ABSTRACT

In this article we consider some topics of the statistical physics of liquid-crystalline phase in the solutions of stiff chain macromolecules. Among these topics are: the problem of the phase diagram for the liquid-crystalline transition in the solutions of completely stiff macromolecules (rigid rods); conditions of formation of the liquid-crystalline phase in the solutions of semiflexible macromolecules; possibility of the intramolecular liquid-crystalline ordering in semiflexible macromolecules; structure of intramolecular liquid crystals and dependence of the properties of the liquid-crystalline phase on the microstructure of the polymer chain.
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I. INTRODUCTION

1.1 Formulation of the problem

Considerable attention has been paid recently to the experimental study of the liquid-crystalline phase in polymer solutions (see, for example, Refs.1-6). At the same time, the theoretical publications in this field are not numerous [7]-[14]. As a matter of fact, up to now only one problem of the theory of polymeric lyotropic liquid crystals has been considered in detail: namely, the problem of the phase diagram for the liquid-crystalline transition in the solution of long rigid rods (see the classical papers by Onsager [7] and Flory [9]). However, as it will be shown below, even for this case the calculations by Onsager and Flory do not give adequate answers to all the questions. As to the problems of the liquid-crystalline transitions in the systems, which are not identical with the solution of rigid rods (for example in the solution of semiflexible macromolecules), they were studied much less. Taking these facts into account, it can be concluded that the theoretical considerations of the liquid-crystalline transition in polymer solutions is rather urgent. The attempt to study some of the problems in this field is made in the present paper.

The aims of this paper are the following.

i) The investigation of the phase diagram for the liquid-crystalline transition in the solution of rigid rods with the help of the method, which uses the ideas of both the Onsager and the Flory methods.

ii) The application of the same method for the study of the liquid-crystalline transition in the solution of semiflexible macromolecules.

iii) The consideration of the intramolecular liquid-crystalline ordering within the semiflexible macromolecules. Although this situation is very interesting from the fundamental point of view and from the point of view of some biological applications, it has not yet been considered in the literature.

The present paper is devoted mainly to the theory itself and not to the interpretation of the experimental results for the specific systems; it is the theoretical aspect that it seldom considered in the literature.

In this article we generalize some of our results published earlier in Refs.15-22.

1.2 Plan of consideration

In Sec.II we shall analyse the orientational ordering in the solution of completely stiff macromolecules (i.e. of the macromolecules with the contour length $L$, which is much smaller than the effective segment $l$, and which is much greater than the characteristic width of the chain $d$: $l >> L >> d$). Such macromolecules can be represented as long thin rods (Fig.1a). Although the phase diagram for this system obtained by Flory [9] is in qualitative agreement with the experimental data, for further generalizations we shall need the more systematic and detailed analysis of this diagram.

In Sec.III we shall consider the orientational ordering in the solution of semiflexible macromolecules (i.e. of the macromolecules with the effective segment $l$, which is much smaller than $L$ and much greater than $d$: $L >> l >> d$). In general, semiflexible macromolecules can have different flexibility distributions along the chain contour: compare, for example, the freely-jointed chain of the long thin rods (Fig.1b) and the persistent chain, which is homogeneous along the contour (Fig.1c). In Sec.III we shall see what properties of the liquid-crystalline transition do depend on the flexibility distribution along the chain contour and what properties are universal for this point of view.

In Secs.II and III the results will be presented in the form of the phase diagrams in the variable temperature $T$-volume fraction of polymer in the solution $\phi$. By comparing the limiting cases $L >> l$ and $L << l$ it will be easy to imagine the form of the phase diagram at the intermediate values of the parameter $L/l$.

With the help of the results of Secs.II and III we shall consider in Secs.IV and V the intramolecular liquid-crystalline ordering of the segments of one semiflexible chain.

We shall show that in the limit of a very long chain the corresponding qualitative properties are practically independent of the details of the chain structure, for example, of the flexibility distribution along the chain contour. At low enough temperatures, the coil formed by the long semiflexible chain suddenly collapses into the dense liquid-crystalline globular state, the corresponding conformational phase transition being of the $I$ order. The properties of this transition and of the appearing liquid-crystalline globule can be studied on the basis of some rather simple qualitative considerations - this will be done in Sec.IV.

Finally, in Sec.V we shall discuss the properties of the intramolecular liquid-crystalline ordering for relatively short chains; in this case the ordering leads to the formation of the so-called small globules. The structure
and the conditions of the stability of such globules depend essentially on the details of the chain structure (in contrast to the case of long chains).

In Sec.V we shall consider in detail the small globules for the following three polymer chain models: chain composed of rods connected by flexible spacers, persistent chain and flexible chain with the rod-like side groups. This consideration will require a rather special formalism generalizing the well-known formalism proposed by Lifshits [23] for the description of the polymeric globules (see also the reviews [24], [25]). It is noteworthy that the small globule for the persistent chain is apparently the convenient model for the so-called compact form of DNA (see below).

II. CONDITIONS OF FORMATION OF THE LIQUID-CRYSTALLINE PHASE IN THE SOLUTIONS OF COMPLETELY STIFF MACROMOLECULES (RIGID RODS)

In this section we shall consider the liquid-crystalline ordering in the well-known system - in the solution of cylindrical rigid rods of the diameter d and of the length L. Since the rods represent the macromolecules, we shall assume that the characteristic asymmetry parameter of the rod p = L/d is much greater than unity; p >> 1.

In this section we shall first of all try to develop the methods, which will remain useful for the subsequent study of the orientational ordering in the solutions of semiflexible macromolecules. At the same time, we shall see that the application of these methods to the rigid rod problem itself leads to some new results.

We begin with the discussion of the limits of validity of the two classical methods of consideration of the liquid-crystalline ordering in the system of rigid rods.

2.1 Limits of validity of the methods by Onsager [7] and Flory [9]

In his paper [7] Onsager has considered the liquid-crystalline transition in the system of rigid rods using two main assumptions: (i) the interaction of rods was assumed to be due to the pure steric repulsion (no attraction); (ii) the virial expansion method was used. Thus, the Onsager results are valid only for good enough solvent (more precisely, in the athermal limit) and at low enough polymer concentrations; at the same time, within the region of their validity these results are asymptotically exact at p >> 1 (see below).

In order to analyse the dependence of the liquid crystalline transition properties on the temperature (i.e. on the solvent quality) it is necessary to introduce the attraction of rods parallel with their steric repulsion. This has been done by Flory in Ref.9. The classical Flory phase diagram for the solution of rods (see Fig.2) corresponds rather well to the experimental results from the qualitative point of view [1]. However, the Flory theory cannot give adequate answers to all the questions connected with the orientational ordering in the system of rigid rods. Indeed:

1) In his paper [9] Flory deals mainly with the numerical results for large (but fixed) value of p (p = 100); at the same time, the analytical dependence of the transition properties on the parameter p >> 1 is given only for the athermal case (no attraction between the rods).

2) The Flory theory is based on the lattice model. It is clear that the use of the lattice model is rather artificial, especially for low polymer concentrations; the results obtained on the basis of this model should be, of course, qualitatively correct, but not exact even in the asymptotic sense (at p >> 1).

3) The expression for the heat of mixing of polymer with the solvent, $\Delta H$, adopted in Ref.9 (Van-Laar form) is generally incorrect 

$\Delta H$ was assumed in Ref.9 to be proportional to the product of the number of solvent molecules and of the polymer volume fraction in the solution. Such an expression for $\Delta H$ would be valid if the polymer molecule would be cut into

$\text{*) This fact can be demonstrated as follows. Let us determine the value of the well-known Flory parameter } x_0 \text{, which corresponds to the 0 point (i.e. to the point of inversion of the second virial coefficient of the solution of rods) in the Flory theory of Ref.9. This can be done by expanding the chemical potential of the solvent in the isotropic phase (formula (16) of Ref.9) in the powers of the polymer volume fraction in the solution, and by equating the coefficient at the quadratic term of this expansion to zero; this procedure gives } x_0 = \frac{1}{2} \text{ independently of } p. \text{ On the other hand, it is well known } [26],[27] \text{ that the value of } x_0 \text{ decreases with the increase in } p \text{ and that } x_0 < 1 \text{ at } p >> 1. \text{ The contradiction obtained shows that the expressions for the thermodynamic functions used in Ref.9 are not always correct.}

\text{**) It is worthy to recall here that in the Flory lattice model the solvent molecule occupies one cell of the lattice and the polymer molecule occupies p successive cells.
p independent pieces in correspondence with the number of cells covered by this molecule. However, as a matter of fact, due to the chain connectivity the probabilities that a given cell and one adjacent to it are covered by the macromolecule are strongly correlated. This fact is not taken into account if $\Delta H$ is written in the Van-Laar form and it is for this reason that the expression for $\Delta H$ adopted in Ref. 9 is generally incorrect. We shall see below that for the dilute solution of rods the main contribution to $\Delta H$ appears from the configurations in which two rods are almost parallel and have a great area of contact. However, the role of these configurations is seriously underestimated if $\Delta H$ is written in the Van-Laar form.

It is clear from the above that although the conclusions of the Flory theory are in qualitative agreement with experiments, they cannot be regarded as indubitable and require some verification.

In this section we shall try to analyse the analytical dependence of the properties of the phase diagram on the asymmetry parameter $p$ in the limit $p \gg 1$. As it has been already noted in the introduction, in our method we shall combine the ideas of both the Onsager method (conveniently generalized to take into account the attraction of rods) and the Flory method. The former method will be used for the dilute solutions, while the latter will be applied at higher concentrations. Such an approach will allow us to obtain some new (in comparison with Ref. 9) information concerning the orientational ordering in the solution of rigid rods.

2.2 Model of the interaction of rods

We begin with the more exact definition of the model of the interaction of rods, which will be adopted in this paper. As in Refs. 7 and 9 we shall assume that the repulsion of the cylindrical rods is solely due to their mutual impenetrability. To introduce the attraction of the rods we shall associate the negative energy to the rods, which approach each other, but do not overlap, this energy being proportional to the area of contact of the rods. It is natural to attribute this attractive energy only to those rods which are in close enough contact. Thus we shall assume that this energy is associated only to the rods whose long axes are separated by the minimal distance between $d$ and $2d$. We shall neglect the direct interaction at the larger distances of the inter-rod separation.

\[
U = -\epsilon \sin \gamma \quad \text{at} \quad \gamma > 1/p, \quad (2.1)
\]

where $-\epsilon$ is the characteristic energy of the contact of two perpendicular rods; if the rods are almost parallel ($\gamma < 1/p$), we shall assume that

\[
U = -\epsilon q \quad \text{at} \quad \gamma < 1/p, \quad (2.2)
\]

where $q_d$ is the "length" of the contact.

The described model dependence of the attractive energy on the angle between the rods is, of course, not exact for any specific interaction of monomers. However, for the case of the short-range interactions, this dependence seems rather reasonable; furthermore, most of the results obtained below are not sensitive to the detailed form of the function $U(\gamma)$.

2.3 Phase diagram for the solution of rods: Preliminary comments

The existence of the attraction of rods leads to the dependence of the properties of the liquid-crystalline transition on temperature (more precisely on the combination $6/T$ in the model described above). At high enough temperatures (i.e. at small $6/T$), the role of attraction is negligible and the transition is solely due to the steric repulsion of rods. We shall refer to this region of the phase diagram as the high temperature region. As was shown in Refs. 7 and 9, in this region the coexistence curves in the $T$-$\delta$ phase diagram form the narrow corridor situated at $\delta \sim 1/p$ (see Fig. 4). The high temperature region will be considered in Subsec. 2.5, whereas in Subsec. 2.4 we shall recall the main steps of the Onsager method in the form which is most convenient for the further generalizations.

In the opposite case of low enough temperatures, the accounting for the attractive interaction of rods is necessary and due to these interactions the solution of rods usually separates into the highly ordered liquid-crystalline phase and the very dilute isotropic phase (Fig. 4). The low temperature behaviour of the phase diagram will be analysed in Subsec. 2.6.

Further, in Subsec. 2.7 we shall determine the position of the triple point in the phase diagram (see Fig. 5) and in Subsec. 2.8 we shall find the $\theta$ point, i.e. the point of inversion of the second virial coefficient for the solution of rods.
Finally, in Subsec. 2.9 we shall show that in some temperature range two

different anisotropic phases for the solution of rods can coexist in equilibrium, and

in Subsec. 2.10 we shall prove that the high temperature corridor of the phase

separation has practically a constant width up to the triple point. These two

results have already been obtained by Flory (Ref. 9); however, we saw above

that the conclusions of Ref. 9 need verification on more systematic grounds.

We now proceed directly to the detailed analysis of the phase diagram.

2.4 Main steps of the Onsager method

Let \( N \) cylindrical rods be situated in the volume \( V \), their concentration

being \( c = N/V \). The polymer volume fraction in the solution is then \( \omega = \rho c d / V \).

