\Phi$ , and an energy term describing the interactions between adjacent molecules. In the mean field approximation the entropy  $S$  is written:

$$-S|_{\text{site}} = \frac{\Phi}{N} \ln \frac{\Phi}{N} + (1 - \Phi) \ln (1 - \Phi) \quad (13.1)$$

The first term is related to the translational entropy of the chain. The second term may be similarly conceived as the translational entropy of the solvent molecules. Instead of considering the full entropy  $S$ , let us consider the entropy of mixing  $S_{\text{mix}}$ :

$$S_{\text{mix}}(\Phi) = S(\Phi) - \Phi S(1) - (1 - \Phi) S(0) = -\frac{\Phi}{N} \ln \Phi - (1 - \Phi) \ln(1 - \Phi) \quad (13.2)$$

The energy term  $E$  contains, in general, three terms that describe: monomer-monomer interactions

$\frac{T}{2} \chi_{\text{MM}} \Phi^2$ ; monomer-solvent interactions  $T \chi_{\text{MS}} \Phi (1 - \Phi)$ ; solvent-solvent interaction

$\frac{T}{2} \chi_{\text{SS}} (1 - \Phi)^2$ . However, we do not need three constants because all terms in the free energy per site which are independent of  $\Phi$ , or linear in  $\Phi$ , drop out when

we consider  $E_{\text{mix}}$

$$\frac{1}{T} E_{\text{mix}/\text{site}} = \chi \Phi (1 - \Phi) + \text{constant} + \text{terms linear in } \Phi \quad (13.3)$$

where  $\chi = \chi_{\text{MS}} - \frac{1}{2}(\chi_{\text{MM}} + \chi_{\text{SS}})$  is the Flory interaction parameter. Finally, we have

$$\frac{1}{T} F_{\text{mix}} \Big|_{\text{site}} = \frac{\Phi}{N} \ln \Phi + (1 - \Phi) \ln(1 - \Phi) + \chi \Phi (1 - \Phi) \quad (13.4)$$

Let us consider first the osmotic pressure  $\pi$  of the macromolecules in the solution. This is defined

by an operation where we change the solution volume (by adding more solvent:  $V_{tot} \rightarrow V_{tot} + \Delta V$ ) while keeping fixed the number of monomers present

$$\pi = -\frac{\Delta F_{tot}}{\Delta V} = \Phi^2 \frac{\partial}{\partial \Phi} \left( \frac{F_{site}}{\Phi} \right) \quad (13.5)$$

where  $F_{tot} = F_{site} V_{tot}/a^3$ . Thus,

$$a^3 \frac{\pi}{T} = \frac{\Phi}{N} + \ln \left( \frac{1}{1-\Phi} \right) - \Phi - \chi \Phi^2 \quad (13.6)$$

In case of polymer – polymer blend segregation effects become important. We start with segregation problems involving two polymers (rather than with the one solvent-one polymer problem) because polymer-polymer systems can be rather correctly described in terms of Flory-Huggins theory; no similar simplification exists for polymer-solvent systems. Our starting point is the Flory-Huggins free energy for a mixture of two polymer species (with degrees of polymerization  $N_A, N_B$ ):

$$\frac{F}{T} \Big|_{site} = \frac{\Phi_A}{N_A} \ln \Phi_A + \frac{\Phi_B}{N_B} \ln \Phi_B + \chi \Phi_A \Phi_B \quad (13.7)$$

where  $\Phi_A, \Phi_B$  are the volume fractions, related by  $\Phi_A + \Phi_B = 1$ . Let us denote  $\Phi_A = \Phi$  and  $\Phi_B = 1 - \Phi$ .

Phase separation can be described in terms of the free energy  $F(\Phi)$ . The essential property is the curvature  $F(\Phi)$ , as explained in Fig. 13.1. Assume first that the sample is homogeneous (single phase), with a certain concentration  $\bar{\Phi}$  (point J). Try then to decompose it into two phases, of concentrations  $\Phi_1$ , and  $\Phi_2$ . The relative weights of the two phases in the mixtures are  $f_1$  and  $f_2$ . We then have  $\bar{\Phi} = f_1 \Phi_1 + f_2 \Phi_2$  and we reach a free energy

$$\bar{F} = f_1 F_1 + f_2 F_2 \quad (13.8)$$

This corresponds to point J in Fig. 13.1. The energy change is positive in case (a) and negative in case (b). Thus, case (b) imposes phase separation.

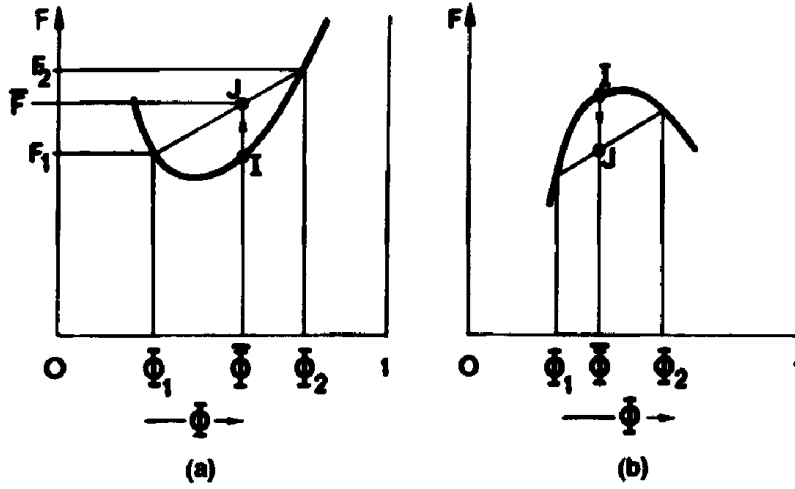


Fig. 13.1. Free energy of the polymer blend.

