

On the Theory of Liquid-Crystalline Ordering of Polymer Chains with Limited Flexibility

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We propose a universal approximate method which enables us to study the statistical mechanics of the liquid-crystalline ordering in the solutions of stiff-chain macromolecules with limited flexibility of arbitrary nature at arbitrary solution concentrations and arbitrary temperatures (solvent quality). In the variables temperature and concentration we construct the full phase diagrams for the nematic transition for the cases of long rigid rods and semiflexible macromolecules with freely jointed, persistent, and rotational-isomeric flexibility mechanisms. The method proposed can be easily generalized for the study of thermotropic polymer liquid crystals, as well as more complex polymer chain models (e.g., copolymers containing stiff and flexible fragments in the chain).

KEY WORDS: Nematic ordering; polymer solution; stiff-chain polymer; phase diagram; chain flexibility mechanism.

1. INTRODUCTION

The ability to form a liquid-crystalline nematic phase is a characteristic property of solutions and melts of sufficiently stiff-chain polymers.^(1,2) A large number of recent papers have been devoted to the theoretical study of the corresponding phase transition.⁽³⁻¹⁴⁾ Naturally, this transition occurs in a different way depending on whether we are considering a dilute polymer solution, concentrated solution or melt, relatively short practically rodlike macromolecules or long semiflexible chains.

In a recent series of papers⁽¹⁵⁻¹⁸⁾ we have analyzed in the framework of a universal approach the liquid-crystalline ordering in dilute solutions of stiff-chain macromolecules (i.e., macromolecules with the Kuhn segment length, l , much larger than the characteristic chain width, d) with partial flex-

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ibility of different character for arbitrary relation between the total contour chain length, L , and the length of the Kuhn segment. In that study only athermal polymer solutions were considered, in which case the interaction of the chain segments is assumed to be purely steric (repulsion due to the mutual segment impenetrability), their attraction being completely neglected. Even in this case it was shown that the properties of the liquid-crystalline transition depend essentially not only on the ratios L/l and l/d , i.e., on the chain length and the degree of partial flexibility, but also on the flexibility mechanism (freely jointed, persistent, or rotational isomeric).

The diversity of possible qualitatively different types of the liquid-crystalline ordering should increase even more if the attraction between the segments is taken into account. In this case, as is well known,⁽⁵⁾ it is necessary to consider not only dilute polymer solutions, but also concentrated orientationally ordered solutions and, consequently, polymer melts. The study of nematic ordering in polymer melts, which occurs when the temperature is lowered (the thermotropic case), is of significant self-dependent interest.

It is clear that the theoretical analysis of the liquid-crystalline phase transition in each specific situation is an independent problem, which should be solved using a most convenient method. However, in different cases these methods may be very different (e.g., for the study of dilute solutions and melts). Thus, to compare most effectively the results for these different cases and to obtain a full picture of available tendencies and qualitative peculiarities it is worthwhile to make an attempt to describe the nematic ordering in polymer solutions of arbitrary concentration and melts for arbitrary values of ratios l/d and L/l and arbitrary flexibility mechanism in the framework of a universal approximate theory able to catch the main qualitative effects. The construction of just such theory is the aim of the present paper.

The majority of available theoretical papers dealing with the liquid-crystalline ordering in polymer systems are based on one of two classical approaches, which were proposed by Onsager⁽¹⁹⁾ and Flory.⁽²⁰⁾ However, it is clear that these approaches are themselves not sufficient to construct a universal theory mentioned above. The Onsager method is valid only at small polymer concentrations in the solution and, consequently, it cannot be used to describe the orientation ordering in polymer melts and concentrated solutions. The Flory method is based on the lattice model, i.e., the chain flexibility mechanism in this method is fixed, and, furthermore, in the majority of cases (except for the case of completely rigid rods or rigid segments included in the chain) the Flory model does not take into account the continuum orientational distribution of the chain links. In Ref. 5 an attempt was made to synthesize the positive features of the Onsager and Flory

approaches; however, the developed theory can be applied only to a limited number of problems.

In the present paper we propose a universal method, which can be used to study the liquid-crystalline nematic ordering in the solutions and melts of polymer chains of arbitrary concentration and solvent quality with arbitrary flexibility mechanism for the cases of completely stiff ($L \ll l$) and semiflexible ($L \gg l$) macromolecules. Generalizations of this method for the case of macromolecules with $L \sim l$, as well as for the case of copolymers including stiff and flexible fragments of the chain (this situation being most interesting from the point of view of thermotropic polymer liquid crystals) do not give rise to any difficulties and will be considered in subsequent publications. The method proposed does not pretend to be absolutely rigorous; however, we believe that it allows us to reveal main tendencies and qualitative peculiarities of the orientational ordering in polymer systems.

Our method is based on the consideration of the papers⁽¹⁵⁻¹⁸⁾ dealing with dilute athermal polymer solutions; it is just the generalization of this consideration for the case of solutions of arbitrary concentration (and melts) and arbitrary quality of solvent. Thus in the next section we will summarize some of the results of Refs. 15-18, which will be used in the further consideration. In Section 3 we will discuss the generalizations necessary to describe solutions of arbitrary concentration. In Section 4 to be able to consider the solvents of arbitrary quality we will take into account the forces of attraction between the chain links. In Sections 5-8 we will use the method proposed here to investigate the nematic ordering in the solutions of stiff-chain macromolecules with different mechanisms of partial flexibility. The application of our method to the study of the liquid-crystalline ordering in polymer melts (thermotropic case) will be the subject of a separate publication.

