Landau-de Gennes free energy expansion for nematic polymers

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Classification
Physics Abstracts
61.30C — 36.20E

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Résumé. — Les coefficients du développement de l'énergie libre de Landau-de Gennes des polymères nématiques sont évalués dans le cadre d'un modèle moléculaire statistique. Nous montrons que le développement obtenu fournit une description qualitative fiable de la transition de phase vers l'état nématique pour des polymères de rigidité et de longueur moléculaire arbitraires. Cette transition est toujours du premier ordre. Le saut du paramètre d'ordre ne dépend que faiblement de la longueur et de la rigidité des molécules.

Abstract. — The Landau-de Gennes free energy expansion coefficients for nematic polymers are evaluated on the basis of a molecular-statistical model. It is proved that the obtained expansion provides a reliable qualitative description of the phase transition to the nematic state for polymers with arbitrary molecular length and rigidity. It is demonstrated that this transition is always of the first-order type and the jump of the order parameter is weakly dependent on the molecular length and rigidity.

1. Introduction.

In the continuum Landau-de Gennes theory the free energy is expanded in powers of the nematic order parameter

$$F = A\eta^2 - B\eta^3 + C\eta^4 , \tag{1}$$

where the coefficients are phenomenological constants. The evaluation of these coefficients in the framework of any appropriate molecular-statistical model is of definite interest because it substantially reduces the number of arbitrary parameters employed in the expansion (1). For example, if one would use the Maier-Saupe model [1, 2], which fits well the theory of low-molecular-weight liquid crystals, it is possible to express all the expansion (1) coefficients in terms of only one parameter, the molecular field constant V_0 [2].

From our point of view, in the polymer liquid crystals theory, an approach of this kind is the only possible one. As a matter of fact, in the case of polymers the Landau-de Gennes expansion coefficients, besides V_0, have to depend on the molecular length and rigidity as well. But there exists no method of purely phenomenological origin which would be capable of determining these dependencies.

The molecular-statistical theory of linear nematic polymers has been discussed in references [3] to [6]. In all these papers the orientational interactions between the chain molecule segments have been treated in a mean-field approximation similar to that of the Maier-Saupe theory. The cited papers employ, however, different models of polymer molecule flexibility. The simplest model — free-linked chain — has been studied in [3]. The orientational phase transition in an assembly of semi-flexible persistent molecules has been considered in [4]. A simplified theory, describing persistent molecule conformations in mean-spherical (Gaussian) approximation, has been developed in [5]. A somewhat more general, in comparison with that of [4], model has been constructed in [6], where the polymer molecule has been approximated by a succession of chain-linked rod-like segments with a finite link rigidity U.

In the present paper a calculation of the expansion coefficients, as functions of U, V_0, the molecular length N and temperature T is given for the model [4]. In this persistent model the uniaxial nematic order parameter is defined as follows

$$\eta = N^{-1} \int_0^N ds < P_2(\mathbf{n}\mathbf{v}_s) >, \tag{2}$$

where $\mathbf{n}$ is the director, $\mathbf{v}_s$ is a unit vector tangent to the s-th part of the chain and $P_2(x)$ is the Legendre polynomial.

In section 2 the expression for non-equilibrium free energy F corresponding to the model [4] is presented and discussed. In section 3 this expression is expanded into powers of the order parameter η i.e. the Landau-de Gennes expansion is constructed. The latter is employed in section 4 for the calculation of nematic-isotropic phase transition characteristics. Then the obtained quantities viz. the transition temperature T_t and the equilibrium order parameter jump η_t are compared with the results of the exact numerical solution of the molecular-statistical model described in section 2.

Calculation of the Landau-de Gennes expansion coefficients on the basis of the persistent model [4] has been carried out in [7]. However, the authors of [7] while expanding the partition function (see Sect. 3) have made some errors and, as a consequence of that fact, their evaluation of the coefficients in (1) turned out to be incorrect. In particular, the results of [7] predict that the transition of semi-flexible molecules ($N \sqrt{V_0/U} \to \infty$) into the nematic state asymptotically approaches the second-order phase transition ($\eta_t \to 0$). This conclusion contradicts the exact solution of the basic model [4, 6] which shows that the nematic transformation is always of the first-order phase transition type and η_t value weakly depends on the molecule length and rigidity (see Sect. 4).