For  $\chi = 0$  (or  $\chi$  non-zero but very small), the plot  $F(\Phi)$  is convex everywhere; entropy effects are dominant, and they favor mixing. However, when  $\chi$  becomes larger than a some critical value  $\chi_c$ , a region of negative curvature exists restricted by certain concentrations  $\Phi'$ ,  $\Phi''$ . In that case single phase exists only outside the interval  $(\Phi', \Phi'')$ , while inside the interval the system breaks up into two phases, of concentrations  $\Phi'$  and  $\Phi''$ .

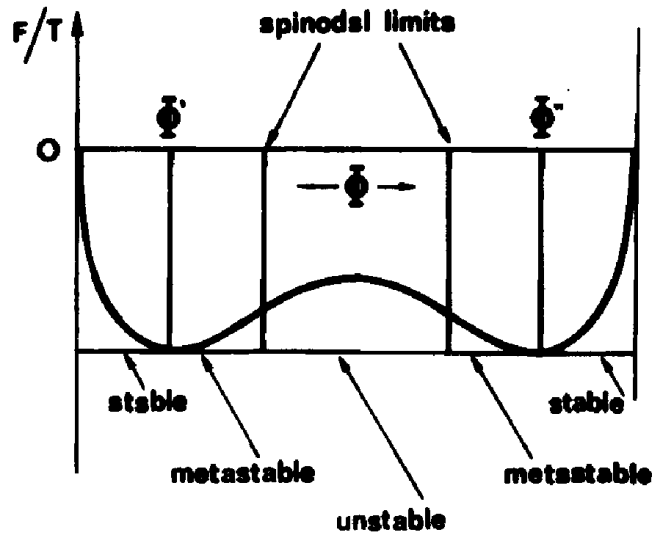


Fig. 13.2. Free energy of the polymer blend in case of  $N_A=N_B=N$ .

Let us define the so called *exchange chemical potential*  $\mu = \frac{\partial F}{\partial \Phi}$ . The two coexisting phases at  $\Phi'$  and  $\Phi''$  have equal  $\mu$  values. For the sake of simplicity let us consider the symmetrical case  $N_A=N_B=N$ . Then the entire free energy diagram is symmetrical around

$\Phi = 1/2$  (see Fig. 13.2) and the coexisting phases at  $\Phi'$  and  $\Phi''$  are defined by condition  $\mu = 0$  that gives the coexistence curve

$$\chi = \frac{1}{N} \frac{(-1)}{1 - 2\Phi} \ln [\Phi/(1 - \Phi)] \quad (13.9)$$

presented in the Fig. 13.3. Phase separation occurs only when  $\chi$  is larger than a threshold value  $\chi_c = 2/N$ .

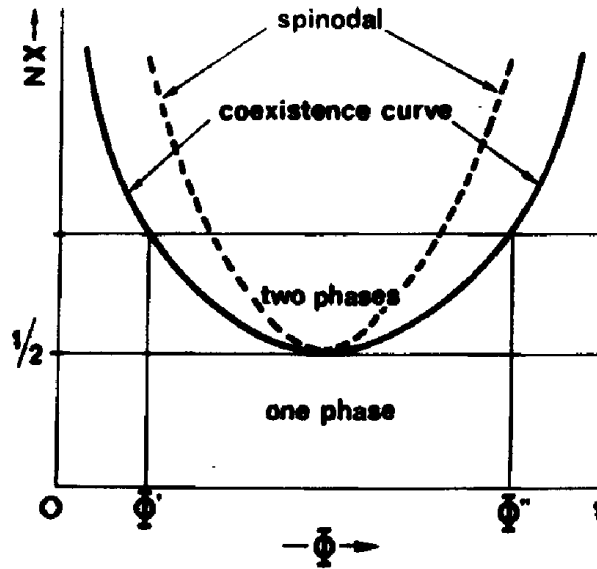


Fig. 13.3. Coexistence curve in case of  $N_A = N_B = N$ .

Equilibrium is reached slowly in polymer melts of high molecular weight. If we enter the two-phase region only slightly, demixing can take place only by nucleation of a droplet of one phase inside the other. This is a thermally activated process, implying the interfacial energy at the droplet surface, and is slow. However, if we go more deeply into the two-phase region, we reach a state where the interfacial energy vanishes (and changes sign). It is then favorable for the system to break up spontaneously into many small domains. This threshold defines what we call the spinodal curve in the  $\chi, \Phi$  plane. From the point of view of Fig. 13.1 the instability occurs whenever the  $F(\Phi)$  plot is concave. The spinodal thus corresponds to the inflection points in Fig. 13.3, and is ruled by the equation

$$0 = \frac{\partial^2}{\partial \Phi^2} \left( \frac{F}{T} \right) = \frac{1}{N_A \Phi} + \frac{1}{N_B (1 - \Phi)} - 2\chi \quad (13.10)$$

The plot of Eq. (13. 10) for the symmetrical case is given in Fig. 13.3.