Let us introduce the orientational distribution function for the rods \( f(u) \); \n
cf(u)d\Omega \) is the number of rods per unit volume, which have the orientations within

the small spatial angle \( d\Omega \) around the unit vector \( u \). It is clear that

in the isotropic state \( f(u) = \text{const} \cdot r^{-2} \). In the liquid-crystalline state

the function \( f(u) \) has two maxima along the anisotropy axis.

In the Onsager approximation the free energy of the solution is written

in the following form:

\[
F(T) = F_0(T) + N T \ln c + N T \int f(u) \ln (4\pi f(u)) d\Omega +
\]

\[
+ \frac{1}{2} N T c \int f(u) f(u') B(\gamma) d\Omega d\Omega',
\]

(2.3)

where \( T \) is the temperature (in the energetic units), \( F_0(T) \) is the irrelevant
term, which depends neither on \( c \) nor on \( f(u) \). The second term of Eq. (2.3)
is the free energy of the relative translational motion of rods; the third
term describes the loss in entropy due to the orientational ordering, i.e. due
to the possible difference between \( f(u) \) and \( 1/4\pi \). The fourth term is the
free energy of the interaction of rods in the second virial approximation.

In this latter term \( B(\gamma) \) is the second virial coefficient of the interaction of
rods, whose long axes (specified by the unit vectors \( u \) and \( u' \)) form the
angle \( \gamma \) with each other.

So the fundamental approximation of the Onsager method is the second

virial approximation, thus this method is valid only at low enough polymer

concentrations in the solution. The estimations for the second \( (B) \) and the

third \( (C) \) virial coefficients of the interaction of rods give \( B \sim p^2d^3 \) and

\( C \sim p^3d^6 \) (see [25]), thus the second virial approximation \( (CC^2 \ll Bc) \) is valid

if \( c \ll 1/pd^3 \), or \( \delta \ll 1 \).\)

In the athermal case (no attraction of rods) the second virial

coefficient can easily be calculated \( [7, 28] \)

\[
B_2(\gamma) = 2 p^2 d^3 \sin \gamma,
\]

(2.4)

where the subscript \( r \) indicates that this coefficient is formed solely by

the repulsive interactions.

The following step in the Onsager method is the determination of

the equilibrium function \( f(u) \), which minimizes the functional (2.2).

Unfortunately, the direct minimization leads to the integral equation, which
cannot be solved in a standard way (see, however, Refs. 29 and 30). So in
Ref. 7 the variational method was used, the trial function being chosen in the form

\[
f(u) = \frac{\omega}{4\pi} \frac{\cosh(\alpha \cos \theta)}{\sin \alpha d\theta} \int f(u) d\Omega = 1,
\]

(2.5)

where \( \theta \) is the angle between the vector \( u \) and the direction of the

anisotropy axis and \( \alpha \) is the variational parameter. The isotropic phase

corresponds to \( \alpha = 0 \), with the increase in \( \alpha \) the maxima of the trial

function (2.5) along the directions \( \theta = 0 \) and \( \theta = \pi \) become more and pronounced.

In Ref. 7 the trial function (2.5) together with the expression (2.4)

were substituted in the expression (2.3), which was then minimized with respect
to \( \alpha \). It was shown that the free energy \( F(\alpha) \) generally has two minima
corresponding to the isotropic and the anisotropic phases. The values of \( F \)
in the minima determine the free energies of these phases. Once these free

energies are obtained, the corresponding phase transition can be analysed in
a standard way (see Ref. 7 for details).

It should be emphasized that the use of the variational procedure in
Ref. 7 is the way to simplify the numerical calculations, so the only fundamental

physical limitation of the Onsager method is connected with the second virial

approximation, i.e. with the condition \( \delta \ll 1 \).

\(* \) It is easy to verify that if \( \delta \ll 1 \) not only \( Bc \gg CC^2 \), but also

\( Bc \) is much greater than any higher order term of the virial expansion.
2.5 Phase diagram: High temperature behaviour

It can be seen that the substitution of Eqs. (2.4) and (2.5) in Eq. (2.3), reduces the free energy to the form in which the parameters \( p \) and \( \beta \) enter only in the combination \( p \beta \). Hence it is clear that in the high temperature region (i.e. in the athermal limit) the liquid-crystalline transition must take place at \( \beta = 1/p \).

Actually, for this case both Onsager [7] and Flory [9] have found that at \( \beta < \beta_0^{(i)} \) the solution is isotropic, at \( \beta > \beta_0^{(a)} \) it is anisotropic and at \( \beta_0^{(i)} < \beta < \beta_0^{(a)} \) it separates into the isotropic and the anisotropic phases, where \( \beta_0^{(i)} \approx \beta_0^{(a)} \approx 1/p \). So the problem amounts to the determination of the numerical coefficients. With the help of the variational procedure described above Onsager has found that

\[
\beta_0^{(i)} = 3.34/p \quad ; \quad \beta_0^{(a)} = 4.45/p \quad ; \quad \beta_0^{(a)}/\beta_0^{(i)} = 1.34. \tag{2.6}
\]

The results obtained by Flory (according to the recent corrected version of his theory [12]) are

\[
\beta_0^{(i)} = 7.89/p \quad ; \quad \beta_0^{(a)} = 11.53/p \quad ; \quad \beta_0^{(a)}/\beta_0^{(i)} = 1.47. \tag{2.7}
\]

Formula (2.6) as well as formula (2.7) were obtained using some approximations. The approximations of the Flory method are connected with the lattice character of his model; it is difficult to estimate the degree of their accuracy. The approximations of the Onsager method are due to (i) the use of the second virial approximation and (ii) the use of the variational procedure. It is rather easy to eliminate the latter approximation by solving numerically with high degree of accuracy the integral equation, which appears as a result of the exact minimization of the expression (2.2). This has been done in Ref. 30; the results are

\[
\beta_0^{(i)} = 3.29/p \quad ; \quad \beta_0^{(a)} = 4.22/p \quad ; \quad \beta_0^{(a)}/\beta_0^{(i)} = 1.28. \tag{2.6a}
\]

As to the second virial approximation, it is valid at \( \beta << 1 \), and, consequently, Eqs. (2.6a) are asymptotically exact at \( p >> 1 \).

Summarizing, we can say that for the athermal case the fundamental advantage of the Onsager method in comparison with the Flory method is due to the fact that by means of the former method it is possible to obtain the results which are asymptotically exact at \( p >> 1 \).

2.6 Phase diagram: Low temperature behaviour

As can be seen from Fig. 1, when the isotropic and the anisotropic phases coexist in equilibrium at low temperatures, the isotropic phase is very dilute and the anisotropic phase is very concentrated. Thus it is natural to write the free energy of the anisotropic phase in the ideal gas form \( *) \)

\[
F = F_o(T^*) + N T \left[ \frac{\beta}{e^2} \right]. \tag{2.8}
\]

On the other hand, in the first approximation the free energy of the anisotropic phase can be calculated assuming that the rods are collinear; furthermore, due to the rather dense packing of the rods, it is possible to use the lattice model. The entropy of mixing of the collinear rods with the solvent in the lattice model was calculated by Flory in Ref. 8. Using Flory's result it is possible to write the free energy of the low temperature anisotropic phase in the form

\[
F = F_o(T^*) + N T \left\{ \frac{T}{\beta} \right\} \ln \left( \frac{T}{\beta} \right) - \frac{T}{\beta} \ln \left( 1 - \frac{T}{\beta} \right) - \frac{T}{\beta} \ln \beta^2 - \chi \rho \beta \right\}, \tag{2.9}
\]

where \( \chi \) is the well-known Flory interaction parameter. In our model \( \chi \) depends on \( \beta \) and on the co-ordination number of the lattice \( Z \) (\( Z = 5 \) for the rods on the lattice) as follows:

\[
\chi = \frac{\beta}{T} \frac{Z-2}{2}. \tag{2.10}
\]

The first two terms in the curly brackets in Eq. (2.9) represent the entropy of mixing, the third term is connected with the loss of the orientational entropy in the anisotropic phase, the fourth term is the energy of contact of the rods.

\( *) \) The possibility of the neglect of the interaction terms in Eq. (2.9) can be verified after the final result (Eq. (2.11)) is obtained.
To obtain the equations for the phase separation curves it is necessary, as usual, to find the chemical potentials \( \mu = \partial F / \partial N \) and the pressures \( \rho = - \partial F / \partial V \) in both phases from Eqs. (2.8) and (2.9). Then one must equate the values of \( \mu \) and \( \rho \) in the coexisting phases - this will provide two equations for the determination of two unknown volume fractions \( g^{(1)} \) and \( g^{(a)} \) in these phases. These equations can be solved by taking into account that \( g^{(1)} \ll 1 \) and \( 1 - g^{(a)} \ll 1 \); the result (valid in the limit \( p \gg 1 \)) is

\[
g^{(1)} = (e^x - 1) \frac{3}{\rho^3} e^{-xp},
\]

\[
1 - g^{(a)} = \frac{1}{\rho (e^x - 1)}.
\]

Equations (2.11) determine the coexistence curves in the low temperature region. With the increase of \( x \) (i.e. with the lowering of the temperature) the polymer concentration in the isotropic phase tends exponentially to zero, while the polymer concentration in the anisotropic phase approaches its maximum possible value.

Equations analogous to (2.11) can also be obtained for the lattice model, however in Ref. 9 the corresponding calculation was not performed.

### Phase diagram: The triple point

In this Subsection we shall find the temperature \( T_3 \), at which the high temperature asymptotic expression for \( g^{(1)} \) matches with the low temperature one. We shall see below that both asymptotic expressions remain approximately valid up to the temperature of matching. Consequently, this temperature must coincide (to the main order) with the triple point temperature of the phase diagram - compare with Fig. 2.

The temperature \( T_3 \) can be determined by the substitution of the high temperature value \( g^{(1)} \sim 1/p \) in the low temperature formula (2.11). Using Eq. (2.10) we obtain in the asymptotic limit \( p \gg 1 \)

\[
\left( \frac{e}{T} \right)^3 \sim \frac{6}{z^2-2} \frac{B_{n,p}}{p}.
\]

The numerical coefficient in Eq. (2.12) is exact in the limit \( p \gg 1 \); it does not depend on the numerical coefficient in Eq. (2.6).

According to Eq. (2.11) the value of \( 1 - g^{(a)} \) at the triple point turns out to be \( \sim 1/(4p) \). This fact proves the validity of the lattice model (and, consequently, of Eqs. (2.11)) for the description of the anisotropic phase at \( T < T_3 \). The validity of the high temperature asymptotic formulae at \( T > T_3 \) will be proved in Subsec. 2.10.

#### Phase diagram: The 0 temperature

Here we shall calculate the second virial coefficient for the solution of rods interacting as described in Subsec. 2.2 and we shall find the point of inversion of this coefficient, i.e. the 0 point. As noted above, the Flory theory [9] gives the incorrect value for the 0 temperature.

The second virial coefficient \( B(\gamma) \) of the interaction of rods, which form the angle \( \gamma \) with each other, is defined by the formula [31]

\[
B(\gamma) = \frac{1}{2} \int \{ 1 - \exp \left[ -U(\varepsilon, \gamma)/T \right] \} d^3 \varepsilon,
\]

where \( U(\varepsilon, \gamma) \) is the energy of the interaction of rods, the centres of which are separated by the vector \( \varepsilon \); this energy can be determined from the formulae (2.1) and (2.2). It is convenient to represent \( B(\gamma) \) in the form

\[
B(\gamma) = B_e(\gamma) + B_a(\gamma),
\]

where \( B_e(\gamma) \) is given by equality (2.4). The coefficient \( B_a(\gamma) \) will then describe the contribution to \( B(\gamma) \) from the integration over the regions of space corresponding to the attraction of the rods.

It is easy to calculate \( B_e(\gamma) \) in the two limiting cases:

(i) If the rods intersect at a large angle \( \gamma \sim 1 \) (more exactly, \( \gamma \gg 1/p_1 \), then according to Eq. (2.1) we have

\[
B_a(\gamma) \sim -p^2 d^3 \sin \gamma \left\{ \exp (e/T/\sin \gamma) - 1 \right\};
\]

(ii) If \( \gamma \ll 1/p_1 \), i.e. if the rods are practically parallel, then according to Eq. (2.2) we obtain
In the intermediate range of angles $\frac{1}{p} < \gamma < \ln p$, the function $B(\gamma)$ varies in a natural way to provide the smooth crossover between the limiting behaviours (2.15) and (2.16).

The $\theta$ temperature can be determined from the equality

$$2\pi \int_0^{\gamma} \left( B_0(\gamma) + B_a(\gamma) \right) \sin \gamma \, d\gamma = 0 \quad (2.17)$$

Using Eqs. (2.4), (2.15) and (2.16) it is possible to obtain after the simple calculation in the asymptotic limit $p \gg 1$

$$\left( \frac{\epsilon}{\theta} \right)_\theta \equiv \frac{\epsilon}{\theta} = \frac{3 \ln p}{\theta} \quad (2.18)$$

As for Eq. (2.12) the numerical coefficient in Eq. (2.18) is exact in the limit $p \gg 1$. From the comparison of Eq. (2.12) and (2.18) we conclude (taking into account also that $Z - 2 > 3$) that the $\theta$ temperature is situated well below the triple point temperature $T_3$. At $p \gg 1$ we have $\frac{\epsilon}{\theta} / (\epsilon / T)_3 = \frac{2 \ln p}{\theta} > 1$.