2. Molecular-statistical model.

In equilibrium the distribution function corresponding to the given macromolecular conformation $\{ \mathbf{v}_s \}$ has the form [4, 7]

$$W_{eq}(\{ \mathbf{v} \}, N) = Z_N^{-1} \left(\frac{V_0 \eta}{T} \right) \exp \left\{ - \int ds \left[\frac{q}{2} \left(\frac{\partial \mathbf{v}}{\partial s} \right)^2 - \frac{V_0 \eta}{T} P_2(\mathbf{n}\mathbf{v}_s) \right] \right\}$$

where $q = U/T$ is the persistent molecule length and V_0 is the molecular-field constant per link. Proceeding to the treatment of non-equilibrium states, we use the idea which was proposed by Leontovitch [8] and is now known in thermodynamics as the « effective » field method. According to this idea some additional field is introduced : this transforms the state previously non-equilibrium (without this field) into an equilibrium state .Concerning the statistics it means that the non-equilibrium distribution function retains the Gibbs form, but in W_{eq} the orienting field

$V_0\, \eta/T$ is changed by the « effective » field ξ :

$$W(\{\,\mathbf{v}\,\}) = Z_N^{-1}(\xi)\, \exp\left\{\int ds\left[-\frac{q}{2}\left(\frac{\partial \mathbf{v}}{\partial s}\right)^2 + \xi P_2(\mathbf{n}\mathbf{v}_s)\right]\right\},$$

$$Z_N(\xi) = \int d\{\text{ conf. }\}\, \exp\left\{-\int_0^N ds\left[\frac{q}{2}\left(\frac{\partial \mathbf{v}}{\partial s}\right)^2 - \xi P_2(\mathbf{n}\mathbf{v}_s)\right]\right\}. \tag{3}$$

Let us calculate the non-equilibrium free energy $F = E - TS$. In the mean-field approximation the internal energy is

$$E = -\frac{NV_0}{2}\,\eta^2 + \frac{U}{2}\left\langle\int_0^N ds\left(\frac{\partial \mathbf{v}}{\partial s}\right)^2\right\rangle,$$

where the angular brackets denote the averaging over all the macromolecule conformations with the distribution function W from (3) while the entropy S is connected with the same function by the relation $S = -\langle \ln W \rangle$. Employing these expressions one gets for the non-equilibrium free energy per molecule of the nematic polymer

$$F = -\frac{NV_0}{2}\,\eta^2 + T\{N\eta\xi - \ln Z_N(\xi)\}. \tag{4}$$

The latter formula includes the non-equilibrium order parameter η which is calculated, according to the definition (2), by averaging over the non-equilibrium distribution (3)

$$\eta = N^{-1}\,\partial \ln Z_N(\xi)/\partial\xi. \tag{5}$$

Thus from the pair of functions — η and ξ — entering the free energy expression (4) only one is independent. It should be noted that the relation between η and ξ, prescribed by the expression (5) is equivalent to the equation $\partial F/\partial\xi = 0$, i.e. in the framework of the employed « effective-field » method the free energy always has an extremum with respect to ξ. Equations (4) and (5) determine the non-equilibrium free energy $F(\eta)$ in the parametric form (ξ is the parameter).

In thermodynamical equilibrium $dF/d\eta_c = 0$ and, as equation (4) yields, the « effective » field coincides with the actual one