## Theme 14. Theory of polymeric globula:

*macromolecule in external field; Lifshits formula, free energy and volume approximation; surface effects; coil - globule transition.*

For the simplest standard Gaussian model of a polymer chain, the microscopic state (i.e., the chain conformation) is specified by the set of coordinates of “bead” links:  $\Gamma = \{x_1, x_2, \dots, x_N\}$ . The probability of a given microscopic state is written

$$\rho(\Gamma) = g(\vec{x}_0, \vec{x}_1)g(\vec{x}_1, \vec{x}_2) \dots g(\vec{x}_{N-1}, \vec{x}_N). \quad (14.1)$$

where the factors  $g(\vec{x}_i, \vec{x}_{i+1})$  describe the bonds between neighboring links. If the beads are interacting, each bead in the field created by another beads. Thus, we can describe the effects of intra – molecular interactions in terms of the effective external field acting on the beads of the chain. Speaking of an effective external field, we do not necessarily mean a real physical (electric, magnetic, and so on) field. We mean only a way to describe a spatial inhomogeneity or anisotropy of the external conditions or to express the dependence of the energy  $\varphi(\vec{x})$  of a link on generalized coordinates. The partition function is obtained by integrating the distribution  $\rho(\Gamma)$  over beads' coordinates. The partition function of the macromolecule whose both terminal links are fixed in space, that is, with the links indexed 0 and  $N$  fixed at the given points  $\vec{x}_0$  and  $\vec{x}_N$  respectively is written

$$G\left(\begin{smallmatrix} 0 \\ x_0 \end{smallmatrix} \middle| \begin{smallmatrix} N \\ x_N \end{smallmatrix}\right) = \int \prod_{i=1}^N \left[ g(x_{i-1}, x_i) \exp\left(-\frac{\varphi(x_i)}{T}\right) \right] d^3x_1 \dots d^3x_{N-1} \quad (14.2)$$

From the latter expression directly follows the next recursive relation

$$G\left(\begin{smallmatrix} 0 \\ x_0 \end{smallmatrix} \middle| \begin{smallmatrix} N+1 \\ x_{N+1} \end{smallmatrix}\right) = \int G\left(\begin{smallmatrix} 0 \\ x_0 \end{smallmatrix} \middle| \begin{smallmatrix} N \\ x_N \end{smallmatrix}\right) Q(x_N, x_{N+1}) d^3x_N, \quad (14.3)$$

where  $Q(x', x) = g(x', x) \exp\left(-\frac{\varphi(x)}{T}\right)$ . The equation (14.3) can be shortly rewritten as

$$G_{N+1}(x_{N+1}) = \hat{Q} G_N(x_N). \quad (14.4)$$

If the integral operator  $\hat{Q}$  has a discrete spectrum, the partition function is written



$$G \left( \begin{matrix} 0 \\ \mathbf{x}_0 \end{matrix} \middle| \begin{matrix} N \\ \mathbf{x}_N \end{matrix} \right) = \sum_m \Lambda_m^N \psi_m^+ (\mathbf{x}_0) \psi_m (\mathbf{x}_N). \quad (14.5)$$

where  $\psi_m$  and  $\psi_m^+$  are “left” and “right” eigenfunctions and  $\Lambda_m$  are eigenvalues of the operator  $\hat{Q}$ . If the maximal eigenvalue, say  $\Lambda_1$  exists, the free energy is estimated as

$$F_N = -T \ln G \left( \begin{matrix} 0 \\ \mathbf{x}_0 \end{matrix} \middle| \begin{matrix} N \\ \mathbf{x}_N \end{matrix} \right) \cong -TN \ln \Lambda_1 \quad (14.6)$$

in the thermodynamics limit  $N \rightarrow \infty$ .

Let us address the conformational entropy of the idel polymer chain in terms of the chain in the effecrive external field. The conformational entropy of a polymer system is independent of the nature of the forces that determine the state of the system; therefore, entropy can be found by considering an ideal chain placed in a fictitious external field that ensures equilibrium for a given macroscopic state. If  $n(\alpha)$  is the density of beads in the state  $\alpha$ , the free energy functional of the polymer chain with the given  $n(\alpha)$  is written

$$\mathcal{F} \{n\} = -T \ln \Lambda = E \{n\} - T S \{n\}, \quad (14.7)$$

where  $\Lambda$  is the maximal eigenvalue of the transfer operator  $\hat{Q}$ . With taking into account  $E \{n\} = \sum_{\alpha} \varphi(\alpha) n(\alpha)$ , entropy is rewritten as

$$S \{n\} = \sum_{\alpha} n(\alpha) [\ln \Lambda + \varphi(\alpha)/T]$$

Any eigenvalue of the operator  $\hat{Q}$  is satisfied by equation  $\hat{Q}\psi = \Lambda\psi$ . Thus, the conformational entropy can be presented by Lifshitz formula

$$S \{n\} = \sum_{\alpha} n(\alpha) \ln (\hat{g}\psi/\psi) \quad (14.8)$$

where the following expression established connection between the density  $n(\alpha)$  and eigenfunctions  $\psi(\alpha)$  and  $\psi^+(\alpha)$

$$\Lambda n(\alpha) = \psi^+(\alpha) \hat{g}\psi \quad (14.9)$$

By physical meaning,  $\psi^+(\alpha)$  and  $\psi(\alpha)$  are the distribution functions of the beginning and the end of the chain.