The $\theta$ temperature is situated in the low temperature region of the phase diagram, as is shown in Fig. 1. Accordingly, the polymer volume fractions in the coexisting phases at the $\theta$ temperature are determined by the formula (2.11).

For the isotropic phase we obtain

$$\frac{\theta}{T} \sim \frac{(3Z - 10)/2}{\theta} \sim \frac{3 \ln p}{\theta} \ll \frac{1}{p} \quad (2.19)$$

The latter inequality means that at the $\theta$ temperature the isotropic phase in coexistence with the anisotropic one is much more dilute than at the high temperatures (above the triple point). The value of $1 - \theta$ at the $\theta$ point turns out to be $\sim 1/n p$.

With the help of the results obtained it is possible to clarify the reason of the invalidity of the Van-Laar approximation for the heat of mixing of polymer with the solvent, $AH$ (see Subsec. 2.1). The phase diagram has its main peculiarities at $\epsilon / T \ll \ln p/p$, since at $\epsilon / T > \ln p/p$ we are in the low temperature region (see Eq. (2.12)). But at $\epsilon / T < \ln p/p$ according to Eq. (2.15) for the intersections at the large angles $\gamma \gg \ln p/p$ we have

$$B_a(\gamma) \sim -\rho^2 \frac{d^2}{\epsilon / T} \quad (2.20)$$

Hence for these angles $|B_a(\gamma)| \ll B_a(\gamma)$, i.e. the attractive part of the interaction for the intersection at large angles is negligible. On the contrary, as it can be seen from Eq. (2.15), at $\gamma \ll 1/p$ the attraction can give the dominant contribution to $B(\gamma)$.

So, for the most interesting region $\epsilon / T \ll \ln p/p$ only the attraction of the parallel rods (which can have a large area of contact) is essential in the dilute solution. It is the conformations of parallel rods in contact that gives the main contribution to the heat of mixing. This is the reason for the invalidity of the Van-Laar approximation, which underestimates the role of these conformations.

2.9 Phase diagram: Coexistence of two anisotropic phases

The conclusion that in the solution of rods the coexistence of two different anisotropic phases is possible was obtained by Flory in Ref. 9. However, it was not clear whether this conclusion has a real physical meaning or it is the artefact of the lattice model. In this section we shall prove the possibility of the coexistence of two different anisotropic phases more accurately and without the use of the lattice model.

We shall apply the Onsager method (see Eq. (2.3)), taking into account both the attractive and the repulsive parts of the virial coefficient $B(\gamma)$. It is necessary to bear in mind that this method is valid only if $\theta \ll 1$, so we shall use it only in this region.

In Sec. 2.8 we have seen that the attraction is essential only between those rods which form a small angle with each other. Since the function $B_a(\gamma)$ enters in the expression (2.3) only in the integrand, it is natural to replace it by the step function

The estimation $\epsilon / T \sim \ln p/p$ has a simple physical interpretation: generally speaking, the type of the liquid-crystalline phase formed depends on the relative importance of the two factors - the entropy loss from the restriction of the orientational degrees of freedom of the rod $\sim T \ln p$ and the gain in energy from the parallel contact of the rods $\sim \epsilon p$. The characteristic points of the phase diagram must lie in the region where these two factors give the contributions of the same order of magnitude.
$$B_a(y) = \begin{cases} \xi = B_a(0) & \text{at } y < \lambda ; \\ 0 & \text{at } y > \lambda , \end{cases} \quad (2.21)$$

where according to the above consideration the value of $\lambda$ must be of order $1/p$ (here accounting for the factor $\sim n^p$ would be the excess of the accuracy). The value of $\xi$ is given by Eq.(2.16).

Let us substitute the value of the virial coefficient determined according to Eqs. (2.4), (2.12) and (2.21) into the expression (2.3) for the free energy and let us perform the integration using the Onsager trial function (2.5). The result has the form

$$F = F_0(T) + \frac{1}{T} \left\{ \ln \frac{\varphi}{e^2} + \ln \frac{\alpha \sinh \lambda}{\sinh \alpha} + \frac{\alpha \sinh \lambda}{\sinh \alpha} \right\} + \frac{\alpha \sinh \lambda}{\sinh \alpha} \left[ \frac{1}{4} \sinh 2\alpha - \frac{1}{2} \right] \frac{\alpha \sinh \lambda}{\sinh \alpha} , \quad (2.22)$$

where $I_0^2$ is the second order Bessel function of the imaginary argument. The first term in the curly brackets represents the translational entropy; the second and the third terms are originated by the entropy term in Eq.(2.3); the fourth term is the contribution of the repulsion of rods to the interaction term - all these terms can be borrowed directly from the Onsager paper [7].

The last term in curly brackets is new in comparison with Ref. 7; it describes the contribution of the attraction of rods to the interaction term. In order to write down this term in the analytic form, the corresponding integral was calculated in the limit $\alpha^2 \gg 1$ (where it is equal to $-C/2$) and in the limit $\alpha^2 \ll 1$ (where it is equal to $-C/2 + \frac{1}{8} \sinh \alpha \left[ \frac{1}{4} \sinh 2\alpha - \frac{1}{2} \right]$), then these two asymptotic expressions were interpolated with the help of the simplest rational fraction in the range $\alpha^2 \sim 1$. The approximation connected with the extrapolation is not essential for the qualitative purposes of this Subsection.

To determine the possible phases which can exist in the system it is necessary to minimize the function $F(\alpha)$ (2.22). The isotropic phase value $\alpha = 0$ always corresponds to the minimum of $F(\alpha)$. The free energy of the isotropic solution (phase I) is

$$F^{(1)}_I = F \bigg|_{\alpha = 0} = F_0(T) + \frac{1}{T} \left\{ \ln \frac{\varphi}{e^2} + \frac{\pi}{4} \varphi \rho d^3 - \frac{1}{4} \varphi \rho d^3 \right\} \quad (2.23)$$

To find other minima of the function $F(\alpha)$ we note that, as was shown in Ref. 7, even in the absence of the attraction between the rods the value of $\alpha$ is rather large ($\alpha \gg 1$) in the whole region of the existence of the anisotropic phase (this fact is due to the numerical reasons and is not connected with any large "letter" parameter). Naturally, the attraction can only reinforce the orientational ordering, i.e. increase the value of $\alpha$. But at large $\alpha$ the expression (2.22) can be simplified

$$F(\alpha)|_{\alpha \gg 1} = F_0(T) + \frac{\alpha \varphi \rho d^3}{\beta} \left[ \ln \frac{\varphi}{e^2} + \frac{\pi}{4} \varphi \rho d^3 \right] C_1 \chi^2 \quad (2.24)$$

The analysis of the function (2.24) can now be performed in a rather simple way. It turns out that this function has either one or two minima at $\alpha \neq 0$ (depending on the values of the parameters); these minima correspond to the anisotropic phases. This proves the existence of two different anisotropic phases (maybe - in the metastable form) at some values of the parameters. We shall denote these phases as phase II and phase III (free energies $F_{II}$ and $F_{III}$, respectively). The phase III being more concentrated, i.e. corresponding to larger $\alpha$.

To prove not only the fact of the existence of two different anisotropic phases, but also the possibility of their coexistence in equilibrium, let us determine, first of all, what minimum of $F$ is more deep, i.e. what is the most stable homogeneous phase. The result of this procedure is demonstrated in Fig. 5, where it is shown what phase - isotropic (I), weakly anisotropic (II) or strongly anisotropic (III) - corresponds to the absolute minimum of $F$ at the given values of $\xi$ and $\zeta$. Since $\xi$ is the function of $T$ (see Eqs. (2.21) and (2.16)), Fig. 5 can also be regarded as the $(\xi, T)$ diagram. The boundaries of the different regions in Fig. 5 are determined by the following equations:

$$\frac{I-II}{I-II} = 3.8 \rho \beta$$
$$\frac{I-II}{I-II} = 3.8 \rho \beta$$
$$\frac{I-III}{I-III} = \rho \beta$$

In Fig. 5 the boundary of the regions II and III is not continued to $\varphi \sim 1$, since the Onsager method is valid only at $\varphi \ll 1$. 
At this stage it is important to note that the curves plotted in Fig. 5 must be situated entirely inside the phase separation region of the actual phase diagram, because outside the separation region the corresponding homogeneous states are the equilibrium ones. This fact together with the known high- and low-temperature forms of the phase diagram (see Subsec. 2.5 and 2.6) determine completely the general qualitative form of the phase diagram. Obviously, this form turns out to be identical with that shown in Fig. 2. So it can be concluded that in spite of some shortcomings of the Flory theory (see Sec. 2.1) the prediction of this theory concerning the qualitative form of the phase diagram is correct. In particular, the equilibrium coexistence of two different anisotropic phases is possible in some temperature range.

2.10 Phase diagram: Constancy of the width of the high temperature corridor of the phase separation

In this Subsection we shall show that at \( T > T_3 \), the width of the high temperature corridor of the phase diagram (see Fig. 2) practically does not depend on the temperature. This conclusion has already been obtained by Flory \[9\] in the framework of the lattice model, below we shall prove it on the basis of the more general and simple considerations.

The independence of \( B^{(a)} \) and \( g^{(a)} \) on \( T \) must be expected in those regions of the phase diagram, where the role of the attraction between the rods is negligible in comparison with their mutual repulsion. Since the high temperature corridor of the phase diagram is situated at \( \beta^{-1}/p \ll 1 \), i.e. in the region of validity of the second virial approximation, this statement can be reformulated as follows: the values of \( B^{(a)} \) and \( g^{(a)} \) do not depend on the temperature if the contribution of the attraction to the second virial coefficient, \( B_a \), is much less than the contribution of the repulsion, \( B_r \).

As we have seen in the previous Subsections the anisotropy parameter \( a \) in the anisotropic phase II near the high temperature corridor is of order unity (in the sense of the independence of \( p \), although \( a \) is numerically large). Hence, in order to estimate the relative importance of the repulsive and attractive interactions for the phase equilibrium of the phases I and II one can simply average \( B_a(\gamma) \) and \( B_a(\gamma) \) over all possible angles \( \gamma \). It turns out that even at the triple point temperature

\[
\frac{\langle B_a \rangle}{\langle \mid B_a \mid \rangle} = \frac{\int B_a(\gamma) \sin \gamma \, d\gamma}{\int \left| B_a(\gamma) \sin \gamma \right| \, d\gamma} \sim \frac{\beta^{-1}}{p} \gg 1 \quad (2.26)
\]

The same estimation can be obtained if we compare the last two terms in the curly brackets of Eq. (2.24). Of course, the increase of the temperature above the triple point will only reinforce the inequality (2.26). Hence, it can be concluded that at \( T > T_3 \), the width of the high temperature corridor does not depend on the temperature.

In this section we have presented the analysis of some features of the phase diagram for the solution of rigid rods with both repulsion and attraction. Besides self-dependent interest, this analysis will be important also for the consideration of the phase diagram for the solution of semiflexible macromolecules. This consideration will be the topic of the next section.

III. ORIENTATIONAL ORDERING IN THE SOLUTIONS OF SEMIFlexible MACROMOLECULES

From the point of view of the method the consideration in this section is analogous to the corresponding consideration of Sec. II, so the plans of Secs. II and III are similar. In Subsec. 3.1 we shall specify the model of the semiflexible macromolecule. Subsec. 3.2 will be devoted to the consideration of the high temperature region of the phase diagram, for this purpose we shall generalize the Onsager method for the case of semiflexible chains. In Subsec. 3.3 we shall use the lattice approximation for the analysis of the low temperature behaviour of the phase diagram. In Subsec. 3.4, by means of the matching of the high and low temperature asymptotic expressions we shall find the triple point temperature and finally in Subsec. 3.5 the general qualitative form of the phase diagram will be analysed.

3.1 Model of a semiflexible macromolecule

As it has already been noted in the Introduction, semiflexible macromolecules can have different flexibility distributions along the chain contour (two limiting cases are shown in Figs. 1b and 1c). Hence, before proceeding further, we must, first of all, specify the model of semiflexible macromolecule which will be dealt with. We shall choose the model shown in Fig. 1b, i.e. we shall assume that the macromolecule consists of freely-jointed cylindrical rods of length \( l \) and diameter \( d \), the asymmetry parameter \( p = l/d \) being much larger than unity. As a matter of fact, the case considered in Sec. II corresponded to the solution of the same rods, but which were not connected in the long chains.
We shall assume that the segments interact in the same way as disconnected rods, i.e. as described in Subsec. 2.2. Although we shall consider explicitly only freely-jointed chain, we shall, nevertheless, always indicate which of the results obtained depend on the flexibility distribution along the chain contour and which results are in this sense universal.