2. FREE ENERGY OF DILUTE ATHERMAL SOLUTIONS OF STIFF-CHAIN POLYMERS

In the present work we will consider the solutions of following objects: (a) completely stiff macromolecules ($L \ll l$), i.e., long rigid rods of length L and diameter d (Fig. 1a); (b) semiflexible macromolecules ($L \gg l$) with freely joint flexibility mechanism, i.e., long chains of freely jointed rigid segments of length l and diameter d (Fig. 1b); (c) semiflexible macromolecules with persistent (homogeneously distributed along the chain contour) flexibility mechanism (Fig. 1c); (d) semiflexible macromolecules with rotational-isomeric flexibility mechanism (Fig. 1d), which consists of elementary subunits of length a and diameter d , the angle γ between the adjacent subunits being equal either to $\gamma_0 = 60^\circ$ (with the probability $p \ll 1$; *gauche*

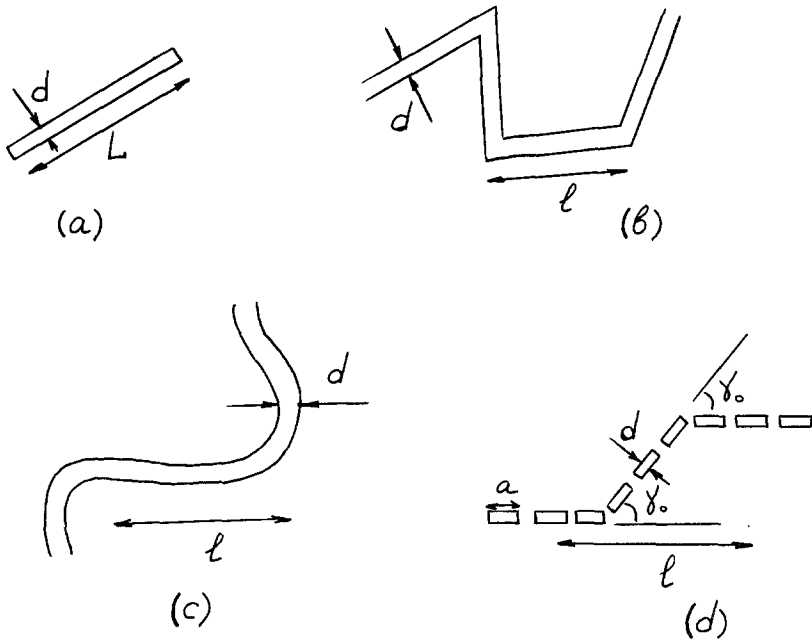


Fig. 1. (a) Completely stiff macromolecule (rigid rod); (b) semiflexible freely jointed macromolecule; (c) semiflexible persistent macromolecule; (d) semiflexible rotational-isomeric macromolecule.

conformation) or to $\gamma = 0$ (with the probability $1 - p$; *trans* conformation).⁽¹⁸⁾

Let us consider an athermal dilute solution of one of the objects described above. Below we will use the term *segment* to denote all the macromolecule (rigid rod), in the case of Fig. 1a; the straight chain segment between two junction points, in the case of Fig. 1b; or the part of the chain whose length is equal to the length of the Kuhn segment, in the case of Figs. 1c and 1d. Let N be the total number of segments dissolved in the volume V , $c = N/V$, T the temperature, and $f(\mathbf{n})$ the orientational distribution function for the unit vector, \mathbf{n} , tangential to the chain (in the cases of Figs. 1a and 1b this function is, as a matter of fact, the orientational distribution function for the straight segments). Let us assume the following normalization condition for $f(\mathbf{n})$: $\int f(\mathbf{n}) d\Omega = 1$, $d\Omega$ being an element of spatial angle.

Then, as shown in Refs. 15–18, the free energy of the solution can be represented as a sum of three terms: $F = F_1 + F_2 + F_3$, where F_1 corresponds to the translational entropy of the motion of the macromolecule as a whole, F_2 describes the entropy of orientational ordering, and F_3 represents the free energy of the steric interaction of segments in the second virial approx-

imation. In Ref. 15 it was shown that the translational entropy should be taken into account only for completely stiff but not for semiflexible macromolecules, thus (here and below indices A, B, C, D correspond to Figs. 1a, b, c, d)

$$F_1^A = NT \ln c, \quad F_1^{B,C,D} = 0 \quad (1)$$

The contribution to the free energy due to the entropy of orientational ordering can be written in the form⁽¹⁵⁻¹⁸⁾

$$\begin{aligned} F_2^{A,B} &= NT \int f(\mathbf{n}) \ln(4\pi f(\mathbf{n})) d\Omega \\ F_2^C &= NT \int \frac{[\nabla f(\mathbf{n})]^2}{4f(\mathbf{n})} d\Omega \\ F_2^D &= -\frac{NTl}{a} \int f(\mathbf{n}) \ln \frac{\hat{g}\psi}{\psi} d\Omega \end{aligned} \quad (2)$$

where the additional function $\psi(\mathbf{n})$ in the latter expression is connected with $f(\mathbf{n})$ by means of the relation

$$\psi \hat{g}\psi = f(\mathbf{n}), \quad \hat{g}\psi \equiv (1-p)\psi + 2p \int \delta(\mathbf{nn}' - \cos \gamma_0) \psi(\mathbf{n}') d\Omega' \quad (3)$$

It is easy to show that for the model of Fig. 1d the length of the Kuhn segment, l , is equal to

$$\frac{l}{a} = \frac{1}{p \sin^2 \gamma_0} - 1 = \frac{4}{p} - 1 \quad (4)$$

It can be noted that in the limit $p \ll 1$ or $l \gg a$ the expression for F_2^D can be significantly simplified (see Ref. 18). However, we will not perform such simplification here (since further in some cases we will deal with not very small values of p); in this case all the formulas written above remains valid not only for stiff-chain ($l \gg d$), but also for flexible ($l \sim d$) macromolecules.

As to the free energy of the steric interaction of segments, F_3 , in Refs. 16-18 it was shown that for all four cases in the second virial approximation (which is valid for the description of the orientational ordering in dilute solution)

$$F_3 = NTc\tilde{l}^2 d \int |\sin \gamma| f(\mathbf{n}_1) f(\mathbf{n}_2) d\Omega_1 d\Omega_2 \quad (5)$$

where $\tilde{l} \equiv L$ in the case of rigid rods and $\tilde{l} \equiv l$ for semiflexible chains, and γ is the angle between the vectors \mathbf{n}_1 and \mathbf{n}_2 . Of course, Eq. (5) is exact only for sufficiently stiff polymer chains, $l \gg d$.

Equations (1)–(5) determine completely the free energy of dilute athermal solution of stiff-chain polymers. Further analysis of the properties of the liquid-crystalline ordering for this case was performed in Refs. 15–18.

3. FREE ENERGY OF ATHERMAL SOLUTIONS OF STIFF-CHAIN POLYMERS OF ARBITRARY CONCENTRATION

Let us assume that now we have a solution of one of the objects shown in Fig. 1, polymer volume fraction in the solution being not obligatory small. Obviously, the free energy of this solution, as before, can be written in the form $F = F_1 + F_2 + F_3$, where for the terms F_1 and F_2 Eqs. (1)–(4) of the previous section remain valid. As to the term F_3 , for the solution of arbitrary concentration it cannot be, of course, written in the form (5) using the second virial approximation.