To find the free energy of the polymeric globula we need to minimize the free energy functional (14.7) over the beads density. The ilternal energy functional can be presented as

$$E \{n\} = \int f^*(n(\mathbf{x})) d^3x,$$

where the free energy density is presented as a virial expansion over beads density

$$f^*/T = n^2 B + n^3 C + \dots$$

To estimate the conformatilonal entropy we need to rewrite Eq.(14.8) for the standard model of polymer chain. If  $n(x)$  varies smoothly, then the substitution  $\hat{g} \rightarrow 1 + \frac{a^2}{6} \nabla^2$  is valid and

$$\begin{aligned} S \{n\} &= (a^2/6) \int n^{1/2}(\mathbf{x}) \Delta n^{1/2}(\mathbf{x}) d^3x = \\ &= \text{const} - (a^2/6) \int (\nabla n^{1/2}(\mathbf{x}))^2 d^3x. \end{aligned} \quad (14.10)$$

The most thermodynamically favorable  $n(x)$  corresponds to the homogeneous globula with the narrow surface layer of the length  $\Delta \ll R_F$ , where  $R_F$  is the Flory radius. Thus, the entoropy loss in the globula state is equal to

$$\begin{aligned} S &= \frac{a^2}{6} \int n^{1/2}(\mathbf{x}) \Delta n^{1/2}(\mathbf{x}) d^3x \sim -a^2 \left( \frac{N}{n_0} \right)^{2/3} \Delta \left( \frac{n_0}{\Delta^2} \right) \sim \\ &\sim -N^{2/3} a^2 n_0^{1/3} / \Delta \end{aligned} \quad (14.11)$$

where  $n_0$  is the density inside the globula. The energy  $E\{n\}$  is additive quantitiy. At the same time entropy is estimated as  $O(N^{2/3})$ . In this so-called *volume approximation*, we totally disregard the conformational entropy as

$$\begin{aligned} F \{n\} &= E \{n\} - T S \{n\} \cong E \{n\} = \int f^*(n(\mathbf{x})) d^3x \cong V f^*(n_0) = \\ &= N f^*(n_0)/n_0. \end{aligned} \quad (14.12)$$

Then, we just need to minimize free energy (14.2) over the densitiy  $n_0$  and obtain in the volume approximation the free energy

$$\mathcal{F}_{\text{vol}} = -NTB^2/4C \quad (14.13)$$

To address the transition into the globular state we need to take into account the surface term  $F_{\text{surf}}$  in the free energy

$$F = F_{\text{vol}} + F_{\text{surf}}$$

It is easy to show that

$$\mathcal{F}_{\text{surf}} \sim N^{2/3} T a (-B)^{4/3} / C^{5/6} \quad (14.14)$$

Near the  $\Theta$  point virial coefficients are estimating as

$$\begin{aligned} B(T) &\cong b\tau, \quad \tau = (T - \theta)/\theta, \\ C(T) &\cong C = \text{const} > 0. \end{aligned}$$

Thus,

$$\mathcal{F} = \mathcal{F}_{\text{vol}} + \mathcal{F}_{\text{surf}} = -N\theta\tau^2(b^2/4C)[1 - |\tau_{\text{tr}}/\tau|^{2/3}], \quad (14.15)$$

where

$$\tau_{\text{tr}} \equiv (T_{\text{tr}} - \theta)/\theta \cong -2,7a^{3/2}C^{1/4}/(bN^{1/2}).$$

Thus, we have the phase transition of the second order between the coil and globular phases at the temperature  $T_{tr}$ .

## Theme 15. Heteropolymers:

*block - copolymers and random heteropolymers (RHP); microphase separation; disordered systems, replica and constrained annealing methods; freezing transition in RHP.*

A heteropolymer or copolymer is a polymer derived from two (or more) monomeric species. While block copolymers comprise two or more homopolymer subunits linked by covalent bonds, random heteropolymer consist on two or more kinds of monomers, randomly distributed along the chain.

The particular chemical structure of block copolymer materials is reflected in the most fundamental and interesting way by incompatibility effects. The most characteristic feature of a block copolymer is the strong repulsion between unlike *sequences* even when the repulsion between unlike *monomers* is relatively weak (see [section 13](#)). As a result sequences tend to segregate, but as they are chemically bonded even the complete segregation cannot lead to a macroscopic phase separation transition as in mixtures of two homopolymers. However, in the case of a sufficiently strong incompatibility, microphase separation (MPS) occurs: microdomains rich in  $A$  (in  $B$ ) are formed.

Let us consider a molten diblock copolymer where all chains have the same index of polymerization  $N$  and the same composition  $f = \frac{N_A}{N}$  ( $N_A \gg 1$  and  $N_B \gg 1$  denote the number of monomers of type  $A$  and  $B$ , respectively;  $N = N_A + N_B$ ); i.e., we neglect the polydispersity of the chains. For the sake of simplicity we will assume that both blocks have the same Kuhn statistical segment length  $a$ . Below is assume the incompressibility of the polymer melt:  $\rho_A(r) + \rho_B(r) = 1$ , where  $\rho_A(r)$  and  $\rho_B(r)$  denote the reduced density of monomers  $A$  and  $B$ , respectively.  $\rho_A(r)$  is defined as the ratio of the local density of monomers  $A$  at the point  $r$  to the overall monomer density averaged over the sample. Although the overall density of monomers is constant,  $\rho_A(r)$  and  $\rho_B(r)$  themselves may exhibit local fluctuations and it is these fluctuations which will be at the very root of the microphase separation. The energy of interaction of different chemical species (per monomer) may be written as

$$\alpha \rho_A \rho_B = kT \chi \rho_A \rho_B \quad (15.1)$$

For  $\chi = 0$  or  $\chi$  finite but sufficiently small, the entropy effects are dominant, and they favor mixing: the system exhibits an isotropic phase with sequences  $A$  and  $B$  of the chains interpenetrating each other so that for all points

$$\langle \rho_A(r) \rangle = f \quad \langle \rho_B(r) \rangle = 1 - f$$

where  $\langle \dots \rangle$  denotes the thermal average. In order to characterize the different phases of a liquid copolymer as well as the transitions between them, we will introduce an order parameter  $\psi(r)$ , defined as