$$\xi = V_0\,\eta/T. \tag{6}$$

The system of equations (5) and (6) determines the orientation state equation $\eta = \eta(T)$. Solving it numerically under the condition of equality of the polymer free energies in the nematic and isotropic phases, one is able to find [6] the phase-transition temperature T_t and the equilibrium order parameter jump η_t. For the semi-flexible molecules ($N \to \infty$), as is shown in [4, 6], $T_t \sim \sqrt{UV_0}$, and so at the transition point the persistent length $q = U/T$ is of the order $q_t \sim \sqrt{U/V_0}$. The model under consideration contains two characteristic lengths : the entire molecule length N and the persistent (correlation) length q_t. In figures 1, 2 the dependencies of T_t and η_t on the reduced molecular length $L = N\sqrt{V_0/U} \sim N/q_t$ are shown by solid lines. As is apparent from figure 1 for small L (rigid molecules, $N \ll q_t$) the transition temperature becomes proportional to the molecular length and for $L \gtrsim 5$ approaches saturation. For the semi-rigid molecules ($L \gg 1$) the exact value is $T_t = 0.388\sqrt{UV_0}$ [4]. As to the order parameter jump, one can see from figure 2 that this quantity weakly depends on the reduced length and varies from 0.429 in the Maier-Saupe limit $L \ll 1$ to 0.356 in the semi-flexible molecule case [4, 6]. Therefore the transition of polymer into a nematic phase for arbitrary molecular length and rigidity is essentially of the first-order type.
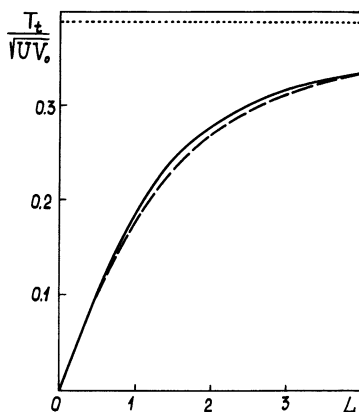
Fig. 1. — Dependence of the transition temperature on the reduced molecular length $L = N\sqrt{V_0/U}$. Solid line : the results of numerical calculation [6] ; broken line : Landau-de Gennes approximation. Dotted line : the asymptote of the function $T_t(L)$ for $L \to \infty$.
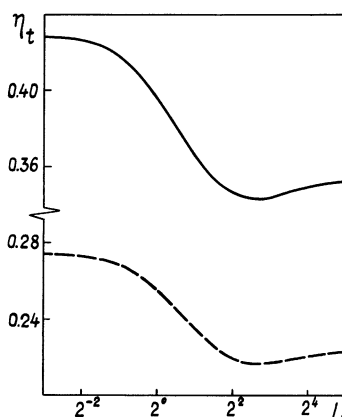
Fig. 2. — Dependence of the order parameter jump at the transition point on the reduced length. Notations are the same as for figure 1.

3. The Landau-de Gennes expansion.

In order to provide the required expansion one has to use formulae (4) and (5) which determine the dependence $F(\eta)$ in parametrical form (with ζ playing the rôle of the parameter). Since the the Landau-de Gennes expansion has to be valid for non-equilibrium states as well, while constructing it one must not use the equilibrium relation (6) between ζ and η.

The proposed expansion procedure includes three steps :

i) the partition function (3) expansion into the powers of ζ with an accuracy up to ζ^4 ;

ii) the evaluation of $\zeta(\eta)$ dependence on the basis of equation (5) to the accuracy level cited in i) ;

iii) the elimination of the parameter ζ from the free energy expression (4) with the aid of the relation obtained in ii).

The partition function (3) is expanded in the powers of ξ as follows

$$Z_N(\xi) = Z_N(0) \left(1 + \sum_{n=2}^{4} I_n \xi^n \right),$$

$$I_n = \int_0^N ds_1 \int_0^{s_1} ds_2 \dots \int_0^{s_{n-1}} ds_n \langle P_2(s_1) P_2(s_2) \dots P_2(s_n) \rangle_0, \quad P_2(s) \equiv P_2(\mathbf{nv}_s).$$

$$(7)$$

The notation $\langle \dots \rangle_0$ in the coefficients I_n indicates the averaging over the isotropic ($\xi = 0$) distribution. Note that the expansion (7) begins from ξ^2 due to the fact that the linear term coefficient is proportional to the order parameter of the isotropic phase and is thus always equal to zero.