3.2 Phase diagram: High temperature behaviour

In the high temperature region the attraction of segments can be neglected and so the liquid-crystalline transition is entirely due to the steric repulsion. As in the case of rigid rods, it is most natural to analyse the phase diagram in this region by means of the Onsager method.

Let us assume that the solution of semiflexible macromolecules occupies the volume V. Let \( \theta \) be the polymer volume fraction in the solution. Then the average concentration of segments is \( c = \frac{\theta}{\rho / p^3} \), the total number of segments is \( N = Vc \), and, finally, the average concentration of macromolecules is \( c_{\ell} = \frac{\ell}{L} \), where \( L \) is the contour length of one macromolecule.

The free energy of the solution of chains in the second virial approximation differs from the free energy of the corresponding solution of disconnected segments (2.3) only in two respects.

First of all, in the solution of disconnected rods each rod has the freedom of the independent translational motion, while in the case under consideration only the chain as a whole (but not each segment) can move independently. Hence the contribution of the translational entropy to the free energy is equal to \( TN (\ell / L) \ln \left[ \frac{\ell}{L} \right] \); for long chains (\( L \gg 1 \)) this is much less than the corresponding contribution in the case of the solution of disconnected rods \( TN \ln \frac{\ell}{c} \). Practically, for long enough macromolecules the contribution of the translational entropy to the free energy can be neglected (see also [15]).

Second, the effective virial coefficient \( B^* \) characterizing the interaction of segments differs from the usual virial coefficient \( B \) of the solution of disconnected rods - the reason is connectivity of segments into long chains. The corresponding renormalization of the virial coefficient was studied in detail in Refs. 32 and 33. In the application to the semiflexible macromolecule under consideration the result \( \ell\beta (\delta - \delta) / B \sim 1 / p \), i.e. for the long rigid rods (\( p \gg 1 \)) the renormalization is unessential.

From the above it follows that the free energy of the solution of semiflexible macromolecules in the high temperature limit can be written in the form

\[
F = F_0 (T) + NT \left[ e^L \frac{\ell}{\ell} + N \int f(\bar{u}) \ln (4 \pi \bar{u}) d\bar{u} \right] + \frac{1}{2} \int N \text{c} \int f(\bar{u}) f(\bar{u}') B_r (\gamma) d\bar{u} d\bar{u}',
\]

where \( B_r (\gamma) \) has the form (2.4). It should be emphasized that, as in the case of disconnected rods, the second virial approximation (3.1) is valid only if \( \theta \ll 1 \).

It is noteworthy that the formula (3.1), as well as the other results of this section (see below), can be applied not only for the model of freely jointed segments, but also for any other model of semiflexible macromolecule; it is necessary only to replace \( p \) in all the formulae by the ratio of the effective segment of the polymer chain to its width. Actually, the translational entropy in the general case has the form of the second term of Eq. (3.1); the loss in entropy due to the orientational ordering is always described by the third term of Eq. (3.1) - according to the definition of the effective segment; finally, the repulsive steric interaction of long thin segments is, obviously, insensitive to the character of their flexibility, because the interaction takes place at the short-range scale \( \delta \) and the flexibility becomes apparent at a much larger scale \( \ell > d \), so the contribution to the free energy due to the interaction of segments in the general case is described in the same way as in Eq. (3.1).

To calculate the actual value of the free energy the expression (3.1) must be minimized with respect to all possible distribution functions \( f(\bar{u}) \). Since the function \( f(\bar{u}) \) enters in the same way in the formulae (3.1) and (2.3), the minimization procedure is performed identically in both cases. Hence the equilibrium distribution functions \( f(\bar{u}) \) for the solutions of separate rods and long chains of rods must coincide.

Thus in the athermal limit the only difference between the equilibrium free energies of the solutions of separate rods and long chains of rods is due to the translational entropy term. Consequently, we can immediately conclude (analogously to Sec. II) that the liquid-crystalline transition for the athermal solution of semiflexible chains takes place at \( \theta \sim 1 / p \).

To perform the minimization of the free energy (3.1) let us use the variational method with the trial function (2.5). After the calculations, which are analogous to those performed in the Onsager paper [7], we arrive at the
following results for the boundaries of the region of phase separation in the
asymptotic limit $L \gg \xi$:

$$J_{(i)}^{(3)} = 3.25/\rho; \, J_{(a)}^{(3)} = 4.86/\rho; \, J_{(a)}/J_{(i)}^{(3)} = 1.50. \quad (3.2)$$

Formulas (3.2) must be compared with the corresponding result (2.6) for the
case of disconnected rods. It can be concluded that the connection of rods
into long chains broadens the region of the phase separation in the athermal
(high temperature) region of the phase diagram (however, numerically this
broadening is not very pronounced).

Similar results can be obtained using the lattice model (see the recent
Flory paper [11]).

3.3 Phase diagram: low temperature

For the solution of semiflexible macromolecules, as well as for the
case of disconnected rods, when the isotropic and the anisotropic phases co-
exist in equilibrium at the relatively low temperatures, the polymer volume
fraction in the isotropic phase is very small, while in the anisotropic
phase it is close to the maximum possible value, the chains in the anisotropic
phase being practically parallel to one another. Thus for the description of
the anisotropic phase it is possible to use the lattice model. The free energy
of the anisotropic phase can be written in the form analogous to Eq.(2.9)
with the only difference that the role of rods is now played by the long
chains of connected rods, thus, in the first two terms of the expression (2.9)
it is necessary to perform the substitutions $p \to p/\ell$, $N \to N/L$. So we
obtain the low temperature expression of the free energy of the anisotropic
phase in the form

$$F = F_0(T) + N T \left( \frac{4.3}{3} \rho \frac{L}{\ell} \right) \ln \left( \frac{4.3}{3} \rho \frac{L}{\ell} \right) \right)
- \left( 1 + \frac{4.3}{3} \rho \frac{L}{\ell} \right) \ln \left( 1 + \frac{4.3}{3} \rho \frac{L}{\ell} \right) + \ln \rho - \chi \rho \frac{L}{\ell} \right). \quad (3.3)$$

As in the case of disconnected rods the free energy of the isotropic phase
can be written in the ideal gas approximation, i.e. instead of (2.8) we have

$$F = F_0(T) + T N \frac{L}{\ell} \frac{\rho}{\ell} \frac{L}{\ell}. \quad (3.4)$$

By equating the chemical potentials and the pressures of the coexisting
isotropic and anisotropic phases, it is easy to find, as usual, in the limit
$p \gg 1$ the following equations for the boundaries of the low temperature
phase separation region:

$$J_{(i)}^{(1)} = \frac{1}{L} \left( e^{x-1} \right) \rho \frac{L}{\ell} + \exp \left( -\frac{X \rho L}{\ell} \right),$$

$$1 - J_{(a)}^{(1)} = \ell + 4 \rho \left( e^{x-1} \right). \quad (3.5)$$

For the case $L = 1$ we return to the result (2.11). Comparing Eqs.(3.5) and
(2.11) one can see that in the low temperature region (i.e. at large $x$) the
connection of segments into long chains leads to the very significant
broadening of the phase separation region.

3.4 Phase diagram: The triple point and the $\theta$ point

Let us now determine the temperature $T_{\theta}$, at which the high temperature
asymptotic expression for $J_{(i)}^{(3)}$ (3.2) matches with the low temperature one
(3.5). We shall show below that, as in the case of disconnected rods, this
temperature corresponds to the triple point of the phase diagram.

Using the definition of $\chi$ (2.10) we obtain after a simple
calculation that

$$\left( \frac{e}{T} \right)_3 = \frac{4 + 2 \frac{L}{\ell} \left( \frac{4}{3} \rho \frac{L}{\ell} \right)}{z - \frac{2}{3} \frac{L}{\ell} \frac{4}{3} \rho \frac{L}{\ell}} \frac{4}{3} \rho \frac{L}{\ell}. \quad (3.6)$$

In particular, for $L = 1$ we return to the formula (2.12) and in the limit of
long chains $L \gg \ell$ we have

$$\left. \left( \frac{e}{T} \right)_3 \right|_{L \gg \ell} = \frac{4}{z - 2} \frac{L}{\ell} \frac{4}{3} \rho \frac{L}{\ell}. \quad (3.7)$$

*) The result (3.6) does not depend (in the limit $p \gg 1$) on the exact value
of the numerical factor in the high temperature formula for $J_{(i)}^{(1)}$ ($J_{(i)} = \text{const} \rho$).
From Eq.(3.6) it can be seen that the triple point temperature increases with
the increase of the ratio \( L/k \) (i.e. with the elongation of the chain).

As to the \( \Theta \) temperature of the solution of semiflexible macromolecules,
in the limit \( p >> 1 \) it practically coincides with the \( \Theta \) temperature of
the solution of disconnected rods with the same \( p \) - the reason is the small degree
of renormalization of the virial coefficients (for a more detailed discussion
see Refs.32 and 33). Thus the result (2.18) for \( \epsilon/\Theta \) also remains valid for
this case. From the comparison of Eqs.(2.18) and (3.6) it can be concluded
that the \( \Theta \) point is always (independently of \( L/k \)) situated in the low
temperature region of the phase diagram, well below the triple point.

3.5 General form of the phase diagram

It should be recalled that the qualitative form of the phase diagram
for the solution of disconnected rods was obtained in Sec.II with the help of
the Onsager method, which was generalized to take into account the attraction
of the rods. The same thing can be done for the solution of semiflexible macromolecules.

For the model of semiflexible macromolecule accepted in Subsec.3.1, the
attractive part of the second virial coefficient of the interaction of segments
is given directly by the formulae (2.16) and (2.21). Thus the procedure of
the determination of the most stable homogenous phase in the solution of
freely-jointed semiflexible macromolecules is absolutely identical to the
corresponding procedure for the solution of disconnected rods (compare
Eqs.(2.3) and (3.1)); consequently, this procedure leads to the results (2.25)
(see also Fig.5).

The general qualitative form of the phase diagram can now be determined
from the known high temperature and low temperature behaviours and from the
fact that the curves of Fig.5 must lie entirely within the phase separation
region (compare with Sec.II). The phase diagram for the solution of semiflexible
macromolecules obtained in this way is shown in Fig.6.

It can be seen that the equilibrium coexistence of two different
anisotropic phases is also possible for this case. As in Sec.II this fact
leads to the existence of the triple point and of the critical point in the phase
diagram, as well as to the sharp broadening of the phase separation region
below the triple point temperature.

The dotted line curves in Fig.6 show the phase diagram for the
corresponding solution of disconnected rods, which was found in Sec.II. We
see that the phase separation region for the solution of semiflexible macromolecules
is generally more broad - this is due to the obvious fact that the
connection of rods into long chains favours their orientational ordering.
It can be noted that as the number of the segments in the chain increases, the
broadening of the phase separation region below the triple point becomes more
and more sharp (see Eqs.(3.5)); when the relative temperature lowering below
the triple point is of order \( \Delta T/T \sim L \ll 1 \), the isotropic phase in co-
existence with the anisotropic one can be considered as practically absolutely
dilute (the polymer volume fraction in this phase is exponentially small).
Such an additional sharpness is connected with the additional large parameter
(in comparison with the case of disconnected rods) - the number of segments
in the macromolecule.

Now let us discuss the applicability of the results obtained for other
models of semiflexible macromolecules. It is clear that the qualitative form
of the phase diagram does not depend on the model adopted. The low temperature
behaviour of the phase diagram is independent of the flexibility distrib-
ution along the chain contour as well, since at low temperature the two phases
in coexistence are: very dilute, nearly ideal solution and the dense phase
of practically completely stretched chains. The high temperature behaviour is
also universal (see Subsec.3.2). So, some unessential dependence of the
parameters of the phase diagram on the chosen polymer chain model (with the
same \( p \)) can be expected only in the intermediate temperature range, i.e. in the
vicinity of the triple point.

3.6 Final remarks

It can be concluded that as the chains become longer the tendency for
the solution of semiflexible macromolecules to form liquid-crystalline phase
increases (since the phase separation region broadens), this effect being more
pronounced at the low temperatures. However, the qualitative form of the phase
diagram practically does not depend on the number of segments in the chain.
At high temperatures the phase separation region forms a narrow corridor, whose
width does not depend on the temperature and changes only slightly (±10%) with the variation of the number of segments in the chain. At low temperatures (below the triple point) the phase separation region broadens in a rather sharp way, especially for long chains.

IV. INTRAMOLECULAR LIQUID-CRYSTALLINE PHASE

In the following sections we shall consider the intramolecular liquid-crystalline ordering of the segments of one macromolecule in the very dilute solution, i.e. the one-chain problem. Correspondingly, below we shall use the letter N to denote the number of segments in the macromolecule.