$$\psi(r) = \langle (1-f)\rho_A(r) - f\rho_B(r) \rangle \quad (15.2)$$

The simplest way to analyze qualitatively the microphase separation is to examine the expansion of the free-energy density  $F$  of an ordered phase in powers of the order parameter  $\psi(r)$ . The quadratic term of the free energy expansion is written

$$F_2 = \frac{1}{V} \sum_q \tilde{S}_q^{-1} \psi_q \psi_{-q}, \quad (15.3)$$

where  $\psi_q$  denotes the Fourier transform of  $\psi(r)$  and  $V$  the volume of the system. near the phase transition  $\tilde{S}_q^{-1}$  has a deep minimum for the wave vectors  $q$  with  $|q| = q^*$ , but the higher order terms  $F_3, F_4, \dots$  have no singular behavior for  $q^*$ . As a consequence the only Fourier components of  $\psi_q$  which are important (near the transition) are those with  $|q| = q^*$ . For  $\chi N > (\chi N)_t$  the free energy is lowered by the presence of a finite  $\psi_q$  ( $|q| = q^*$ ) - a periodic ordered mesophase appears. The periodicity of the ordered phase is equal to  $2\pi/q^*$  and is of the order of the radius of gyration of copolymer molecules. The detailed structure and magnitude of the coefficients  $\psi_q$  ( $|q| = q^*$ ) for various orientations of  $q$  will depend crucially on the higher order terms  $F_3, F_4, \dots$ . Near the spinodal the important fluctuations should be those with wave vectors  $|q| = q^*$  and that  $\psi(r)$  may be approximated by

$$\psi(r) = \sum_{q \in \{Q_i\}} \psi_q e^{iqr}, \quad (15.4)$$

where  $|Q_i| = q^* (i = 1..n)$  and  $\psi_q = \psi_{-q}$ .

Radiation scattering experiments provide a very attractive method for studying the various aspects of the microphase separation. In case of MPS, the scattering by the periodic microdomain structure gives the characteristic diffraction spectrum. The scattering intensity for the disordered phase of the block copolymer is proportional to the correlation function  $\tilde{S}(q)$ . There is a certain critical value of  $\chi N$ ,  $(\chi N)_s$ , for which the correlation function  $\tilde{S}(q)$  diverges with  $|q| = q^*$ ; this is the spinodal point. Thus, from the definition of the spinodal point

$$F_2 = \tilde{S}_q^{-1} \sum_{q \in \{\pm Q_i\}} \psi_q \psi_{-q} = 2N(\chi_s - \chi) \sum_{q \in \{\pm Q_i\}} |\psi_q|^2 \quad (15.5)$$

If  $\chi > \chi_s$  the microphase separation transition (MST) occurs. Subsequent analysis of the free energy shows that there are two microdomain structures that may appear after the MST: the hexagonal and bcc mesophases. In order to decide which mesophase will actually appear, it is necessary to analyze the free energy of these phases in more detail.

Biological macromolecules (proteins, RNA, DNA) are heteropolymers, where the sequence of monomers are evolutionary selected. These non-random (evolution selected) macromolecules can be modelled by disordered polymers of various sorts. In these models, the relevant interactions (monomer-monomer or monomer-solvent) are disordered, and the disorder is quenched, to account for the fixed character of the chemical sequence. The approach to macromolecules with quenched sequence disorder is based on the spin glass theory. We will restrict ourselves with the minimum amount needed for the heteropolymer folding problem. The spin glass problem originally arose in the study of disordered magnetic alloys, where magnetic impurities (e.g. Mn), quenched at random positions in the host lattice (e.g. Cu) interact with one another through competing interactions. The essence of the spin glass problem (i.e. frustration + quenched disorder) is captured by the Edwards-Anderson model:

$$H = - \sum_{i < j} J_{ij} S_i S_j, \quad (15.6)$$

where  $S_i = \pm 1$  and  $J_{ij}$  are the random coupling between impurities  $i$  and  $j$ , distributed with a law  $P(\{J_{ij}\})$ . for a given set of  $\{J_{ij}\}$ , the free energy  $F(\{J_{ij}\})$  at temperature  $T$  is obtained as:

$$F(\{J_{ij}\}) = -T \log Z(\{J_{ij}\}) \quad (15.7)$$

with

$$Z(\{J_{ij}\}) = \text{Tr} \{ S_i \exp(-\beta H(\{J_{ij}\})) \} \quad (15.8)$$

with  $\beta = 1/T$  (throughout this article, we set Boltzmann's constant  $k_B = 1$ ). Note that  $F(\{J_{ij}\})$  is also a random variable; for short range interactions, we now show that, when the number  $N$  of spins becomes very large,  $F(\{J_{ij}\})$  is sharply peaked around its (disorder) averaged value  $\bar{F}$ , where

$$\bar{F} = \int d(\{J_{ij}\}) P(\{J_{ij}\}) F(\{J_{ij}\}) \quad (15.9)$$

This property is called self-averageness of the free energy.

Two main lines have been pursued in the (static) study of mean field spin glasses:

1) the replica method where one averages a priori over all disorder configurations, through the identity:

$$\bar{F} = -T \overline{\ln Z} = -T \lim_{n \rightarrow 0} \frac{\overline{Z^n} - 1}{n} \quad (15.10)$$

2) the TAP equations, which give, for each disorder configuration the free energy local minima. These equations are difficult to study either analytically or numerically, except in certain limits.