Let us at first consider the problem of approximate calculation of the free energy F_3 in the solution of arbitrary concentration for the case of long rigid rods (Fig. 1a). In this consideration we will follow the ideas developed by Parsons in Ref. 21.

Let \mathbf{n}_1 and \mathbf{n}_2 be the orientations of two rods, and \mathbf{r} the vector between their centers of mass (Fig. 2). In Ref. 21 it was shown that a reasonable approximation for the pair correlation function of the solution of rods, $g(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2; c)$, which gives a qualitatively correct description of the solution behavior in all the concentration range, is based on the assumption that

$$g(\mathbf{r}, \mathbf{n}_1, \mathbf{n}_2; c) = g(r/\sigma; c) \quad (6)$$

where $r = |\mathbf{r}|$, $\sigma = \sigma(\mathbf{n}, \mathbf{n}_1, \mathbf{n}_2)$ is the distance of closest approach of the rods, and $\mathbf{n} = \mathbf{r}/r$. The assumption (6) is exact for dilute solutions; in the concen-

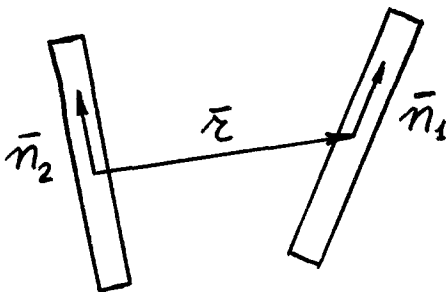


Fig. 2

trated system it corresponds to a mean-field-type approximation, which separates the orientational and translational degrees of freedom.⁽²¹⁾ Since, as was already emphasized, our aim is not an absolutely rigorous theory, but rather an approximate consideration describing main qualitative tendencies, we will adopt the approximation (6) in the further consideration. In this case, as shown in Ref. 21, the free energy F_3 can be written in the form [cf. Eq. (5)]:

$$F_3 = NT\mathcal{E}(c) L^2 d \int |\sin \gamma| f(\mathbf{n}_1) f(\mathbf{n}_2) d\Omega_1 d\Omega_2$$

$$\mathcal{E}(c) = \int_0^c g(1; c) dc \tag{7}$$

Thus, the problem of determination of the term F_3 amounts to the calculation of the function $g(1; c)$.

The approximation (6) in the case of a purely steric interaction can be interpreted somewhat more broadly as the assumption of independence of the function $g(r/\sigma; c)$ of the specific form of the solute particles (see Ref. 21). Thus, as soon as we adopt this approximation, the function $g(1; c)$, which is necessary for the calculation of the free energy F_3 , can be directly borrowed from the well-developed theory of sterically interacting spheres. The thermodynamic characteristics of the solution of rigid spheres were calculated in the superposition approximation in Ref. 22. The results of the corresponding calculation, shown in Fig. 3, can be conveniently approximated by the expression

$$g(1; c) = \frac{1}{1 - \vartheta} \tag{8}$$

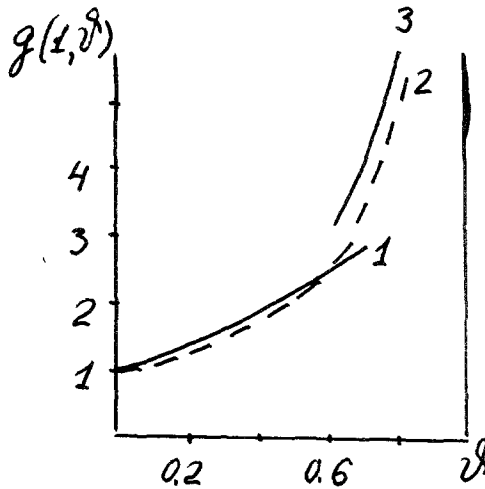


Fig. 3. Function $g(1; c)$ for the system of sterically interacting spheres: 1, Kirkwood theory; 2, approximation (8); 3, theory of free volume.

where $\vartheta = c/c_{\max}$ is the packing degree of rigid spheres. The accuracy of the approximation (8)—15%—does not exceed the discrepancies between different modifications of the superposition approximation.⁽²³⁾ It should be also noted that the theory of free volume,^(24,25) which is often used in the case of large densities, gives similar behavior for $g(1; c)$ at the values of ϑ close to unity: $g(1; c) = 3/2 \cdot (2\pi)^{1/2} \vartheta^2 / (1 - \vartheta^{1/3})$ (see Fig. 3). Thus, the relation (8) is, apparently, the simplest relation, which describes qualitatively correctly the behavior of the solution of rigid spheres in the whole concentration region. For the aims of the present paper the approximation (8) is quite sufficient, thus we will not use here more accurate modern theories (see Ref. 26).

Substituting Eq. (8) in Eqs. (7) we obtain finally the approximate expression for the free energy of the steric interaction of rods, F_3^A , in the solution of arbitrary concentration:

$$F_3^A = N T c_{\max} L^2 d \ln \left(\frac{1}{1 - c/c_{\max}} \right) \int |\sin \gamma| f(\mathbf{n}_1) f(\mathbf{n}_2) d\Omega_1 d\Omega_2 \quad (9)$$

where c_{\max} is the maximal packing degree for the system of rods. In the limit $c \ll c_{\max}$ we return to Eq. (5).

It should be noted that the most frequently used approach to the calculation of the steric part of the free energy, F_3 , in polymer liquid-crystalline problems is the lattice approach of Flory.⁽²⁰⁾ The expression (9) is, as a matter of fact, a continuum analog of the corresponding expression in the Flory theory. Actually, Flory theory in his notation (see Ref. 20) gives

$$F_3^A/T = n_1 \ln v_1 - (n_1 + \bar{y}n_x) \ln [1 - v_x(1 - \bar{y}/x)] - n_x \bar{y} \quad (10)$$

where $\bar{y} = x(4/\pi) \langle \sin \psi \rangle$, ψ is the angle between the direction of the rod and the ordering axis. For the sake of the convenient comparison of this expression with Eq. (9) let us consider a strongly ordered and dense state, in which case $\langle \sin \psi \rangle \ll 1$, and let us return to our notation; then Eq. (10) takes the form

$$F_3^A = N T c_{\max} L^2 d \ln \left(\frac{1}{1 - c/c_{\max}} \right) \langle \sin \gamma \rangle \quad (11)$$

which is identical to Eq. (9). Thus, the expression (9) retaining all the advantages of the corresponding expression in the Flory theory, is free from the shortcomings of this theory connected with the lattice character of the model.