In this section we shall deal with the case of a very long chain. The particular features of the intramolecular liquid-crystalline phase for the relatively short chains will be considered in Sec.V.

4.1 Phase transition coil-liquid-crystalline globule

Let us begin with the estimation of the polymer volume fraction inside the coil formed by one long semiflexible macromolecule. It is well known [25], that this estimation depends essentially on the strength of the excluded volume effect, i.e. on the value of the parameter $Z = V_{M}^{1/2} / a$, where $V$ is the excluded volume of a monomer and $a$ is the distance between two subsequent along the chain monomers. To be definite let us adopt for a moment the model shown in Fig.1b. Then, if we choose one segment as an elementary monomer, $V \sim a^{2}$ (see formula (2.4)) and $a \sim 1$, i.e. $Z \sim P^{-1/2}$. Consequently, the excluded volume effect is pronounced at $N \gg P^{2}$ and is negligible at $N \ll P^{2}$ (see also [31]). The size of the coil in these cases is $\sim N^{1/2}$ or $\sim N^{1/2}$, correspondingly; so for the polymer volume fraction inside the coil we obtain

$$\phi_{\text{coil}} \sim \begin{cases} P^{-7/5} N^{-4/5} & \text{at } N \gg P^{2}, \\ P^{-2} N^{-1/2} & \text{at } N \ll P^{2}, \end{cases} \tag{4.1}$$

where we have used the value $\xi = 3/5$ for the critical exponent (for more details see [34]).

From the result (4.1) one can see, first of all, that $\phi_{\text{coil}} \ll 1/P$ at $P \gg 1$ and at any $N \gg 1$, so at the temperatures above the triple point temperature the polymer volume fraction within the coil is not sufficient for the formation of the intramolecular liquid-crystalline phase.

On the other hand, for the temperatures slightly below the triple point the result (3.5) for $\phi_{(1)}$ can be written in the form (in the limit $p \gg 1$)

$$\phi_{(1)} \sim P^{-1 - 2N / T_{3} - T} \tag{4.2}$$

apart from the logarithmic factor. We see that at large $N$ small temperature lowering below the triple point $dT / T \sim \ln N / \ln p$ $p \ll 1$ is sufficient to make the polymer volume fraction in the coil (4.1) essentially larger than the stability limit of the isotropic phase (4.2). It is clear that in this case the loose fluctuating coil must collapse and form the dense highly ordered liquid-crystalline globule (since the density of the anisotropic phase at $T < T_{3}$ is close to its maximum possible value - see Sec.III).

So at $T > T_{3}$ the long semiflexible macromolecule is in the coil state, while at $T < T_{3}$ it is in the globular state. Consequently, the temperature $T_{3}$, which is determined by Eq.(3.7) is the temperature of the coil-globule transition for the long freely-jointed macromolecule (see Fig.6). It is clear that this transition is the 1 order phase transition with the considerable bound of the coil dimensions, it leads simultaneously to the transformation of the coil into the globule and to the formation of the liquid-crystalline ordering in the globule.

It should be emphasised that these features of the transition coil-liquid-crystalline globule, as well as the expression (3.7) for the temperature of this transition, are not sensitive to the specific polymer chain model in the limits $p \gg 1$ and $N \gg 1$. In particular, the above results remain valid for each of the models shown in Figs.7b,c,d, the chain composed of rods connected by flexible spacers (Fig.7b), the flexible chain with the rod-like side groups (Fig.7c) and the persistent chain (Fig.7d). Such universality can be proved by means of the following simple arguments.

The translational entropy of the system does not vary at the point of the coil-globule transition. So this transition occurs as a result of the competition between the gain in energy of the contact of segments in the dense liquid-crystalline phase $\sim T / \chi N p$ and the loss in the orientational entropy in this phase $\sim T \ln p$. Taking into account the definition of $\chi$ (2.10) and the equality (3.7) for $T_{3}$, we obtain that at $T > T_{3}$ the entropy loss is larger than the gain in energy and vice versa. In the long macromolecule even the slight temperature lowering below $T_{3}$ is enough to make the gain in energy much larger (since $N \gg 1$) than the loss in entropy, i.e. to induce the transition coil-liquid-crystalline globule. It is clear that the above consideration is valid for each of the models shown in Figs.7b,c,d.
So for all the polymer chain models under consideration the temperature of the transition coil-liquid-crystalline globule is determined by the formula (3.7) and the transition itself is the 1 order phase transition. It should be emphasised that this transition takes place above the $\theta$ temperature.

### 4.2 Spatial structure of a large liquid-crystalline globule

According to the general definitions of the coil and the globule [24] the macromolecule is in the coil state if the fluctuations of the monomer concentration within the macromolecule are of order of the monomer concentration itself and the correlation radius of the fluctuations of concentration is of order of the macromolecular dimensions, while in the globular state the fluctuations of the concentration are small compared with the concentration and the correlation radius is much less than the globular dimensions.

In other words, in the coil state all the monomers are correlated, while in the globular state the chain can be considered as consisting of a large number of effectively independent portions. Thus, the small region inside the large liquid-crystalline globule formed by the semiflexible macromolecule can be regarded from the local point of view simply as the solution of semiflexible chains in the condensed liquid-crystalline state. We have shown in Sec.III that in this state at $T < T_\theta$ (i.e. in the region of existence of a liquid-crystalline globule) the polymer volume fraction is always close to unity. Thus, in the first approximation for the polymer volume fraction inside the globule, $\phi$, we have $\phi \approx 1$. Correspondingly, the volume of the globule, $V$, is $V = N\rho a^3$ and the spatial distribution of the polymer volume fraction is of the form shown in Fig.8a (compare with Ref.24).

To find the corrections to the result $\phi \approx 1$, it is necessary to first of all determine the function $\psi(\alpha)$ — the free energy per unit volume of the liquid-crystalline solution of infinitely long semiflexible chains. For each of the models shown in Figs.7b,c,d the free energy of the anisotropic solution at $T < T_\theta$ (and hence the function $\psi(\alpha)$) can be found by means of the method, which is completely analogous to that developed in Sec.III for the low temperature behaviour of the solution of freely-jointed chains (Fig.1b). After that the free energy of the large globule can be written in the form

$$F = V \psi(\alpha) = \frac{3}{8} \rho a^3 \psi(\alpha)/\beta .$$

To obtain $\psi$ the equilibrium value of $\alpha$, this expression must be minimized with respect to $\alpha$. As a result we obtain for the determination of $\psi(\alpha)$ the following equation:

$$\psi(\alpha) = 0 ,$$

where $\psi(\alpha)$ is the osmotic pressure of the solution of the long macromolecules of a given type. For example, for the chain composed of rods connected by flexible spacers (Fig.7b) basing on the results of Secs.II and II, we obtain

$$\psi(\alpha) \approx \left\{ \begin{array}{ll}
1 - \frac{a}{\epsilon} \left( \frac{\alpha^2}{\epsilon^2} \right) & \text{if } a \ll \ell \\
1 - \frac{d^2}{\epsilon(\ell^2 - 1)} - \frac{\alpha^2}{\epsilon^2} & \text{if } a \gg \ell
\end{array} \right.$$
4.3 **Metastable isotropic state**

Since the surface energy of the globule is positive, the temperature of the phase transition coil-liquid-crystalline globule decreases with the decrease in the chain length. Thus when the coil is slightly supercooled below the phase transition temperature $T_3$, small parts of the chain are not able to form the globular structures themselves, i.e., to initiate the new phase. In other words, the formation of the globule at slight supercooling requires correlated motion of a large number of monomers. Of course, this situation is typical for the I order phase transitions. However, in the polymer systems due to the connection of monomers into long chains the corresponding relaxation times are especially large. Thus semiflexible macromolecules can actually exist in the metastable state without the liquid-crystalline ordering at the temperatures well below $T_3$. In this Subsection we shall consider some properties of this metastable state.

Since $T_3 > 0$, at slight supercoolings below $T_3$ we still remain in the good solvent region. By further supercooling it is possible to pass to the $0$ solvent region and even to the region of a very poor solvent (precipitant). As was shown in Refs. 33 and 34, in the absence of the liquid-crystalline ordering it is possible to reduce the description of the conformational characteristics of a given macromolecule in each of these regions to the corresponding description for the standard Gaussian model of "beads" (for the definition of this model see the caption to Fig.7a) with some effective parameters (for the method of calculation of these parameters see Ref. 33).

Thus upon lowering the temperature, the semiflexible macromolecule in the metastable isotropic state undergoes the same conformational changes as the corresponding effective chain of "beads". The theory of the conformational changes for the model of "beads" is now well developed (see, for example, Ref. 24) and so it is possible to apply the results of this theory for the isotropic phase of a semiflexible macromolecule.

In particular, it is well known that when the macromolecule is supercooled below the $0$ temperature, the phase transition isotropic coil-liquid-crystalline globule occurs; we emphasize that for the semiflexible macromolecule this is the peculiar phase transition between two metastable states. It should be recalled that the theory of the transition isotropic coil-liquid-crystalline globule for the model of "beads" is formulated in terms of the second and the third virial coefficients of the interaction of "beads", $b$ and $c$ [24]. This transition takes place slightly below the $0$ point and its type depends on the value of the ratio $c^{1/2}/a^3$. If $c^{1/2}/a^3 \ll 1$ the coil globule transition is of the I order phase transition with the bound of the macromolecular dimensions, and if $c^{1/2}/a^3 \sim 1$, it is the smooth II order phase transition (see [24] and [25]).

The parameters of the effective model of "beads" for the polymer chain models under consideration (Figs. 7b, c, d) can easily be found using the methods of Refs. 25 and 33. We shall omit here the corresponding trivial analysis and present only the final results for the value of $c^{1/2}/a^3$ which determines the type of the transition isolated coil-liquid-crystalline globule. For the models of Figs. 7b and 7d it turns out that at $t \gg 1$ always $c^{1/2}/a^3 > 1$, so the coil-globule transition is always of the I order. At the same time, for the model of Fig. 7c the type of the transition depends on the ratio $t/a$; at $t/a < 0$ this is the I order phase transition and at $t/a > 1$ the transition is of the II order.

When the temperature is further lowered below the $0$ point, the density of rods in the isotropic globule increases, the instability of the metastable phase becomes more pronounced and finally the macromolecule undergoes the transition to the liquid-crystalline state.

It is noteworthy that even in the isotropic phase (in the coil, as well as in the globule) there exists a weak orientational ordering (not of the liquid-crystalline nature) due to the inhomogeneity of the spatial density distribution in the macromolecule. This ordering will be considered in the Appendix.

We see that the properties of the intramolecular liquid-crystalline phase in the long macromolecules are rather universal, i.e. not sensitive to the polymer chain models (compare the results of this section for the models shown in Figs. 7b, c, d). It is due to this universality that it became possible to establish the main properties of the large globules on the basis of the general considerations and without referring to the special formalism.

V. **SMALL GLOBULES**

In this section we shall consider the intramolecular liquid-crystalline ordering in the relatively short macromolecules. We shall see that the properties of the globules in this case (small globules) are not universal. As was already noted in the introduction, the analysis of the structure of small globules requires the use of the formalism of the self-consistent theory of polymer globules, which was proposed by Lifshits in Ref. 23.

However, it must be recalled that the Lifshits theory was originally formulated [23]-[25] for the model of "beads" (see Fig. 7a). In this model each monomer is represented as a material point, so, obviously, this model cannot be used to describe the intramolecular liquid-crystalline phase. In
order to be able to describe the orientational ordering, it is necessary to
generalize the Lifshitz consideration for the models in which the state of
an elementary monomer is defined not only by its spatial position, but also by
its orientation (see for example the models of Figs.9c,d). Such a generalization
will be our first aim in this section.

5.1 Conformational entropy of the globule

Let us consider some polymer chain and let \( \xi \) be the set of parameters,
which describe completely the state of the \( i \)th link. This set can, in
principle, include not only the co-ordinates and orientations, but also some
other intrinsic parameters of the monomer (if necessary). Let \( n(\xi) \) be the
"density" of monomers in the state \( \xi \) normalized by the condition

\[
\int n(\xi) \, d\xi = N, \tag{5.1}
\]

and let \( \psi(\xi) \) and \( \psi'(\xi) \) be the probability distributions for two monomers
at the ends of the chain \( \xi \). Finally, let us introduce the matrix of conditional
probabilities \( g(\xi,\xi') \) and the corresponding integral operator \( \hat{g} \) [23]:

\[
\hat{g} \psi = \int g(\xi,\xi') \psi(\xi') \, d\xi', \tag{5.2a}
\]

where \( g(\xi,\xi') \) is the conditional probability that the monomer is in the state
\( \xi' \) provided the previous one is in the state \( \xi \). Since \( \hat{g} \) is the probability

\[
\int g(\xi,\xi') \, d\xi' = \hat{g} = 1 = \hat{g}, \tag{5.2b}
\]

Using the notation introduced, it is possible to formulate the following
result, which can be proved analogously to the corresponding result for the
model of "beads" (see Refs.23-25). If the macromolecule is in the globular
state, i.e. if the fluctuations of the generalized density \( n(\xi) \) are weak,
the macromolecular conformational entropy is equal to

\[
S\{n^i\} = \int n(\xi) \ln \hat{g} \frac{\psi}{\psi} \, d\xi, \tag{5.3}
\]

where the functions \( n, \psi \) and \( \psi^* \) are connected by means of the following
formulas:

\[
\lambda n = \psi^* \hat{g} \psi = \psi^* \hat{g} + \psi. \tag{5.4a}
\]

In Eq.(5.4a) the parameter \( \lambda \) specifies the normalization of the functions \( \psi \)
and \( \psi^* \) (the value of \( S(n) \) does not depend on \( \lambda \)) and \( \hat{g}^* \) is the operator,
which is Hermitian-conjugated to \( \hat{g} \) with respect to the scalar product

\[
\langle \psi_1, \psi_2 \rangle = \int \psi_1(\xi) \psi_2(\xi) \, d\xi. \tag{5.5}
\]

It is noteworthy that from the physical point of view the Hermitian conjunction
means in this case simply the change of the order of monomer numeration along
the chain (for a more detailed discussion of this point see Ref.20). Thus the
chains which are not symmetric with respect to this change, are characterized
by the non-Hermitian operators \( \hat{g} \).