Disordered systems like spin glasses or random heteropolymers are characterized by two types of degrees of freedom: annealed, which arrange themselves to minimize the free energy, and quenched, which can be considered as constant in time. In case of macromolecules, annealed degrees of freedom are spatial coordinates of monomers. The monomers sequence can be addressed as a set of quenched degrees of freedom. The free energy of the macromolecule with random quenched sequence can be estimated as

$$f \geq g(\mu, T) \geq f_A \quad (15.11)$$

where  $f$  and  $f_A$  are the quenched and annealed free energy per monomer, correspondingly and

$$g(\mu, T) = -\frac{T}{N} \ln \overline{Z(seq) e^{-N\mu\alpha(seq)}}, \quad (15.12)$$

where  $Z(seq)$  is the partition function of macromolecule with given sequence realization  $seq$  and  $\alpha(seq)$  is the appropriate self-averaging quenched quantity.  $\overline{\phantom{x}}$  means the average over sequence distribution function. We will refer to this approach as a "constraint annealing approach".

Let us consider the Hamiltonian:

$$\beta\mathcal{H}(\{w_{ij}\}) = \frac{1}{2} \sum_{i \neq j} (v_0 + \beta w_{ij}) \delta(\vec{r}_i - \vec{r}_j) + \frac{1}{6} \sum_{i \neq j \neq k} w_0 \delta(\vec{r}_i - \vec{r}_j) \delta(\vec{r}_i - \vec{r}_k) \quad (15.13)$$

where the couplings  $\{w_{ij}\}$  are random independent couplings, and  $v_0$  represents the overall effect of the solvent, as well as the direct non random pair interactions. For the sake of simplicity, we use a Gaussian probability distribution for the couplings:

$$h(w_{ij}) = \frac{1}{\sqrt{2\pi w^2}} \exp\left(-\frac{w_{ij}^2}{2w^2}\right) \quad (15.14)$$

The partition function is:

$$Z(\{w_{ij}\}) = \int \mathcal{D}\vec{r}_i \prod_i g(\vec{r}_i, \vec{r}_{i+1}) e^{-\beta\mathcal{H}(\{w_{ij}\})} \quad (15.15)$$

where the function  $g(\vec{r}_i, \vec{r}_{i+1})$  enforces the chain constraint. Replicating and averaging the latter equation yields:

$$\begin{aligned} \overline{Z^n} = & \int \prod_a \mathcal{D}\vec{r}_i^a \prod_{i,a} g(\vec{r}_i^a, \vec{r}_{i+1}^a) \exp\left(-\tilde{v}_0 \sum_{i < j} \sum_a \delta(\vec{r}_i^a - \vec{r}_j^a) + \frac{\beta^2 w^2}{2} \sum_{a \neq b} \sum_{i < j} \delta(\vec{r}_i^a - \vec{r}_j^a) \delta(\vec{r}_i^b - \vec{r}_j^b)\right) \\ & \times \exp\left(-\frac{w_0}{6} \sum_{i \neq j \neq k} \sum_a \delta(\vec{r}_i^a - \vec{r}_j^a) \delta(\vec{r}_j^a - \vec{r}_k^a)\right) \end{aligned} \quad (15.16)$$

where  $\tilde{v}_0 = v_0 - (\beta w)^2 / 2$ .

The proposed model is possessed by two main features:

(i) a possible  $\theta$  point if  $\tilde{v}_0$ .

(ii) a possible freezing transition due to the a  $a \neq b$  term of (15.16).

Since we wish to emphasize here the freezing transition, we will assume that  $\tilde{v}_0$

Is indeed negative, so that the system is in the collapsed phase. The Eq.(15.16) can be easily generalized for the continuous case as

$$\begin{aligned} \overline{Z}^n = & \int \prod_{a=1}^n \mathcal{D}\vec{r}_a(s) \exp \left( -\frac{d}{2a^2} \int_0^N ds \sum_a \left( \frac{d\vec{r}_a(s)}{ds} \right)^2 - A \right) \\ & \times \exp \left( \frac{\beta^2 w^2}{2} \int_0^N ds \int_0^N ds' \sum_{a < b} \delta(\vec{r}_a(s) - \vec{r}_a(s')) \delta(\vec{r}_b(s) - \vec{r}_b(s')) \right) \end{aligned} \quad (15.17)$$

where

$$\begin{aligned} A = & \frac{1}{2}(\tilde{v}_0) \int_0^N ds \int_0^N ds' \sum_a \delta(\vec{r}_a(s) - \vec{r}_a(s')) \\ & + \frac{w_0}{6} \int_0^N ds \int_0^N ds' \int_0^N ds'' \sum_a \delta(\vec{r}_a(s) - \vec{r}_a(s')) \delta(\vec{r}_a(s') - \vec{r}_a(s'')) \end{aligned} \quad (15.18)$$

Introducing density – like parameters

$$\begin{aligned} q_{ab}(\vec{r}, \vec{r}') &= \int_0^N ds \delta(\vec{r}_a(s) - \vec{r}) \delta(\vec{r}_b(s) - \vec{r}') \\ \rho_a(\vec{r}) &= \int_0^N ds \delta(\vec{r}_a(s) - \vec{r}) \end{aligned} \quad (15.19)$$

obtaining

$$\overline{Z}^n = \int \mathcal{D}q_{ab}(\vec{r}, \vec{r}') \mathcal{D}\hat{q}_{ab}(\vec{r}, \vec{r}') \mathcal{D}\rho_a(\vec{r}) \mathcal{D}\phi_a(\vec{r}) \exp (G(q_{ab}, \hat{q}_{ab}, \rho_a, \phi_a) + \log \zeta(\hat{q}_{ab}, \phi_a)) \quad (15.20)$$