Let us now proceed to the case of the solutions of semiflexible chains with various flexibility mechanisms (Figs. 1b, c, d). It should be recalled that

in the dilute limit the expression for the free energy was determined by Eq. (5) independently of the chain flexibility mechanisms, the only difference between rigid rods ($L \ll l$) and semiflexible chains ($L \gg l$) lying in the fact that the rod length, L , should be replaced by the Kuhn segment length, l . Arguments in favor of this statement were adduced in Ref. 16. These arguments without any change can be applied for the case of the solutions of arbitrary concentration as well (the main idea lying behind these arguments is the fact that semiflexible chains can be always divided into such elementary subunits of length λ ($l \gg \lambda \gg d$), that these subunits can be regarded as practically long rigid rods). Thus, the general expression for the steric part of the free energy in the solution of objects shown in Fig. 1 can be written in the form

$$F_3 = NTc_{\max} \tilde{l}^2 d \ln \left(\frac{1}{1 - c/c_{\max}} \right) \int |\sin \gamma| f(\mathbf{n}_1) f(\mathbf{n}_2) d\Omega_1 d\Omega_2 \quad (12)$$

where, as before, $\tilde{l} \equiv L$ for rigid rods and $\tilde{l} \equiv l$ for semiflexible chains.

This expression depends essentially on the value of concentration c_{\max} corresponding to the maximally dense packing of the links. Obviously, $c_{\max} \sim 1/d^2 \tilde{l}$. In this paper we will assume, to be definite, that

$$c_{\max} = \frac{4}{\pi} \frac{1}{d^2 \tilde{l}} \quad (13)$$

The choice of any other numerical coefficient of order unity in Eq. (13) does not lead to the change of the qualitative conclusions of the present paper.

4. FREE ENERGY IN THE PRESENCE OF THE FORCES OF ATTRACTION

Now let us assume that the solution of stiff-chain macromolecules is no longer athermal, i.e., that in addition to the forces of steric repulsion there exist also forces of attraction of arbitrary nature between the links. It is clear that in this case we must add a new term, F_4 , to the free energy, which would describe the influence of the forces of attraction.

It is easy to show that in the case when the characteristic radius of the attraction forces, r_a , exceeds considerably the characteristic width of the chain, d ($r_a \gg d$), the influence of the attraction forces can be described by the mean field of the type

$$U(\mathbf{n}) = -u_0 c - u_a c \eta P_2(\mathbf{nn}_0) \quad (14)$$

where u_0 and u_a are the constants characterizing the isotropic and the anisotropic part of the attraction forces, correspondingly, $\eta = \langle P_2(\mathbf{nn}_0) \rangle \equiv$

$\int f(\mathbf{n}) P_2(\mathbf{nn}_0) d\Omega$ is an order parameter defined in a usual way, $P_2(\mathbf{nn}_0)$ the second Legendre polynomial, \mathbf{n}_0 the direction of the anisotropy axis. In the orders of magnitude $u_0, u_a \sim W\tilde{l}^2d$, where W is the characteristic energy of the intermolecular interaction. The free energy $F_4 = \frac{1}{2}N \int f(\mathbf{n}) U(\mathbf{n}) d\Omega$ is, thus, equal to

$$F_4 = -\frac{1}{2}Nc(u_0 + u_a\eta^2) \quad (15)$$

In spite of the fact that Eq. (14) is strictly valid only in the limit $r_a \gg d$, we will use it below also for the general case ($r_a \sim d$). We believe that the corresponding errors of order unity change the results only quantitatively and do not influence the qualitative effects in the systems under consideration.

Equation (15) can be conveniently rewritten as follows. Let us note that very dilute polymer solution is deliberately isotropic, thus in this limit the free energy of the interaction is given by

$$F_{\text{int}} = F_3 + F_4 = \frac{\pi}{4} NTc\tilde{l}^2d - \frac{1}{2}Ncu_0 \quad (16)$$

This value is equal to zero at the temperature $\theta = (2/\pi)(u_0/\tilde{l}^2d)$, which in the framework of our theory plays the role of the θ temperature of polymer solution and determines the characteristic scale of energetic interactions in the system. Taking into account this notation the free energy F_4 can be rewritten in the form

$$F_4 = -N\theta \frac{\pi}{4} \tilde{l}^2dc(1 + \kappa\eta^2) \quad (17)$$

where $\kappa = u_a/u_0$. As a rule, the anisotropic part of the attraction is much smaller than the isotropic one^(27,28); further we will use in specific calculations $\kappa = u_a/u_0 = 0.1$ as a reasonable estimation (calculations have shown that the properties of the liquid-crystalline transition depend very weakly on κ , thus the specific assignment of the exact value of κ is not essential).

Equations (1), (2), (12), and (17) determine completely the free energy, F , of a polymer solution. To find equilibrium characteristics of the nematic ordering in this solution the expression for F should be minimized with respect to all possible orientational distribution functions, $f(\mathbf{n})$. For this purpose we have used, following Refs. 15–18, an approximate variational method. For the cases shown in Figs. 1a, b, c the trial function was chosen in the form (cf. Refs. 15–18)

$$f(\mathbf{n}) = \text{const} \cdot \exp(-\alpha \cos^2 \varphi) \quad (18)$$

where φ is the angle between the vector \mathbf{n} and the orientation axis, α the variational parameter and const a normalizing constant. For the case of Fig. 1d it is convenient to represent in the form (18) not the function $f(\mathbf{n})$ itself, but the additional function $\psi(\mathbf{n})$ [see Eq. (3)]. The minimization of the free energy and the determination of possible phases and the transition characteristics between these phases can be performed for the present problem in a standard way. Omitting all the intermediate calculations, in the next sections we will describe the main results obtained.

5. NEMATIC ORDERING IN THE SOLUTION OF RIGID RODS

At first let us consider the results, which can be obtained using the theory described above for the well-studied case (see Refs. 5 and 20) of the solutions of long rigid rods of arbitrary concentration at the arbitrary temperatures.