5.2 Self-consistent system of equations for globules

If the globular state of a macromolecule with the given generalized
density distribution \( n(\xi) \) would be somehow prepared in the absence of the interactions
between the monomers, the macromolecular free energy would be equal to

\[
-T S(n). \tag{5.6a}
\]

The contribution of the interactions to the macromolecular free energy
(in reality it is due to the interactions that the globule is formed) is
also some functional of \( g(\xi) \): \( E = E(n) = F(n) + T S(n) \).

In the self-consistent field approximation the equilibrium distribution \( n(\xi) \) can be determined by means of the minimization of \( F(n) \) with the
additional condition (4.1). Performing the variational procedure and taking
into account Eqs.(5.3) and (5.4a) it is easy to find the following equation
in complete analogy with the corresponding calculation in Ref.24:

\[
\hat{g} \psi = \lambda \psi \exp \left\{ \frac{\delta E}{\delta n} / T \right\}. \tag{5.6b}
\]

In Eq.(5.6b) we have connected in a special way the normalization parameter \( \lambda \)
with the Legendre multiplier and thus, we have specified the normalization of
the function \( \psi \) (compare with [24]). The value of \( \delta E/\delta n \) plays the role of
the self-consistent field in Eq.(5.6).
From Eqs. (5.1) and (5.6) the following local relation between the equilibrium functions \( n, \psi \) and \( \psi^\dagger \) can be obtained:

\[
\psi(n, \xi) = \psi(n, \xi') \exp \left\{ \frac{\delta E}{\delta n} (\xi) / T \right\}.
\] (5.7)

Eqs. (5.6) and (5.7) together with the normalization condition (5.1) form the self-consistent system of two equations and one additional condition for the determination of two unknown functions \( n \) and \( \psi \) and one unknown number \( A \) (in Eq. (5.7) \( \psi^\dagger \) is the function Hermitian conjugated to \( \psi \)), i.e. for the complete description of the equilibrium spatial structure of the globule.

5.3 Examples of the specific macromolecular models

Let us now specify the general notation of the two preceding sections for some concrete macromolecular models.

1. Models of "beads" (see Fig. 7a and the figure caption). For this model it is natural to choose one "bead" as an elementary monomer; then the state of a monomer is completely defined by its co-ordinates, i.e. \( \xi = \bar{x} \). Usually it is assumed that the connecting filaments do not have the orientational memory; in this case the kernel of the operator \( \hat{\mathcal{g}} \) depends only on the distance between the monomers

\[
\mathcal{g}(\xi, \xi') = g_0 \left( \| \bar{x} - \bar{x}' \| \right).
\] (5.8)

The most important characteristics of the kernel \( g_0 \) is the mean-square distance between subsequent monomers

\[
a^2 = \int x^2 g_0(\bar{x}) \, d\bar{x}.
\] (5.9)

Obviously, in the model of beads \( g = g^\dagger \) and \( \psi = \psi^\dagger \). This model can be used for the consideration of those effects, which are not connected with the orientational ordering.

2. Flexible chain with the rod-like side groups (see Fig. 7c and the figure caption). In this model it is natural to choose one rod as an elementary monomer; then the state of a monomer is defined by the co-ordinates of the origin of the rod \( \bar{x} \) and by the unit vector specifying the orientation of the rod \( \bar{u} \). To be definite we shall assume that for this model (as well as for the model of "beads") flexible filaments connecting the monomers (i.e. rods) do not have the orientational memory. In this case the kernel of the operator \( \hat{\mathcal{g}} \) is equal to the kernel \( (5.6) \) multiplied by the factor \( (4\pi)^{-1} \). As before, the mean-square distance between the origins of two subsequent along the chain rods is determined by the formula (5.9). We shall assume that the rods can rotate freely with respect to their origins, in this case the operator \( \hat{\mathcal{g}} \) does not act on the variable \( \bar{u} \). For this model the operator \( \hat{\mathcal{g}} \) remains Hermitian and \( \psi = \psi^\dagger \).

The formula (5.3) for the conformational entropy has the simple interpretation for this model. Let us write the generalized density in the form \( n(\bar{x}, \bar{u}) = C(\bar{x}) n(\bar{u}) \), where \( \int f(\bar{u}) \, d\bar{u} = 1 \). Then according to (5.4) we shall have \( \psi(\bar{x}, \bar{u}) = \psi(\bar{x}) n(\bar{u}) \) and so

\[
S = \int C(\bar{x}) \ln \frac{\bar{u}}{\bar{u}' \bar{u}} \, d\bar{x} - \int C(\bar{x}) \left[ \int f(\bar{u}) \, d\bar{u} \right] \ln (4\pi f(\bar{u})) \, d\bar{u}.
\]

Thus, for this model the conformational entropy can be represented as the sum of two independent contributions: one from the spatial packing of the origins of the rods and the other from the orientational distribution of the rods.

3. Chain composed of rods connected by flexible spacers (see Fig. 7b and the figure caption). For this model, as well as for the previous one, it is natural to choose one rod as an elementary monomer, i.e. \( \xi = (\bar{x}, \bar{u}) \). However, now the rods are inserted between the flexible spacers, so the kernel of the operator \( \hat{\mathcal{g}} \) must depend on the distance between the end of the preceding rod and the beginning of the following one, i.e.

\[
\mathcal{g}(\xi, \xi') = g_0 \left( \| \bar{x} - \bar{x}' - \ell \bar{u} \| \right).
\] (5.10)

In this notation the mean-square distance between the ends of a flexible spacer is given by Eq. (5.9).

It is easy to understand that for this model \( \hat{\mathcal{g}} + \hat{\mathcal{g}}^\dagger \) and

\[
\psi^\dagger(\bar{x}, \bar{u}) = \psi(\bar{x} + \ell \bar{u}) \bar{u}.
\] (5.11)
As it has already been noted, the model of freely-jointed rods (Fig.1b) is the particular case of this model for which $g_0(x) = S(x)$.

4. Persistent model (see Fig.7d and the figure caption). The continuous persistent model can be obtained by means of some smoothing of the properties of the suitable discrete model on the microscopic level. For this purpose let us consider the discrete model, which differs from that shown in Fig.7b only in one respect: namely, let us attribute to the spacers some finite stiffness with respect to the bending, i.e. for this model

$$g(x, x') = g_0 \left( \frac{1}{2} \frac{x}{x'} - \left< u_x' \right> \right) g_1 \left( \frac{1}{2} \frac{u_x'}{u'_x} \right),$$

(5.12)

where $\Delta_{uu}$ is the angle between the orientations $u$ and $u'$ and $\bar{u}$ is the notation for the length of the rod in this model. The smoothing procedure is possible if the states of the adjacent rods are close to each other, i.e. if the integral operator $g$ with the kernel (5.12) is close to the unit operator. But in this case the integral operator can be approximated by the differential one. It is the use of the differential operator instead of the integral one that corresponds to the smoothing on the microscopic level, i.e. to the consideration of the persistent model.

Expanding the function $\Psi(x', u')$ with respect to $(x-x')$ and $(u-u')$ in the expression

$$\hat{g} \Psi = \int g_0 \left( \frac{1}{2} \frac{x}{x'} - \left< u_x' \right> \right) g_1 \left( \frac{1}{2} \frac{u_x'}{u'_x} \right) \Psi(x', u') d \frac{x'}{x'} d \frac{u_x'}{u'_x},$$

(5.13)

and keeping only the main non-zero terms, we obtain

$$\hat{g} \Psi = \int g_0 \left( \frac{1}{2} \frac{x}{x'} - \left< u_x' \right> \right) g_1 \left( \frac{1}{2} \frac{u_x'}{u'_x} \right) \Psi(x', u') d \frac{x'}{x'} d \frac{u_x'}{u'_x},$$

(5.14)

where

$$\hat{g} = 1 + \left< u_x' \right> \frac{1}{2} \theta^2 \Delta_{uu},$$

(5.15)

$\Delta_{uu}$ is the operator of the partial derivative with respect to the co-ordinate along the direction $u$, $\Delta_{uu}$ is the angular part of the Laplace operator in the space of orientations.

Expression (5.14) gives the operator $\hat{g}$ for the persistent model.

The operator of the similar form has already been used for the analysis of the persistent coils in Refs.35 to 37. In particular, in these references it was shown that the effective segment of the persistent chain described by the operator (5.14) is equal to

$$\ell = \frac{\bar{\ell}}{\theta^2}.$$  

(5.16)

It is clear that the macroscopic characteristics of the persistent chain can depend only on the combination (5.16) of the microscopic parameters $\bar{\ell}$ and $\theta$.

Operator (5.14) is not Hermitian: $\hat{g} \neq \hat{g}^\dagger$. For the function $\Psi^+$ it is easy to find

$$\Psi^+ = \Psi(x', u') = \Psi(x', -u').$$

(5.17)

In the next Subsections we shall use the formalism described above for the analysis of the intramolecular orientational ordering in the relatively short macromolecules, in which case this ordering is accompanied by the formation of the so-called small globules. As has already been noted, the structure of small globules depends essentially on the macromolecular model chosen (in contrast to the case of the large globules, which was considered in Sec.IV). Thus, below we shall consider the structure of small globules for each of the models of Figs.7b,c,d separately. The whole set of these models describes a rather broad area of situations, which are frequently encountered in the real cases.

5.4 Small globule for the chain composed of rods connected by flexible spacers (Fig.7b)

We say that the polymer chain of this type forms a small globule if in the equilibrium conformation due to the attraction rods the average spatial distance between the ends of the flexible spacer is much less than $a$.

*) It must be noted that the expression (5.14) was obtained in Ref.36 not as a result of the smoothing procedure, but with the help of some other more formal consideration. The main idea of this consideration can be outlined as follows. It is well known [24] that the smoothing procedure for the model of "beads" leads to the operator of the type $g = \frac{1}{2} \theta^2 \Delta_{uu}$ and in the same approximation the partition function reduces to the Wiener integral [37]. In Ref.36 it was shown that the role of the operator (5.14) for the integration over the space of smooth curves is the same as the role of the Laplace operator for the usual Wiener integral.
the small globule has the form of the "sheaf" (Fig. 9). The majority of the rods belong to this "sheaf" and form the cylindrical core of the globule. Its length is \( L \), its radius \( R \). A relatively small fraction of rods does not belong to the core, these form the defects of the globular structure. We shall say that these rods form the "fringe" of the globule.

It is clear that the structure described can be stable only if the attraction of rods is strong enough - in any case it must be \((\delta^2/\pi) > (4/\pi^2)\). Thus the volume of the globular core \( V_1 \) must be of the same order as the self-volume of the macromolecule \( \sim N \delta^2 \), i.e. \( R \sim \delta^{1/2} \). Consequently, the condition ensuring that the globule formed is actually small has the form

\[
N \ll \left( \frac{a}{d} \right)^2
\]

(5.18)

The structure of the small globule shown in Fig. 9 is rather simple and can be described on the basis of the simple considerations. However in order to give the example of the solution of general equations obtained in Subsecs. 5.1 and 5.2, we shall analyse the properties of the small globule with the help of the formal theory. Another reason to do this is that in this case Eq. (5.16) has the exact solution.

The rods forming the globular core occupy the following small region in the five-dimensional configurational space of coordinates and orientations: all the terminal points of the rods are situated in two small volumes \( V \sim \delta^3 \) separated by the distance \( \delta \); the orientations fill two small spatial angles \( \pm \theta \) around \( \pm \varphi \) (see Fig. 9). We shall call this region the five-dimensional globular core. Inside the five-dimensional core the density \( n(x, u) \) is practically constant.