The isotropic part of the partition function may be rearranged as follows

$$Z_N(0) = \int d\mathbf{v} \int d\mathbf{v}' \, G_N(\mathbf{v}, \mathbf{v}'),$$

$$(8)$$

where G_N is the partition function of the persistent molecule of the length N with the fixed orientation $\mathbf{v}$ and $\mathbf{v}'$ of its ends in the isotropic phase of the polymer. This function may be expressed in the form of a series in the full orthonormal basis of spherical harmonics [9]

$$G_N(\mathbf{v}, \mathbf{v}') = \sum_{l,m} \exp\left[-\frac{l(l+1)}{2q} N \right] Y_{lm}(\mathbf{v}) \, Y_{lm}(\mathbf{v}').$$

$$(9)$$

The expansion (7) coefficients include the correlation functions ordered along the chain ($N \geqslant s_1 \geqslant s_2 \dots$), which are calculated with the aid of the propagator (9). The result of calculation is

$$K_2(s_1, s_2) \equiv \langle P_2(s_1) P_2(s_2) \rangle_0 = \frac{1}{5} \exp\left[-\frac{3}{q}(s_1 - s_2) \right],$$

$$K_3(s_1, s_2, s_3) = \frac{2}{35} \exp\left[-\frac{3}{q}(s_1 - s_3) \right],$$

$$(10)$$

$$K_4(s_1, s_2, s_3, s_4) = \frac{1}{5} \exp\left[-\frac{3}{q}(s_1 + s_3 - s_2 - s_4) \right] \times$$

$$\times \left\{ \frac{1}{5} + \frac{4}{49} \left[\exp\left(-\frac{3}{q}(s_2 - s_3) \right) + \frac{9}{5} \exp\left(-\frac{10}{q}(s_2 - s_3) \right) \right] \right\}.$$

Substituting these correlators into (7) and performing integration, one obtains the coefficients I_n and thus gets

$$\ln \{ Z_N(\xi)/4\pi \} = N(a\xi^2 + b\xi^3 + c\xi^4),$$

$$a = \frac{I_1}{5} \left(\frac{q}{3} \right), \qquad b = \frac{2\,I_2}{35} \left(\frac{q}{3} \right)^2,$$

$$(11)$$

$$c = \frac{1}{25} \left(\frac{q}{3} \right)^3 \left\{ I_3 - \frac{\rho}{2} I_1^2 + \frac{20}{49} \left(I_4 + \frac{9}{5} I_5 \right) \right\}.$$

Here the following notations are introduced

$$I_1 = 1 - \varphi, \qquad I_2 = 1 + e^{-\rho} - 2\varphi, \qquad I_3 = \frac{\rho}{2} - 2 - e^{-\rho} + 3\varphi,$$

$$I_4 = 1 + \left(2 + \frac{\rho}{2}\right) e^{-\rho} - 3\varphi,$$

$$I_5 = 3\left(\frac{1}{10} + \frac{1}{7} e^{-\rho} - \frac{11}{49}\varphi - \frac{9}{490}\psi\right), \tag{12}$$

$$\varphi = (1 - e^{-\rho})/\rho, \qquad \psi(\rho) = \varphi\left(\frac{10}{3}\rho\right),$$

where $\rho = 3N/q$. For very rigid molecules ($\rho \to 0$) the preceding formulae yield

$$a_0 = N/10, \qquad b_0 = N^2/105, \qquad c_0 = -N^3/700, \tag{13}$$

which corresponds to the low-molecular-weight nematics [2]. In this limiting case the dominating contribution to the partition function is provided by straight-lined molecular conformations and hence expression (3) acquires the well-known form of the Maier-Saupe model partition function

$$Z_N(\xi) = \int_0^1 dx \exp\{N\xi P_2(x)\}.$$

The expansion of this function in a power series of $N\xi$ immediately leads to the result (13). (For very rigid molecules the expansion parameter is $N\xi$ because the orienting field rotates such a molecule as a whole.)

For semi-flexible molecules ($\rho \to \infty$) from (11) and (12) one finds

$$a_\infty = q/15, \qquad b_\infty = \frac{2}{35}\left(\frac{q}{3}\right)^2, \qquad c_\infty = -\frac{13}{875}\left(\frac{q}{3}\right)^3. \tag{14}$$

In this case formula (11) takes the form

$$\ln\{Z_N(\xi)/4\pi\} = \frac{N}{q}\left\{\frac{3}{5}\left(\frac{q\xi}{3}\right)^2 + \frac{6}{35}\left(\frac{q\xi}{3}\right)^3 - \frac{39}{875}\left(\frac{q\xi}{3}\right)^4\right\}.$$

From the latter it is apparent that for semi-flexible molecules, as could be expected, the expansion parameter is $q\xi$. The orientational properties of such a molecule are similar to those of the free-linked chain, containing N/q segments with equal lengths q.