Some results for the athermal solution ($\theta = 0$) are shown in Table I. It can be seen that the increase of concentrations corresponding to the nematic ordering with the decrease of the ratio L/d is somewhat slower than it would follow from the asymptotic Onsager theory, which is valid in the limit $L/d \gg 1$. This conclusion agrees with the Flory theory.⁽²⁰⁾ However, the numerical values of c_i and c_a represented in Table I remain (even for finite values of L/d) essentially lower than in the Flory theory. It is worthy also to note the fact of some relative narrowing of the transition region (decrease in w) with the decrease in L/d and the fact of the practical independence of the order parameter at the transition point, η_0 , of the value of L/d .

Now we proceed to the general case of the solvent of arbitrary quality ($\theta \neq 0$). The calculated phase diagrams for the liquid-crystalline transition in the variables $\theta/T - c/c_{\max}$ for several value of L/d are shown in Fig. 4.

Table I. Nematic Ordering in Athermal Solutions of Rigid Rods

L/d	c_i/c_{\max}^a	c_a/c_{\max}^a	w^b	η_0^c
$\rightarrow \infty$	$3.31 d/L$	$4.22 d/L$	0.275	0.800
100	0.0326	0.0415	0.273	0.802
20	0.152	0.193	0.270	0.809
5	0.483	0.580	0.201	0.817

^a c_i and c_a , polymer concentrations in the isotropic and anisotropic phases coexisting at the transition point.

^b $w \equiv (c_a - c_i)/c_i$, relative width of the phase separation region.

^c η_0 , order parameter at the transition point.

At large L/d phase diagram has the characteristic form shown in Fig. 4a. In the high-temperature region there is a narrow corridor corresponding to the separation of the solution into the isotropic and the nematic phases. At low temperatures, on the contrary, we have a very broad separation region between the isotropic and concentrated highly ordered phase. These two regimes are separated by the interval between the triple point temperature, T_t , and the critical temperature, T_c , ($T_c > T > T_t$), within which there are two phase separation regions: between the isotropic and the anisotropic phases and between two anisotropic phases. The temperatures T_t and T_c exceed essentially the θ temperature. The phase diagram of similar form was obtained in the early work of Flory⁽²⁰⁾ (see also Ref. 5).

With the decrease in L/d the interval between T_c and T_t becomes narrower (Fig. 4b) and disappears at $(L/d)_{c1} = 15$. At $L/d < 15$ there are no critical or triple points in the phase diagram (Fig. 4c) and it is possible to speak only about the crossover temperature, T_{cr} , between the narrow high-temperature phase separation corridor and the very broad low-temperature separation region. The temperature T_{cr} decreases with the decrease in L/d ; at $(L/d)_{c2} = 3.5$,² when this temperature becomes noticeably lower than the θ temperature, the situation changes qualitatively once more: now we have the triple and critical points corresponding to the additional phase transition between two isotropic phases (Fig. 4d). The physical meaning of this result is rather obvious: at small values of L/d the properties of the solution of rods must approach the properties of the solution of isotropic particles, in particular, at low temperatures we must have a region corresponding to the ordinary isotropic phase separation.

The nematic ordering in the solution of rigid rods of finite length was considered in detail in Ref. 4 with the help of the lattice method. In that paper the phase diagrams of the type of Figs. 1a, b [at $L/d > (L/d)_{c1}$] and of Fig. 1c [at $L/d < (L/d)_{c1}$] were obtained; the value of $(L/d)_{c1}$ was shown to be equal to 20—this is rather close to our result $(L/d)_{c1} = 15$ obtained using a completely different method. Main differences of the results of Ref. 4 from that shown in Fig. 4 concern low values of L/d . First of all, the regime shown in Fig. 4d was not found in Ref. 4. Apparently, this is connected with the fact that in Ref. 4 the isotropic part of the attraction forces, which is, as a matter of fact, predominant, was not taken into account. For the same reason the phase separation curves found in Ref. 4 in the high-temperature corridor at not very large values of L/d are strongly inclined. Second, according to Ref. 4 at $L/d < 6.4$ in the purely athermal case the liquid-

² The possibility of using our theory at such small values of L/d is not clear. However, we present here this result since further the phase diagrams of analogous type will appear for the solutions of semiflexible macromolecules at significantly higher values of the asymmetry parameter.

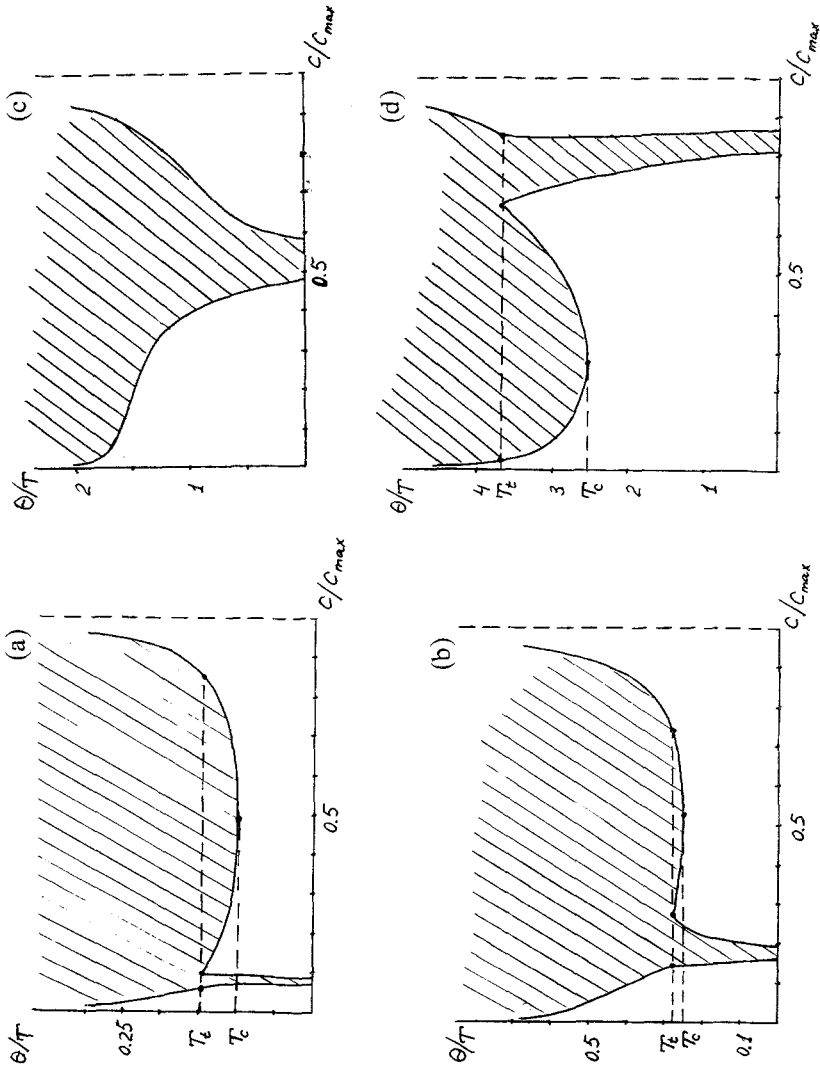


Fig. 4. Phase diagrams for the nematic ordering in the solution of rigid rods with (a) $L/d = 50$, (b) $L/d = 20$, (c) $L/d = 5$, (d) $L/d = 2$. Phase separation region is shaded.