Using the terminology introduced, we can say that the rods, which are outside the five-dimensional core, form the defects of the globular structure. The interactions of these rods can be neglected (compare with Ref. 38) both with each other (because the concentration of rods outside the core is small) and with the rods of the core (because the rods of the fringe either do not intersect the core, or intersect it only by the small portion of their length).

So,

\[
\frac{dn}{dx} = \begin{cases} \text{const} & \text{inside the five-dimensional core} \\ 0 & \text{outside the five-dimensional core} \end{cases}
\]

(5.19)

Taking into account Eq. (5.19), it is possible to solve Eqs. (5.6) and (5.7) in complete analogy with the solution obtained in Ref. 38 for the model of "beads". The main steps are the following.

Let us introduce the notation

\[
\psi(x, \varphi) = \begin{cases} \psi_+ = \text{const} & \text{inside the five-dimensional core} \\ \psi_{\text{out}}(x, \varphi) & \text{outside the five-dimensional core} \end{cases}
\]

\[
\psi_+ \equiv \psi_{\text{out}} \left( \frac{L}{2} \varphi, -\varphi \right) = \psi_{\text{out}} \left( -\frac{L}{2} \varphi, \varphi \right)
\]

(5.20)

where we have chosen the origin of the three-dimensional \( \tilde{x} \)-space in the middle point of the "sheaf". The value of \( \psi_+ \) is proportional to the probability that the last monomer of the chain is situated inside the five-dimensional core, while the value of \( \psi_- \) is proportional to the probability of the fact that the last monomer is situated outside the five-dimensional core, but near its boundary.

From Eqs. (5.7), (5.11) and (5.20) we obtain (using the natural notation)

\[
n_- = \psi_- \psi_+^*, \quad n_+ = \psi_+^2,
\]

\[
n_{\text{out}} (x, \varphi) = \psi_{\text{out}} \psi_{\text{out}}^* = \psi_{\text{out}} (x, \varphi) \psi_{\text{out}} (x + \ell, -\varphi)
\]

(5.21)

Using the smallness of the five-dimensional globular core and the smoothing properties of the integral operator \( \hat{g} \), we can rewrite the main equation (5.6) in the form of the linear II order integral equation (compare with Ref. 38):

\[
\hat{g} \psi_{\text{out}} + V \omega \left( \psi_- - \psi_+ \right) \left\{ g_0 (x + \ell, -\varphi) + g_0 (x - \ell, \varphi) \right\} = \lambda \psi_{\text{out}}
\]

(5.22)

It is easy to verify that the eigenfunctions and the eigenvalues of the integral operator \( \hat{g} \) with the kernel (5.10) are equal to, correspondingly, \( \exp(\pm ik(x + \ell)) \) and \( g_{\text{out}} \sin kx/\ell \), where \( g_{\text{out}} = \int g_0 (x) \exp(i2k) \, dx \). As soon as the eigenfunctions and the eigenvalues are known, it is possible to find the resolvent operator (see, for example Ref. 39) and with the help of this operator it is easy to write down the solution of Eq. (5.22):

\[
\psi_{\text{out}} = \int g_{\text{out}} (x, \varphi) \psi (x, \varphi) \, dx
\]
The expression obtained for $\Psi_\text{out}$ and the corresponding result for $n_\text{out}$ (see (5.21)) describe, correspondingly, the formation of the "tail" defects and of the "loop" defects of the globular structure (see Fig.9). It is possible to show that the $m^{th}$ term of the expansion of $\Psi_\text{out}(x,u)$ in the powers of $1/A$ is proportional to the probability of the fact that the end monomer of the "tail" defect involving $m$ monomers is in the state $(x,u)$. Analogously, the $m^{th}$ term of the expansion of $n_\text{out}$ is proportional to the generalized density at the point $(x,u)$ due to the "loop" defects involving $m$ monomers (compare with Ref.38).

To complete the solution it is still necessary to find four constants: the volume of the five-dimensional core $V_0$ (the constants $V$ and $\omega$ enter always in this combination) $A$, $n_-$ and $n_+$. The former two constants can be determined from the definition (5.20) and from the normalization condition (5.1). The corresponding equations can be written in the form

$$n_+ a^3 = N Q(A, l/a),$$  

(5.24)

$$2 V \omega (n_- - n_+) = N P(A, l/a),$$  

(5.25)

where

$$J_1(A, l/a) = \frac{2}{(2\pi)^3} \int \frac{g e^2 \cos \frac{l}{2} k u}{A - g e^2 \sin k l} d^3k,$$  

(5.26)

$$J_2(A, l/a) = \frac{2}{(2\pi)^3} \int \frac{g e^2 \cos \frac{l}{2} k u}{A - g e^2 \sin k l} \left[ \frac{g e^2 \cos \frac{l}{2} k u}{A - g e^2 \sin k l} \right] d^3k,$$  

(5.27)

$$P(A, l/a) = \frac{J_1}{J_1 + J_2}, \quad Q(A, l/a) = \frac{J_2}{J_1 + J_2},$$  

(5.28)

Finally, to determine two still unknown constants $n_-$ and $n_+$ it is necessary to find the boundary conditions for the generalized density and to apply these conditions for the density bound between the core and the fringe. We note that the microcrations of the rods inside the five-dimensional core are not hindered by the flexible spacers, since the average distance between the ends of the spacers is much less than $a$. Consequently, there must be a local equilibrium with respect to two elementary acts: 1) parallel moving out of one rod from the core to the fringe; 2) expansion of the core as a whole. Correspondingly, $n_-$ and $n_+$ can be determined from the conditions of the continuity of local chemical potential and pressure at the boundary between the core and the fringe (compare with Ref.21). This means that $n_-$ and $n_+$ are equal to the concentrations of the phases coexisting in equilibrium in the system of disconnected rods. Using the notation of Sec.II we can write $n_+ = \beta(1)/a^2 pd^3$ and $n_- = \beta(a) \ell(0)/a^2 pd^3$. So the values of $n_-$ and $n_+$ can be considered as known functions of temperature.

Using the obtained complete solution of the small globule problem it is easy to write down the expression for the equilibrium globular free energy

$$F = N T \left\{ P(A, l/a) - \ln A \right\},$$  

(5.29)

where $A$ is the root of the equation (5.24).

It is easy to show that when the temperature is lowered the small globule is formed by means of the 1st order phase transition (the transition temperature can be determined from the condition $F = 0$). Practically, in the whole region of existence of the small globule the value of $A$ turns out to be rather large, so it is possible to keep only a few first terms in the expansion of the functions (5.26) to (5.28) in the powers of $1/A$. In this approximation for the transition temperature $T_0$ we have

$$J^{(i)}(T_0) \equiv \text{const} \cdot \frac{N l^2}{(a^2 \ell^3)^{3/2}},$$  

(5.30)

The results can be interpreted as follows. The coil-globule transition takes place when the number of rods in the fringe becomes $\sim N$ (the dimensions of the fringe are $\sim (a^2 \ell^3)^{1/2}$).
From Eqs. (5.18) and (5.30) it can be seen that in the whole region of the existence of the small globule the polymer volume fraction in the fringe is very small (much less than unity) and that the temperature of the coil-globule transition increases with the increase of the chain length (the latter fact is rather natural).

5.5 Small globule for the flexible chain with the rod-like side groups (Fig.10c)

The short enough macromolecules of this type can also form the "sheaf-like" small globule, Eq. (5.18) being the criterion of the small globule. General lines of the analysis of the globular structure are analogous to those in the previous section. In particular, the values of $\varepsilon_0$, $\varepsilon_1$, $\varepsilon_2$ and $\varepsilon_3$ coincide with those found earlier.

However, from the very beginning it is clear that for this model two structures of the "sheaf" type are generally possible (Figs. 10a,b): the structure A for which the flexible chain is situated near one of the ends of the "sheaf", i.e. all the rods are oriented in the same way along the "sheaf", and the structure B for which the rods have no preferential direction along the "sheaf". Obviously, the structure B is more favourable from the point of view of the entropy, but its formation requires the presence of at least one defect of the globular structure (see Fig. 10b), which is unfavourable from the energetic point of view. So an additional problem arises: under what conditions does the globule have the structure A (or B)?

Using the considerations analogous to those of the previous section it is possible to reduce Eq. (5.17) to the linear equation for the function $\Psi_{out}(\tilde{x}, \tilde{u})$:

for the structure A

$$\tilde{g} \Psi_{out} + \sqrt{\omega} \left( \Psi_{-} - \Psi_{+} \right) \tilde{g}_{0}(\tilde{x}) = \Lambda \Psi_{out}(\tilde{x}, \tilde{u}) ; \quad (5.31)$$

for the structure B

$$\tilde{g} \Psi_{out} + \sqrt{\omega} \left( \Psi_{-} - \Psi_{+} \right) \left[ \tilde{g}_{0}(\tilde{x} - \frac{\tilde{u}}{2}), \tilde{g}_{0}(\tilde{x} + \frac{\tilde{u}}{2}) \right] = \Lambda \Psi_{out}(\tilde{x}, \tilde{u}) ; \quad (5.32)$$

In the first case the origin is chosen at the end of the "sheaf", in the second case the origin is in its middle point. The solutions of these equations are:

for the structure A

$$\Psi_{out} = \frac{\sqrt{\omega} (\Psi_{-} - \Psi_{+})}{(2\pi)^{3}} \int e^{-i\tilde{r}\tilde{u}} \frac{g_{0}^{\lambda}}{\Lambda - \frac{\partial^{2}}{\partial \tilde{u}^{2}}} d^{3}\tilde{r} , \quad (5.33)$$

for the structure B

$$\Psi_{out} = \frac{\sqrt{\omega} (\Psi_{-} - \Psi_{+})}{(2\pi)^{3}} \int e^{-i\tilde{r}\tilde{u}} \frac{g_{0}^{\lambda}}{\Lambda - \frac{\partial^{2}}{\partial \tilde{u}^{2}}} \cdot 2 \cos(\tilde{k} \tilde{u}) \; d^{3}\tilde{r} . \quad (5.34)$$

It is noteworthy that in both cases the distribution of orientations outside the core remains isotropic.

The obtained formulae give some idea about the equilibrium conformation of both structures. Using these formulae it is possible to calculate and compare the free energies of these structures. Omitting the corresponding lengthy calculations we shall present only the main results.

The transition between both globular structures and the coil state turns out to be the I order phase transition. The relation between the free energies of the structures A and B depends on the temperature and on the characteristic dimensionless parameter $\varepsilon_{0}$. The latter dependence is manifested already at the temperatures which are much lower than the coil-globule transition temperature, i.e. formally at $\varepsilon_{0} \gg 1$. In this region the following simple result can be obtained:

$$\Delta F = F_A - F_B \approx \frac{T}{N} \ell_{0} \left[ \int_{\kappa}^{\varepsilon_{0}} \frac{\kappa^{2} \sin^{2} \frac{\kappa L}{2}}{\kappa L / 2} d \kappa \right] \quad (5.35)$$

In particular, for the Gaussian function $g_0(x)$, i.e. for $g_{0} = \exp \left( - \frac{x^2}{2} \right)$, we find

$$\frac{\Delta F}{NT} = \ell_{0} \frac{2}{3} - \frac{3}{8} \left( \frac{L}{\varepsilon_{0}} \right)^{2} \quad (5.36)$$

* From Eqs. (5.33) and (5.34) it is clear that the value of $\Lambda$ increases upon the lowering of the temperature (since the fraction of rods in the fringe decreases).
Just as it was expected the parallel orientation (the structure A) is more stable for large \( i \) and small \( a \) and vice versa.

The temperature dependence of \( \Delta F \) is described by somewhat more complex formulae, which we shall not consider here for the sake of brevity. The result of the analysis of these formulae is illustrated in Fig.12. The main conclusion which can be drawn from Fig.12 is physically obvious: when the temperature is increased the structure B becomes more and more favourable; the transition A\( \rightarrow \)B is the \( \frac{1}{2} \) order phase transition. It is noteworthy that this transition takes place at the temperature, at which the typical number of rods is one "loop" defect (Fig.10b) becomes of order \( \frac{1}{i/a} \).

5.6 Small globule for persistent chain

In the persistent chain there are no points of easy bending; persistent molecule prefers the conformations with the constant small curvature. So as soon as the chain elements in the liquid-crystalline globule are oriented mainly in the tangential direction (see Sec.IV), the small globule formed by the persistent chain must have the tendency to form the cavity in the middle of the globule. Thus, in this case the globule has the form of either the torus or the spherical layer.

We shall show below that the structure of the torus type (or of the spherical layer type) with the cavity in the middle of the globule can be stable only for the persistent molecules, which are not very long. This is the reason for calling this structure the small globule.

It is clear that the average curvature in the torus conformation is smaller than in the conformation of the spherical layer (in the case of the dense packing). Thus the equilibrium structure is actually the toroidal one (Fig.12); it is this structure that will be considered below. The structure of the spherical layer type is metastable and can be analysed along the same lines.