Substituting the expansion (11) into the order parameter definition (5), one obtains an equation for ξ

$$4c\xi^3 + 3b\xi^2 + 2a\xi = \eta. \tag{15}$$

Since we intend to consider the free energy expansion in the order parameter powers only with an accuracy up to η^4 (see Eq. (1)) then while determining ξ from the latter equation we omit the terms higher than η^3, i.e. $\xi = \alpha\eta + \beta\eta^2 + \gamma\eta^3$. Substitution of this expansion into (15) allows one to express the coefficients α, β and γ through a, b and c from (11). Substituting $\xi(\eta)$ into the free energy expression (4), one finds the Landau-de Gennes expansion coefficients (1) :

$$A = \tfrac{1}{2} NV_0(T/T_c - 1), \qquad B = NTb(2a)^{-3}, \qquad C = NT(9b^2/4a - c)(2a)^{-4}. \tag{16}$$

Here $T_c = 2 a V_0$ is the Curie temperature below which the isotropic phase is absolutely unstable. It is worth noting that the coefficients B and C do not depend on the molecular field constant V_0. The latter, as can be seen from equation (4), enters only the bilinear in η energetic component E of the free energy $F = E - TS$; the terms with η^3 and η^4 in the expansion (1) are of pure entropy origin.

4. The nematic ordering of the polymer.

Substitution of expansion (1) into the stability condition $\partial F / \partial \eta = 0$ yields the orientation state equation

$$4 C \eta^2 - 3 B \eta + 2 A = 0. \tag{17}$$

The parameters of the equilibrium transition of the isotropic polymer into the nematic phase are determined by compatible solution of equation (17) and the condition of free energy equality of both phases which reads :

$$C \eta^2 - B \eta + A = 0. \tag{18}$$

For the transition temperature T_t and the order parameter jump η_t one finds

$$\begin{aligned}
\eta_t &= B/2\,C = 4\,a^2\,b/(9\,b^2 - 4\,ac)\,, \\
T_t &= T_c[1 + b^2/(8\,b^2 - 4\,ac)]\,,
\end{aligned} \tag{19}$$

where a, b and c are defined by equation (11). Since these coefficients are temperature-dependent, we have to substitute into equation (19) their values corresponding to the T_t point. Therefore the second relation of (19) turns out to be the equation determining the transition temperature. This equation is easy to solve in the limiting cases of rigid and semi-flexible molecules for which the coefficients a, b and c are determined by formulae (13) and (14) respectively. The results are as follows :

— for short chains ($\rho \to 0$)

$$\begin{aligned}
T_t &= 0.214\,N V_0 \quad &(T_t &= 0.220\,N V_0)\,, \\
\eta_t &= 0.275 \quad &(\eta_t &= 0.429)\,;
\end{aligned} \tag{20}$$

— for semi-flexible molecules ($\rho \to \infty$)

$$\begin{aligned}
T_t &= 0.381\,\sqrt{U V_0} \quad &(T_t &= 0.388\,\sqrt{U V_0})\,, \\
\eta_t &= 0.222 \quad &(\eta_t &= 0.356)\,.
\end{aligned} \tag{21}$$

The results of numerical evaluation of the original molecular-statistical model [4, 6] described in section 2 are given in parentheses for comparison. For the intermediate values of ρ the equation for T_t has been solved numerically. The T_t and η_t dependencies on the reduced molecule length obtained from equations (11) and (19) are plotted in figures 1, 2 (broken lines). As is apparent from these figures, where the solid lines represent the exact results, the Landau-de Gennes expansion is qualitatively correct for the description of $T_t(L)$ and $\eta_t(L)$ curves in the whole range $0 < L < \infty$ of the relative molecular length. This good agreement achieved may be considered to be an important confirmation of the validity of the proposed method. In the paper quoted above [7] due to an error, which has probably been made during the symmetrization of the correlator K_4, the coefficient c in expansion (11) has been calculated uncorrectly.