crystalline ordering does not occur even at the highest concentrations. Apparently, this result is an artifact of the lattice model, since in the real system of so strongly asymmetric particles with an absolutely rigid steric interaction the orientational ordering at sufficiently high concentrations should appear at least from the packing considerations. A more detailed discussion of this point we postpone until the following publication devoted to the thermotropic case. Finally, we emphasize that for large values of L/d in the high-temperature region the method used here is asymptotically exact (see Refs. 5 and 29), while the Flory method overestimates significantly the transition concentrations in the asymptotic limit $L \gg d$.

6. NEMATIC ORDERING IN THE SOLUTION OF SEMIFLEXIBLE FREELY JOINTED MACROMOLECULES

Now we proceed to the consideration of the solutions of long chains of freely jointed segments of length l and diameter d (Fig. 1b), i.e., of semiflexible macromolecules with the freely jointed flexibility mechanism.

In Table II we present the results obtained for the liquid-crystalline transition in athermal solutions of such macromolecules. The general tendencies of the variation of the transition properties with the decrease of the asymmetry parameter l/d are here practically the same as for the solution of disconnected segments. In accordance with the conclusion obtained in Ref. 9 the phase separation region for freely jointed chains is always somewhat broader than in the corresponding solution of disconnected segments.

Phase diagrams for the case under consideration at several values of the parameter l/d are shown in Fig. 5. In general these diagrams are similar to those shown in Fig. 4. However, an important qualitative difference lies in the fact that the left branch of the separation curves intercepts the ordinate axis at some finite temperature, T_g —at lower temperatures the isotropic phase is unstable even at very low polymer concentrations (this is connected

Table II. Nematic Ordering in Athermal Solutions of Semiflexible Freely Jointed Macromolecules (Notation the Same as in Table I)

l/d	c_i/c_{\max}	c_a/c_{\max}	w	η_0
$\rightarrow \infty$	$3.25 d/l$	$4.62 d/l$	0.422	0.858
100	0.0319	0.0454	0.423	0.858
20	0.150	0.208	0.387	0.856
5	0.480	0.595	0.240	0.841

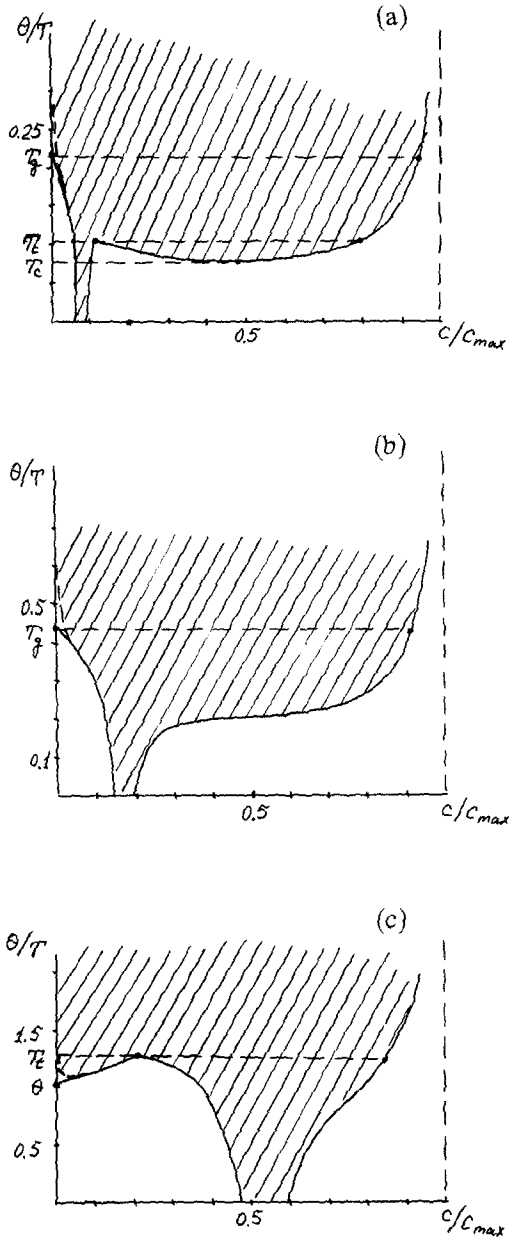


Fig. 5. Phase diagrams for the nematic ordering in the solution of semiflexible freely jointed macromolecules with (a) $l/d = 50$, (b) $l/d = 20$, (c) $l/d = 5$. Solid lines, limit $L/l \rightarrow \infty$; dotted lines, large finite value of L/l . Phase separation region is shaded.

with the fact that, as soon as we are considering the limit of very long semiflexible chains $L/l \gg 1$, the macromolecule itself turns out to be a macroscopic object). If we assume the value of L/l to be large but finite, at $T < T_g$ we will have a narrow region of stability of isotropic phase near the ordinate axis (dotted lines in Fig. 5); however, the width of this region even at $T \cong T_g$ will be small (to the extent to which the parameter L/l is small) and will further decrease exponentially with the decrease in temperature.

At $l/d > (l/d)_{c1} = 20$ (Fig. 5a) the phase diagram for the nematic transition has a usual form with the triple and critical points (cf. Fig. 4a). At $(l/d)_{c1} > l/d > (l/d)_{c2} = 6.8$ the right branch of the phase separation curves is monotonous and does not exhibit any peculiarities (Fig. 5b). Finally, at $l/d < (l/d)_{c2}$ (Fig. 5c), when the temperature T_g becomes lower than the θ temperature, the critical point corresponding to the usual isotropic separation appears (cf. Fig. 4d). It is worthwhile to note that the values of $(l/d)_{c1}$ and $(l/d)_{c2}$ corresponding to the transitions between different regimes increase somewhat in comparison with the case of disconnected segments considered in the previous section.