Since the toroidal globule can be formed only as a result of strong enough attraction of the parts of the molecule (in any case it must be \((\delta/T)>\frac{4}{3}\bar{\gamma}L^2\)) the volume of the torus is approximately equal to the self-volume of the molecule, i.e.

\[ Rz^2 \sim Ld^2, \quad (5.37) \]

where \( L \) is the contour length of the molecule, \( R \) and \( r \) are the torus radii (see Fig.12). It is also clear that the volume part of the energy of the interaction between the parts of the chain does not depend on the form of the torus, i.e. on the radii \( R \) and \( r \) separately, and is equal to \(-\gamma Ld/d\) (see Eq.(2.10)).

Besides the volume part of the energy, the free energy of the globule contains two other contributions - the conformational entropy \((5.3)\) and the surface energy.

Performing the smoothing procedure (see Subsec.3.3) in the formula \((5.3)\) it is possible to find the following expression for the conformational entropy of the globule formed by the persistent chain:

\[ S = \int \left( \Psi(\mathbf{x}, \mathbf{u}) \left[ \nabla \cdot \mathbf{u} + \frac{2}{\gamma} \Delta \mathbf{u} \right] d^3 \mathbf{x} \right), \quad (5.38) \]

\[ \mathcal{A} \ln \mathcal{E} = \Psi \cdot \mathbf{u}. \quad (5.39) \]

The entropy given by Eqs.(5.38) and (5.39) can be easily estimated for the torus conformation (see Ref.16). The result is \( S \sim -4\pi/(\pi)^{1/2} \).

As to the surface free energy, obviously it is of order \( \Delta \mathcal{F}_{sur} \sim \bar{\gamma} Rr/d^2 \). So we can write down the expression for the total free energy of the toroidal globule in the form

\[ F \sim -\text{const} \cdot \bar{\gamma} L/d + \text{const} \cdot \bar{\gamma} L (d^2)^{1/3} + \text{const} \cdot \bar{\gamma} L \bar{\gamma}/d \], \quad (5.40) \]

where we have taken into account the additional condition \((5.37)\). Minimizing this free energy with respect to \( r \), we can find the equilibrium radii of the toroidal structure

\[ R \sim \left( \frac{T}{\bar{\gamma}} \right)^{1/3} \frac{\bar{\gamma} L^{1/3}}{d^{1/3}} \quad ; \quad \varepsilon \sim \left( \frac{\bar{\gamma} L}{T} \right)^{1/3} \frac{d^{1/3} \bar{\gamma}^{1/3}}{\bar{\gamma}^{2/3}}. \quad (5.41) \]

The obvious condition \( R \gg r \) means

\[ \text{const.} \left( \frac{\bar{\gamma} L}{T} \right) < \frac{d}{L}. \quad (5.42) \]
As was expected, the toroidal globule can be formed only by stiff enough chains (large \( p = l/d \)). The inequality (5.42) specifies the low temperature boundary of the region of existence of the toroidal globule. The existence of the low temperature boundary is the natural manifestation of the fact that the existence of the cavity in the middle of the globule is due to the chain rigidity with respect to the bending, which is of the entropic nature. When the temperature is lowered below this low temperature boundary, the globule takes its usual form without the cavity (it must be kept in mind, however, that in reality the persistent length \( l \) is also dependent on the temperature).

By substituting the equilibrium torus radii (5.41) in the formula (5.40) we obtain the expression for the equilibrium value of the globular free energy, from which it can be seen that under heating the toroidal globule transforms into the coil state, the corresponding phase transition being of the first order. For the temperature and the heat of the transition we obtain, correspondingly,

\[
\frac{\epsilon}{T} \sim l / (4d)^{1/2} ,
\]

\[
Q \sim \epsilon l / d .
\]

It should be noted that the toroidal globule can be stable only if the formation of the structural defect of the "loop" type (compare with the structures A and B in the previous section) is improbable. (In the presence of this defect two parts of the chain can twist round the torus cavity in the opposite directions). Indeed, if such defects were possible, the following equalities would be valid: \( \psi(x,\theta) = \psi(x,-\theta) = \psi(x,0) \) and in this case the first term of the conformational entropy (5.38) would turn into zero. From the physical point of view, this fact means that due to these defects the cavity in the middle of the globule is destroyed. The detailed analysis shows (see Ref.16) that the formation of the defects of this type is practically forbidden until

\[
L / l \ll \rho^2
\]

So the inequality (5.45) is, as a matter of fact, the criterion of the small globule for the persistent model. If this inequality is satisfied (i.e. if the macromolecule is not too long), the globular structure with the cavity in the centre is formed, for longer chains this cavity is destroyed by the structural defects.

5.7 Concluding remark

We see that in contrast to the case of long macromolecules the spatial structure of the small globules depends essentially on the details of the chain structure. The relative universality of the three-dimensional globular structure of long macromolecules and rather strong dependence of this structure on the microscopic details for the shorter macromolecules is apparently the general characteristic feature of polymer globules. A more profound understanding of this feature would probably be interesting for molecular biophysics.

VI. CONCLUSION

In conclusion, let us make some remarks concerning the correspondence between the theoretical results obtained above and the experimental data.

Quantitative experimental results in the field of lyotropic polymeric liquid crystals are now available mainly for the solutions of completely stiff macromolecules [1,2,4,6]. These results are in good qualitative agreement with the conclusions of the Flory theory [9] and, thus, with the results of Sec.II. To reveal the deviations from the Flory theory found in this paper, more accurate and systematic measurements are needed.

The orientational ordering in the solutions of semiflexible macromolecules which was considered in Sec.III is now poorly studied from the experimental point of view. The direct measurements of the properties of the corresponding liquid-crystalline transition are practically absent in the literature in spite of the general interest to this problem.

Some experimental data [40]-[42] show that the double-helix DNA macromolecules exist in the polyethylene glycol solution in the so-called compact form, which is very similar to the toroidal globule considered in Sec.V. The electron microscopy photographs definitely show the existence of cavities in the middle of the globules. Of course, to develop an adequate theory of the compact form of DNA it is necessary to take into account some more refined peculiarities of the system and, primarily, the role of polyethylene glycol (see recent works [43]-[45]). However, we emphasize that the fact of the existence of the cavity in the middle of the globule is, apparently, the fundamental consequence of the absence of the points of easy bending in the polymer chain and so more refined theories must use as a starting point the simple considerations of Subsec.5.6 of this paper.
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APPENDIX

Intramolecular orientational ordering in the isotropic phase

The formation of the liquid-crystalline globule is always accompanied by the significant orientational ordering of the segments. Nevertheless, the orientational ordering is not always connected with the liquid-crystalline phase, it exists also in the isotropic macromolecule (either in the coil or in the globular state). This orientational ordering, which is not liquid-crystalline in its nature, is caused by the inhomogeneity of the density distribution in the macromolecule; the effect of the inhomogeneous density distribution is from a certain point of view analogous to the effect of the external orientational field.

At first let us consider the orientational ordering in the isotropic globule. Since the monomer density profile in this case has the form shown in Fig.8a, the orientational ordering is most pronounced in the globular surface layer, where the density gradient is maximal. However, it is natural to assume that the corresponding non-liquid-crystalline anisotropy is small, so that it is possible to expand the angular dependence of the generalized density $n(\mathbf{r}, \mathbf{u})$ in the Legendre polynomials and to keep only the term with the second polynomial $P_2$:

$$n(\mathbf{r}, \mathbf{u}) \cong c(r) \left( 1 + s(r) P_2 (\cos \beta) \right), \quad \text{(A.1)}$$

where $r$ is the co-ordinate along the radius of the globule, $\beta$ is the angle between $\mathbf{u}$ and $\mathbf{x}$ (the origin is chosen in the centre of the globule), $c(r)$ is the spatial concentration of monomers and $s(r)$ is the parameter of the orientational ordering defined in a usual way [28] (to be definite we shall imply here and below that we are dealing with the model shown in Fig.7b). The calculation based on the expansion of Eq.(5.6) in the Legendre polynomials leads to the following results. The profile of the spatial concentration $c(r)$ coincides with one found in Ref.24 for the model of "beads" (see Eq.(4.16) of Ref.24 and Fig.13a). As to the function $s(r)$, slightly below the $\theta$ temperature (where it is enough to take into account only the second and the third virial coefficients of the interaction of monomers, $\Lambda$ and $\Lambda'$) it is equal to

$$s(r) = \frac{a^2}{a^2 + \zeta^2} \frac{c(r) \left[ \Lambda + 2 \zeta C \right]}{c(r) \left[ \Lambda + 2 \zeta C \right]}. \quad \text{(A.2)}$$
For the persistent model we must put here $a = 0$. It should be recalled that in the centre of the globule $B + 2 C_0 = 0$ (compare with Eq. (A.3)). Taking into account also the fact that $B$ is negative below the $S$ temperature, it is easy to understand that the function $s(r)$ has the form shown in Fig. 13b.

These results show that in the surface layer of the isotropic globule the segments are oriented mainly parallel to the surface (as in the liquid-crystalline globule, although the corresponding order parameter is much smaller). In both cases such a situation is due to the fact that if the chain enters the surface layer, it must finally return back to the globular core. Thus it is natural that the function $s(r)$ increases with the increase of the ratio $I/a$.

Now let us consider the orientational ordering in the isotropic coil with the excluded volume (i.e. in the coil dissolved in the good solvent). The surface anisotropy in the isotropic globule is, as a matter of fact, due to the fact that the globule is more dense than the Gaussian coil and so when the chain enters the surface layer it has the tendency to return inside the globule. In the swollen coil with the excluded volume it is natural to expect the orientational ordering of the opposite sign - the segments must be oriented mainly in the radial direction.

The degree of the orientational ordering in the swollen coil can be estimated with the help of the Edwards equation (see Ref. 24)

\[
\frac{\partial Z_N \left( \vec{x}, \vec{u} \right)}{\partial N} = (g - 1) Z_N \left( \vec{x}, \vec{u} \right) - 2 C(\vec{x}) B,
\]

(A.3)

which plays for the coils the same role as Eq. (5.6) for the globules. In Eq. (A.3) $Z_N \left( \vec{x}, \vec{u} \right)$ is the partition function of the $N$-link chain with the beginning fixed at the origin and end monomer fixed at the point $\vec{x}$ and oriented in the direction $\vec{u}$. Of course, the application of the self-consistent theory of the Edwards type to the coils is not exact (for more details on this point see Refs. 24 and 25), but it can be used for the rough estimations.

The calculation based on the expansion of Eq. (A.3) in the Legendre polynomials, which is completely analogous to the corresponding calculation for the globular case, shows that the parameter of the orientational ordering $s(r) \sim N \langle \xi^2 \rangle / R^2$, i.e. at the typical distance $r \sim \langle \xi^2 \rangle^{1/2}$

\[
s \sim (p^2 N)^{1/5},
\]

(A.4)

As was expected, $s > 0$, i.e. the segments are oriented mainly along the radii. We emphasise that the result (A.4) is valid only for the coil with the excluded volume, i.e. for the case $N \gg p^2$ [34]; consequently, the orientational ordering is weak: $s \ll 1$.

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FIGURE CAPTIONS

Fig.1 a) Completely stiff macromolecule; b) semiflexible freely-jointed macromolecule; c) semiflexible persistent macromolecule.

Fig.2 T-9 phase diagram for the solution of rods obtained in Ref.9. I - isotropic solution; II - anisotropic solution; III - phase separation region.

Fig.3 a) The area of contact is proportional to 1/sin y; b) area of contact is proportional to qd.

Fig.4 Phase diagram: coexistence curves in the high temperature and low temperature limits.

Fig.5 Regions of the stability of homogeneous phases.

Fig.6 Phase diagram for the solution of semiflexible macromolecules. I - isotropic phase; II - anisotropic phase; III - phase separation region. Dotted line curves - phase diagram for the solution of rigid rods with the same p (see Fig.2).

Fig.7 a) Model of "beads": polymer chain is represented as a long flexible immaterial filament, on which interacting "beads" are strung, a - mean square spatial distance between subsequent along the chain "beads"; b) chain composed of rods connected by flexible spacers: rods have the length l and the diameter d, p = l/d >> 1, a is the mean square distance between the ends of a flexible spacer; c) flexible chain with the rod-like side groups: notations are the same as in the previous case; d) persistent chain of width d and of effective segment l, p = 1/d >> 1.

Fig.8 a) Spatial distribution of the polymer volume fraction in the large globule; b) field of orientations of the director of mesophase.

Fig.9 "Sheaf-like" small globule. Rods outside the "sheaf" form the defects of the globular structure. Both the defects of the "loop" type (left) and of the "tail" type (right) are shown.
Fig. 10 Two possible structures of the small globule for the model of Fig. 7c.

Fig. 11 Phase diagram for the macromolecule with the flexible main chain and rod-like side groups.

Fig. 12 Toroidal small globule for persistent macromolecule.

Fig. 13 Functions $c(r)$ and $s(r)$ in the isotropic globule.
**Fig 11**

isotropic coil

**Fig 12**

**Fig 13**

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