For the limiting cases $\rho \to 0$ and $\rho \to \infty$ the results of [7] provide $c_0 \sim q^3$, $c_\infty \sim Nq^2$ while the correct asymptotics of this coefficient (see Eqs. (13) and (14)) are $c_0 \sim N^3$, $c_\infty \sim q^3$. The above mentioned error had produced the paradoxical conclusion that the η_t value tends to zero in the limiting cases of rigid and semi-flexible molecules.

One more remark is worth regarding reference [7]. As has already been explained in section 3, while constructing the Landau-de Gennes expansion one ought to use the unequilibrium free energy (4) with the order parameter defined by expression (5). The authors of [7] took another way : they have eliminated the parameter ζ from (4) with the aid of the equilibrium relation (6). The expression thus obtained

$$\tilde{F} = \frac{NV_0}{2}\eta^2 - T \ln Z_N\!\left(\frac{V_0\,\eta}{T}\right) \tag{22}$$

coincides with the real free energy function only at the extremum point $\partial \tilde{F}/\partial \eta = 0$. If one would use equation (22) for the evaluation of the expansion coefficients (1), then it would turn out that in the limiting cases of rigid and semi-flexible molecules the order parameter jumps are $\eta_t(0) = 0.772$ and $\eta_t(\infty) = 0.981$ respectively. It is apparent that the latter values by no means can pretend to be even in qualitative agreement with the results of the exact evaluation of the original model (see Eqs. (20) and (21)).

5. Discussion.

The present paper is based on the molecular-statistical model of nematic polymers [4, 6], where the molecules are approximated by finite-length elastic threads and intermolecular orientational interactions are taken into account with the aid of mean-field approach. After expanding the free energy in power series of the order parameter η with η^4 accuracy the Landau-de Gennes expansion coefficients have been determined. It has been demonstrated that near the phase transition point the obtained expansion retains all the essential features of the original molecular-statistical model. The phase transition of the polymer into the nematic state is always accompanied by a finite jump η_t of the order parameter (the first-order phase transition) and the η_t value weakly depends on the molecule length and rigidity. At the transition point the orientation of semi-flexible molecules is only 20 % less than that of the most rigid ones. The transition temperature T_t grows with the molecule length N and approaches saturation for semi-flexible molecules ($N \gg q$). This very type of the $T_t(N)$ dependence was observed in experiments [4, 10].

The presented method of constructing the Landau-de Gennes expansions turns out to be a systematic one and may be used in the investigation of other problems — the case of external fields influence, mixtures, polydispersedness... First of all it is relevant to the description of liquid-crystalline polymer behaviour in external fields. With the aid of the Landau-de Gennes expansion it is quite simple to take the external fields into account. For example, in the case of mechanical stress-fields, it is sufficient to add into the right side of the expansion (1) a term proportional to the contraction of the tensors of stress σ_{ik} and of order parameter η_{ik}. This scheme may be applied to study polymer orientational ordering in non-uniform stress-fields with no additional complications. Note however that if tensor σ_{ik} is not uniaxial, as it is in the case of shear stress, then the resulting orientational tensor will be biaxial as well. It is important that under these conditions the expansion coefficients do not change, it is necessary only to substitute in (1) the order parameter powers by the corresponding invariants of the tensor η_{ik} :

$$\eta^2 \to \mathrm{Sp}\,\eta_{ik}^2, \quad \eta^3 \to \mathrm{Sp}\,\eta_{ik}^3, \quad \eta^4 \to (\mathrm{Sp}\,\eta_{ik}^2)^2 .$$

In future research the authors intend to apply the obtained expansion for studying the effect

of polymer polydispersity on the orientational phase transition into the nematic state. More or less wide molecular-mass distribution is inherent to any real polymer system. Therefore consider the corresponding averaging of the theoretical parameters to be of importance.

Acknowledgments.

The authors are indebted to Dr. Yu. L. Raikher for the critical reading of the manuscript.

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