Using the results obtained we can determine the properties of the coil-globule transition in a single freely jointed macromolecule at $L/l \gg 1$ (see Refs. 30 and 31). Obviously, this transition occurs at $T \cong T_g$, since at $T < T_g$ the segment concentration inside the coil exceeds the maximal concentration corresponding to the thermodynamically stable dilute isotropic phase (cf. Ref. 5). Thus, from the above results it follows that at $l/d > 6.8$ the coil-globule transition in the freely jointed macromolecule takes place above the θ temperature and somewhat lower than the triple point temperature, T_t , being a pronounced first-order phase transition with the formation of an orientationally ordered globule. If $l/d < 6.8$ the succession of phase transitions in a single macromolecule when the temperature is lowered is the following: at first a usual transition coil-isotropic globule⁽³¹⁾ takes place near the θ temperature; the liquid-crystalline ordering inside the globules appears only at lower temperatures ($T \cong T_t$).

It may be noted that some of the above-mentioned properties of the phase diagram of the solution of freely jointed chains in the limit $l/d \gg 1$ were obtained using other method in Ref. 5.

7. NEMATIC ORDERING IN THE SOLUTION OF SEMIFLEXIBLE PERSISTENT MACROMOLECULES

Now let us consider a solution of semiflexible persistent chains of diameter d with the length of the Kuhn segment equal to l (Fig. 1c). Table III contains the results for the nematic phase transition in this solution in athermal case ($\theta = 0$). It can be seen that, in agreement with the conclusions

Table III. Nematic Ordering in Athermal Solutions of Semiflexible Persistent Macromolecules (Notation the Same as in Table I)

l/d	c_t/c_{\max}	c_a/c_{\max}	w	η_0
$\rightarrow \infty$	10.38 d/l	11.06 d/l	0.0650	0.431
100	0.986	0.1047	0.062	0.431
20	0.405	0.424	0.047	0.428
5	0.877	0.887	0.012	0.408

drawn in Ref. 16 for the limit $l/d \gg 1$, in this case the ordering takes place at significantly higher concentrations, the relative width of the transition region and the order parameter at the transition point are much smaller than for the solutions of freely jointed macromolecules or rigid rods with the same parameters \bar{l} and d . With the decrease of the ratio l/d these peculiarities of the persistent case become even more pronounced (see Table III).

Phase diagrams for the solutions of semiflexible persistent chains at several values of l/d are shown in Fig. 6. When the parameter l/d is lowered these diagrams undergo the same sequence of transformations as in Figs. 4 and 5. However, the critical values $(l/d)_{c1}$ and $(l/d)_{c2}$ separating different regimes for the case of persistent chains turn out to be significantly higher: $(l/d)_{c1} = 125$; $(l/d)_{c2} = 50$. This means that the usual isotropic phase separation, as well as the phase transition coil-isotropic globule, can be realized even in the solutions of persistent chains with rather high degree of stiffness ($l/d \lesssim 50$). Moreover, it can be seen from Fig. 6 that all the characteristic temperatures (T_g, T_c, T_l) are for this case essentially lower than for the cases of Figs. 1a, b (at the same values \bar{l} and d). It is possible to draw a general conclusion that it is much more difficult to obtain an orientationally ordered phase (i.e., we need much higher concentrations) for the solution of persistent chains than for the solution of freely jointed chains. The reasons for this difference were analysed in Ref. 16 for the athermal solution in the limit $l/d \gg 1$; the considerations of Ref. 16 remain valid in the present case as well.

8. NEMATIC ORDERING IN THE SOLUTION OF SEMIFLEXIBLE MACROMOLECULES WITH ROTATIONAL-ISOMERIC FLEXIBILITY MECHANISM

Finally, let us discuss the properties of the orientational ordering in a solution of rotational-isomeric semiflexible chains for the model shown in Fig. 1d. It should be recalled that this problem was considered for the athermal case in the limit $l \gg d$ in Ref. 18, where it was shown that in this

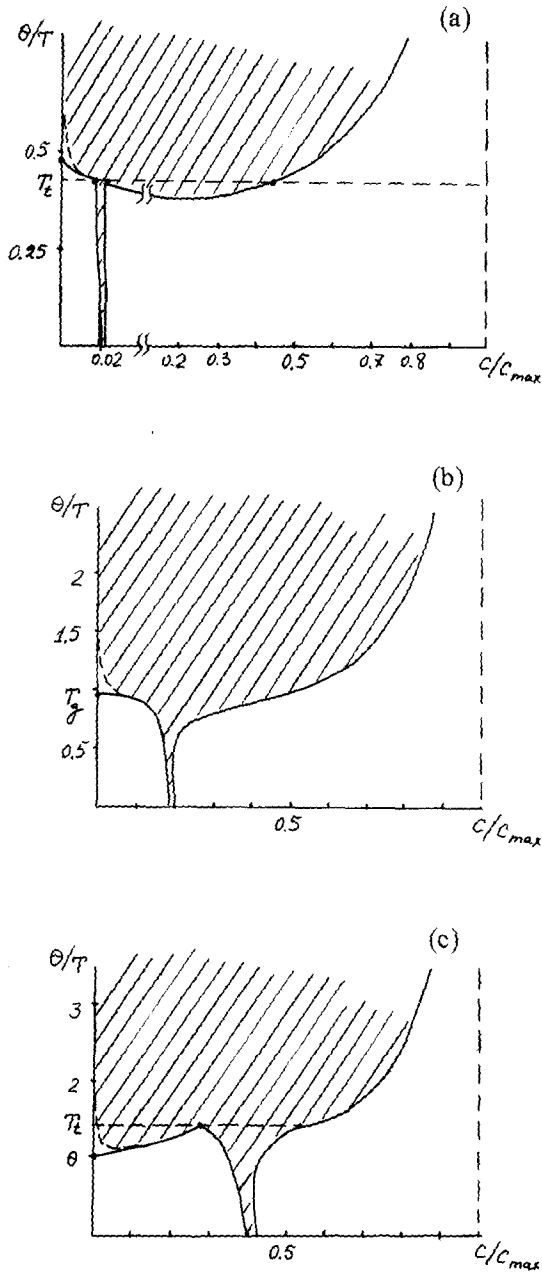


Fig. 6. Phase diagrams for the nematic ordering in the solution of semiflexible persistent macromolecules with (a) $l/d = 500$, (b) $l/d = 50$, (c) $l/d = 5$. Solid lines, limit $L/l \rightarrow \infty$; dotted lines, large finite values of L/l . Phase separation region is shaded.

case the liquid-crystalline ordering is the transition between the isotropic phase and the completely concentrated and completely ordered (in the limit $L/l \rightarrow \infty$) phase. In this latter phase macromolecules are practically completely elongated, thus effectively they can be considered as rigid rods of very large length $L \gg l$. These anomalous transition features are especially pronounced for the chains with "pure" rotational-isomeric flexibility mechanism (Fig. 1d); if some small flexibility component of persistent character is present (which is always the case for real chains) these features are manifested in a not so extreme form (remaining, nevertheless, very essential).⁽¹⁸⁾ However, we will not take into account the persistent flexibility component here, keeping in mind that in the presence of the latter the qualitative properties of the orientational ordering in the solution of semiflexible rotational-isomeric chains will be defined by the combination of the tendencies described in this and in the previous sections (cf. Ref. 18).