with

$$\begin{aligned} G(q_{ab}, \hat{q}_{ab}, \rho_a, \phi_a) = & \int d^d r \sum_a \left( i \rho_a(\vec{r}) \phi_a(\vec{r}) - (\tilde{v}_0) \frac{\rho_a^2(\vec{r})}{2} - \frac{w_0}{6} \rho_a^3(\vec{r}) \right) \\ & + \int d^d r \int d^d r' \sum_{a < b} \left( i q_{ab}(\vec{r}, \vec{r}') \hat{q}_{ab}(\vec{r}, \vec{r}') + \frac{\beta^2 w^2}{2} q_{ab}^2(\vec{r}, \vec{r}') \right) \end{aligned}$$

and

$$\begin{aligned} \zeta(\hat{q}_{ab}, \phi_a) = & \int \mathcal{D}\vec{r}_a(s) \exp \left( -\frac{d}{2a^2} \int_0^N ds \dot{\vec{r}}_a^2 \right) \\ & \times \exp \left( -i \int_0^N ds \sum_a \phi_a(\vec{r}_a(s)) - i \int_0^N ds \sum_{a < b} \hat{q}_{ab}(\vec{r}_a(s), \vec{r}_b(s)) \right) \end{aligned}$$

Then, we need to get the limit  $n \rightarrow 0$  to estimate the free energy (15.10). The subsequent analysis



of the obtained free energy shows the close similarity between the model with Hamiltonian (15.13) and Random Energy Model (REM). This model can then be solved by a one-step replica symmetry breaking scheme. The chain undergoes a freezing transition at a temperature  $T_c$ . Above  $T_c$ , the system has a finite entropy, whereas below  $T_c$ , it vanishes. The system is then frozen in a small number of dominant states.

## Theme 16. Liquid crystalline ordering:

*Onsager approximation for the semiflexible macromolecules; order parameter and nematic ordering.*

Let us start with the case of semiflexible macromolecules with  $L \gg \ell \gg d$ , where  $L$  is the contour length,  $\ell$  is the persistence length and  $d$  is the diameter of chain. The free energy of a solution of these macromolecules in the Onsager approximation must consist of the contribution  $F_{conf}$  describing the entropy losses upon orientational ordering and the free energy  $F_{ster}$  of steric interaction of the macromolecules in the second virial approximation (the translational free energy for long polymer chains is generally inessential).

To write the expression for  $F_{ster}$  we note that, since  $\ell \gg d$  for semiflexible macromolecules, one can always divide the polymer chains into regions of length  $\lambda$  so that  $d \ll \lambda \ll \ell$ , and call these regions elementary links. In essence, the elementary links thus defined are long rigid rods. Therefore the second virial coefficient of interaction of two links having the orientations  $n_1$ , and  $n_2$  is  $B(\gamma) = 2\lambda^2 d |\sin \gamma|$ . Upon allowing for this, we can write the expression for  $F_{ster}$  in the form as:

$$\begin{aligned} F_{ster} &= \frac{NL}{2\lambda} T \frac{4\varphi}{\lambda d^2} \int d\Omega_{n_1} d\Omega_{n_2} 2d\lambda^2 |\sin \gamma| f(n_1) f(n_2) = \\ &= NTL \frac{4\varphi}{\pi d} \int d\Omega_{n_1} d\Omega_{n_2} |\sin \gamma| f(n_1) f(n_2) \end{aligned} \quad (16.1)$$

where  $N$  is the total number of macromolecules in the solution,  $\varphi = \pi c L d^2 / 4$ ,  $c = N/V$  and  $f(n)$  is the orientation distribution of the unit vectors  $n$  tangential to the chain. For the semiflexible persistent macromolecules we have

$$F_{conf} = NT \frac{L}{\ell} \int d\Omega_n \frac{(\nabla_n f)^2}{4f} \quad (16.2)$$

The next step in the Onsager method is to find the equilibrium distribution function  $f(n)$  by minimizing  $F = F_{ster} + F_{conf}$ . Direct minimization yields an integral equation that can be solved only numerically. Therefore, an approximate variational method can be used with the trial function

$$f(n) \propto \cosh(\alpha \cos \vartheta), \quad (16.3)$$

where  $\vartheta$  is the angle between the vector  $n$  and the direction of the anisotropy axis, while  $\alpha$  is the variational parameter. One must substitute the trial function of (16.3) into Eqs. (6.1, 6.2) and minimize it with respect to  $\alpha$ . The found minima correspond to possible phases (isotropic and liquid-crystalline). One can study the transition between these phases by the usual method by

equating the pressures  $\pi = (c^2 / N) \partial F / \partial c$  and chemical potentials  $\mu = \frac{1}{N} (F + c \partial F / \partial c)$  of the two phases. As a result it turned out that the orientational ordering of the athermal solution has the character of a first-order phase transition and occurs at low concentrations of the polymer in solution. More exactly, when  $\varphi < \varphi_i$ , the solution is homogeneous and isotropic, when  $\varphi > \varphi_a$  it is homogeneous and anisotropic, while when  $\varphi_i < \varphi < \varphi_a$  it separates into isotropic and nematic phases, with  $\varphi_i \cong \varphi_a \cong d / \ell \ll 1$ .