Table IV contains some of the characteristics of the liquid-crystalline ordering for the athermal solution of rotational-isomeric macromolecules obtained using the method of this paper. Complete phase diagrams for several values of the parameters l , a , and d are shown in Fig. 7. It can be seen that the anomalous transition properties mentioned above are well apparent in the presence of attraction forces (and for finite values of l/d) as well. In the system under consideration the value of $(l/d)_{c1}$ is meaningless since the only possible anisotropic phase is the completely ordered one. At $l/d > (l/d)_{c2}$ the phase diagram has the form shown in Figs. 7a, b, if $l/d < (l/d)_{c2}$ a critical point corresponding to the isotropic phase separation appears (Fig. c). In the latter case in a single macromolecule the coil-isotropic globule phase transition takes place near the θ temperature, and only upon further temperature lowering we reach the point ($T \cong T_l$), at which the intramolecular liquid-crystalline ordering takes place. The value of $(l/d)_{c2}$

Table IV. Nematic Ordering in Athermal Solutions of Semiflexible Rotational-Isomeric Macromolecules (Notation the Same as in Table I)

l/d	a/d	c_l/c_{\max}	c_a/c_{\max}
$\rightarrow \infty$	Arbitrary	$2d/l$	1
100	5	0.0210	1
100	1	0.0201	1
20	5	0.154	1
20	1	0.103	1
5	1	0.468	1

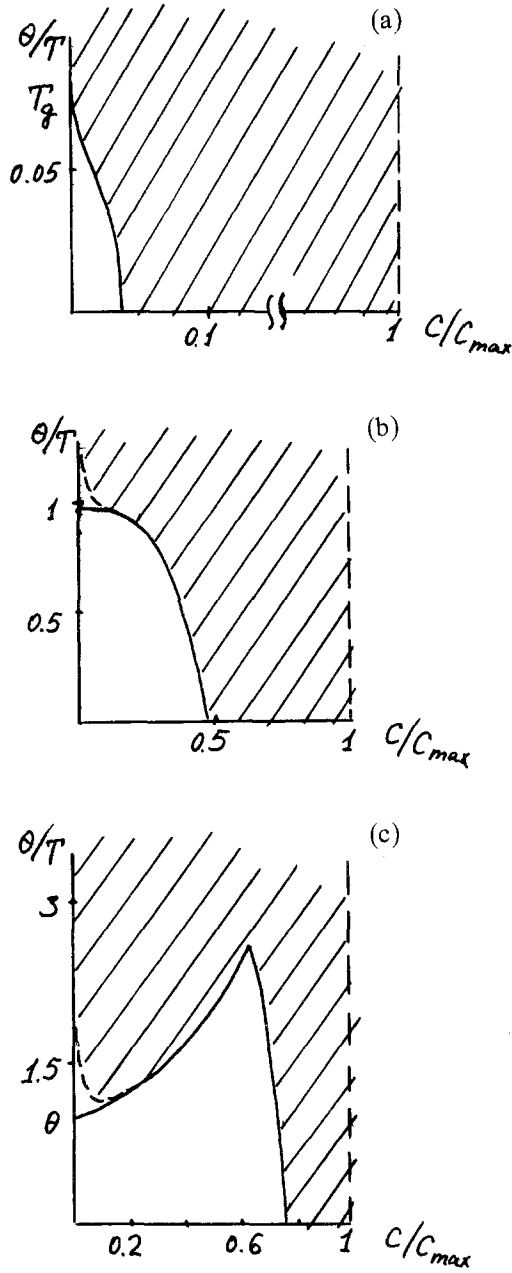


Fig. 7. Phase diagrams for the nematic ordering in the solution of semiflexible rotational-isomeric macromolecules with (a) $a/d = 1$ and $l/d = 50$, (b) $l/d = 5$, (c) $l/d = 3.5$. Solid lines, limit $L/l \rightarrow \infty$; dotted lines, large finite values of L/l . Phase separation region is shaded.

is not universal (as for the models of Figs. 1a, b, c), but depends on the relation between the length of a monomeric link, a , and its diameter, d :

$$(l/d)_{c2} = \frac{a}{d} \left[\frac{4}{1 - \exp(-1.1a/d)} - 1 \right] \quad (19)$$

Moreover, it can be noted (see Table IV) that in general for the model of Fig. 1d with finite value of l/d the transition properties depend not only on the value of l/d , but on the ratio a/d as well.

As the probability of the *gauche* conformation, p , further increases and approaches unity, the completely ordered state becomes less and less favorable and the usual liquid-crystalline phase with finite anisotropy degree can appear. It turns out that the corresponding phase transitions take place at the concentrations so close to c_{\max} that with good reason they can be considered as thermotropic. Thus these transitions will be analyzed in the future publication.

9. CONCLUSION

With the help of a universal method we have considered specific features of the liquid-crystalline ordering in the solutions of semiflexible macromolecules with different flexibility mechanisms (and in the solutions of rigid rods) at arbitrary solution concentrations and arbitrary temperatures (solvent quality). The properties of the corresponding phase transitions were shown to be strongly dependent on the degree and type of the flexibility of solute macromolecules.

It is worthwhile to emphasize that the tendency to form an orientationally ordered phase in the systems under consideration is connected mainly with the shape anisotropy of macromolecules, which becomes more and more important with the increase of the solution concentration and of the forces of isotropic attraction. The anisotropy of attraction forces does not play an essential role: even the complete neglect of this anisotropy ($u_a = 0$) lead only to the insignificant changes in the form of the phase diagrams.

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