The following characteristics of nematic ordering were obtained for an athermal solution of persistent semiflexible chains

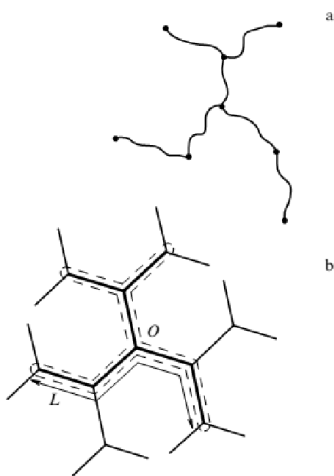
$$\varphi_i = \frac{10.48d}{\ell}, \quad \varphi_a = \frac{11.39d}{\ell}, \text{ and order parameter } s = \frac{1}{2} \langle 3 \cos^2 \vartheta - 1 \rangle = 0.49.$$

## Theme 17. Branched polymers:

*dimensions of branched chains; chains with quenched and annealed branching; Flory theory and radius of gyration.*

Branched polymers are of significant interest both for synthetic polymer chemists and for biophysicists. Most of the synthetic polymers are somewhat branched. Also, RNA molecules form clover leaf structures that can be viewed as branched polymers, with elements of secondary structure forming branches. An even better example of a branched polymer is super-coiled DNA.

To begin with, let us disregard volume interactions and ask what is the size of an ideal randomly branched polymer,  $R_{id}$ ? This was answered by B Zimm and W Stockmayer as early as in 1949. Their result reads  $R_{id} \propto N^{1/4}$ . There are several ways to derive it; one of the simplest is based on the estimate of the ‘chemical diameter’ of the branched structure, that is, the chemical interval, or contour distance, between two arbitrary ends of the structure, and it is done by mapping the branched structure on a Cayley tree graph (see Fig. 17.1). By choosing an arbitrary origin point  $O$  on the Cayley tree, the branched structure can be viewed as a one dimensional random walk with possible steps to and from  $O$ . This yields an estimate that the chemical diameter,  $L$ , scales as the square root of the number of monomers in the macromolecule,  $N$ , or more accurately,



*Fig. 17.1. The branched structure without cycles (a) can be mapped onto the Cayley tree graph (b). On the graph, the image can be encircled with the ‘ring polymer’ (dashed line), its characteristic distance from the origin  $O$  scales as the chemical diameter of the structure,  $L$ .*

$$L \propto g \sqrt{\frac{N}{g}} \propto \sqrt{Ng} \quad , \quad (17.1)$$

where  $g$  is the characteristic number of monomers in the linear part of the structure, between two neighboring branch points. As each diameter in the ideal polymer represents a Gaussian linear chain, we arrive at

$$R \sim aL^{1/2} \sim a(Ng)^{1/4}, \quad (17.2)$$

where  $a$  is the monomer length. Thus, the density of monomers can be estimated as

$$\rho \approx \frac{N}{R_{id}^3} \cong N^{1/4} \quad (17.3)$$

The density  $\rho$  is diverged in the thermodynamic limit  $N \rightarrow \infty$ . Thus, in three dimensions, branched polymers are very compact and dense, and it is necessary to take into account the effects of excluded volume. For the branched polymers we need to distinguish between two extremes. To explain it, let us say that the branched polymer corresponds to the tree-like graph embedded in real space. In one extreme, the branched polymer is far from equilibrium such that the structure of the graph is fixed. The opposite extreme is the situation where the positions of the branches fluctuate and are in thermal equilibrium. These two extremes are called *quenched* and *annealed*, respectively. The physical reason for the difference between quenched and annealed branches is simple. The excluded volume leads only to the stretching of subchains in the case of quenched branches, but it is accompanied by the rearrangement of branches in the annealed case.

Let us construct the Flory type theory for the quenched branched polymer. The free energy in dependence on the size of the polymer is written

$$F(R) = F_{int}(R) + F_{el}(R), \quad (17.4)$$

where

$$F_{int}(R) \approx Tv \frac{N^2}{R^d} \quad (17.5)$$

is the interaction part of the free energy and  $v \sim a^d$  is the excluded volume of monomer. The entropic part of the free energy  $F_{el}(R)$  is written

$$F_{el}(R) \approx T \left( \frac{R}{R_{id}} \right)^2 \quad (17.6)$$

Minimization of the free energy (17.4) yields the characteristic size of the branched polymer

$$R \cong aN^{\nu_Q} g^{\mu_Q}, \quad (17.7)$$

where

$$\nu_Q = \frac{5}{2(d+2)}, \quad \mu_Q = \frac{1}{2(d+2)} \quad (17.8)$$

In case of the the annealed branched polymer the entropic contributions to the Flory type free energy (17.4) is written

$$F_{el}(R) \approx T \frac{R^2}{a^2 L} + T \frac{L^2}{Ng}, \quad (17.9)$$

where the first term has the same meaning as (17.6), but the second one is responsible for the rearrangement of the branching pattern. How many configurations are there for the diameter  $L$ ? As was already mentioned, these configurations can be mapped onto a one dimensional random walk (to or from the origin  $0$  on the Cayley tree), and thus the answer is given by the entropy of a linear polymer stretched out to the end-to- end distance  $L$ , because, on the Cayley tree,  $L$  plays the role of spatial size. Thus, we get

$$F_{br}(R) \approx T \frac{\left(\frac{L}{g}\right)^2}{N/g} = T \frac{L^2}{Ng} \quad (17.10)$$

Minimizing by  $L$  yields

$$L \cong \left(\frac{R}{a}\right)^{2/3} (Ng)^{1/3}$$

and free energy (17.4) is transformed as

$$F \cong Tv \frac{N^2}{R^d} + T \frac{\left(\frac{R}{a}\right)^{4/3}}{(Ng)^{1/3}} \quad (17.11)$$

Minimizing the latter expression in respect to  $R$  obtaining

$$R \cong a N^{\nu_A} g^{\mu_A}, \quad (17.12)$$

where

$$\nu_A = \frac{7}{3d+4}, \quad \mu_A = \frac{1}{3d+4} \quad (17.13)$$

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