

Nonlocal nature of the Landau free energy in the theory of polymer systems

S. V. Panyukov and S. I. Kuchanov

P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, 117924, Moscow

(Submitted 5 September 1991; resubmitted 2 October 1991)

Pis'ma Zh. Eksp. Teor. Fiz. **54**, No. 9, 499–502 (10 November 1991)

It is shown, for the first time, that the nonlocal nature of the density functional must be taken into consideration for polymers with a fairly general chemical structure.

Phase transitions in low-molecular systems are customarily described by the Landau method, which starts from an expansion of a free-energy functional $F\{\rho_\alpha\}$ of the system in powers of $\varphi_\alpha(\vec{x}) = \rho_\alpha(\vec{x}) - \bar{\rho}_\alpha$, which are the deviations of the densities $\rho_\alpha(\vec{x})$ of the various components α from their values in the disordered phase.^{1,2} Several authors have formally extended this method to the description of polymer systems.^{3,4} However, this formal use of the standard Landau theory turns out to be incorrect for real polymer systems, as we will demonstrate below. A rigorous analysis shows that the functional $F\{\rho_\alpha\}$ is very nonlocal, despite the short-range nature of the van der Waals interactions between the monomer units of the polymer molecules.

The reason for the appearance of an effective long-range effect is that the monomer units M_α are coupled with each other by chemical bonds in the macromolecule and thus cannot be treated as independent thermodynamic components within the framework of standard statistical physics. Nevertheless, one might suggest a thermodynamic description based on a density-functional method in which these units play the role of quasicomponents. When a description of this sort is used for the statistical ensemble of units M_α , and the constraints imposed by the bonds are taken into account, we no longer have the concept of a chemical potential for these quasicomponents, and the corresponding functional $F\{\rho_\alpha\}$ turns out to be very nonlocal.

To illustrate the physical meaning of this effect, we consider the simple example of a system with molecules of species i in concentrations $c_i(\vec{x})$. These molecules consist of l_i units. For given total numbers of these molecules, n_i , the entropy of this system is well known:

$$S = - \sum_i \int d\vec{x} c_i(\vec{x}) \ln \frac{c_i(\vec{x})}{e}, \quad n_i = \int d\vec{x} c_i(\vec{x}). \quad (1)$$

In a less detailed description of the system, it can be characterized by a resultant density $\rho(\vec{x}) = c_1(\vec{x})l_1 + c_2(\vec{x})l_2 + \dots$. The functional $S\{\rho(\vec{x})\}$ is found from the condition for a maximum of S in (1) with respect to $c_i(\vec{x})$ for given $\rho(\vec{x})$ and n_i . As a result, we find the following expression for the case of low-molecular systems ($l_i = 1$ for all i):

$$S\{\rho(\vec{x})\} = S_{\text{mix}} + S_{\text{loc}}\{\rho(\vec{x})\}, \quad S_{\text{loc}}\{\rho(\vec{x})\} = - \int d\vec{x} \rho(\vec{x}) \ln \frac{\rho(\vec{x})}{e}, \quad (2)$$

where the mixing entropy is related to the numbers n_i in the standard way.⁵ In the case of polymers, S_{mix} becomes a nonlocal functional of the density $\rho(\vec{x})$. The first nonvanishing term of a Landau expansion in $\varphi(\vec{x})$ of the functional is

$$S_{\text{mix}}\{\rho\} - S_{\text{mix}}\{\bar{\rho}\} = -\frac{1}{8} \int d\vec{x} d\vec{x}' K(\vec{x} - \vec{x}') \varphi^2(\vec{x}) \varphi^2(\vec{x}'), \quad K(\vec{x}) = \gamma/V. \quad (3)$$

The coefficient γ is proportional to the quantity $m_4 m_2 - m_3^2$, where $m_K = n_1 l_1^K + n_2 l_2^K + \dots$, which is expressed in terms of the moments m_K of the distribution of the polymer molecules with respect to the number of units they contain, l_i . The quantity V is the volume of the system. The local term S_{loc} in (2) has the standard form of a power series in $\varphi(\vec{x})$ in the Landau theory.

One of the most significant manifestations of a nonlocal nature is that the phase coexistence line on the (P, T) diagrams broadens out into a region of finite dimensions. As a result, at certain values of the pressure P there is a finite temperature interval on this diagram in which both phases are at thermodynamic equilibrium.

The simple arguments presented above, for the case in which the molecules are treated as point molecules, are incapable of describing superstructures with scales comparable to the size of the polymer molecules. To describe such effects, we have developed a general approach for calculating the functional

$$F(n(c), \{\rho_\alpha(\vec{x})\}) = \Omega(\mu(C), \{\rho_\alpha(\vec{x})\}) + \sum_C n(C) \mu(C), \quad (4)$$

for a given distribution of the numbers $n(C)$ of molecules of chemical structure C , where the potential $\mu(C)$ of molecule C is found from the condition

$$n(C) = -\partial \Omega(\mu(C), \{\rho_\alpha(\vec{x})\}) / \partial \mu(C). \quad (5)$$

To calculate the thermodynamic potential Ω as a functional of (generally nonequilibrium) density distributions $\rho_\alpha(\vec{x})$, it is convenient to use the Leontovich-Lifshitz formalism^{6,7}

$$\Omega(\mu(C), \rho_\alpha(\vec{x})) = \Omega_e(\mu(C), \{h_\alpha(\vec{x})\}) - \sum_\alpha \int d\vec{x} h_\alpha(\vec{x}) \rho_\alpha(\vec{x}) + \int d\vec{x} f^*(\rho_\alpha(\vec{x})), \quad (6)$$

which relates Ω to Ω_e , the thermodynamic potential of the equilibrium system of molecules whose units do not interact with each other and which are in an external field $h_\alpha(\vec{x})$ that shapes the same density distribution:

$$\rho_\alpha(\vec{x}) = \delta \Omega_e(\mu(C), \{h_\alpha(\vec{x})\}) / \delta h_\alpha(\vec{x}). \quad (7)$$

The interaction of the units with each other is taken into account by the function $f^*(\rho_\alpha)$ here. This function is well known in the theory of low-molecular liquids.⁷

The chemical potential for molecules C found from the solution of Eqs. (5) for a system with a nonequilibrium distribution $\{\rho_\alpha(\vec{x})\}$ is, for given $n(C)$, a functional of this distribution. In the case of low-molecular systems, however, there is no such functional dependence. This point can be verified easily with the help of (5)–(7), since in this case the functional Ω_e depends on its arguments only in the combinations $h_\alpha(\vec{x}) - \mu_\alpha$. In an analysis of high-molecular systems, in which the number of thermodynamic components C is usually greater than the number of quasicomponents M_α , the dependence of $\mu(C)$ on $\{\rho_\alpha(\vec{x})\}$ must be dealt with when the functional $F(n(C), \{\rho_\alpha(\vec{x})\})$ in (4) is found.

To find an explicit expression for the functional $\mu(C, \{\rho_\alpha(\vec{x})\})$, we expand the potential Ω in (6) in a functional series in powers of $\psi_\alpha(\vec{x}) = \rho_\alpha(\vec{x}) - \rho_\alpha^s$, where ρ_α^s is the density of the spatially homogeneous state of the system with a given set of chemical potentials $\mu(C)$ of all molecules C . An expansion of this sort is well known in the fluctuation theory of phase transitions,¹ in which ρ_α^s means the extent of the spontaneous ordering. The expansion coefficients $T_{\alpha_1 \dots \alpha_n}^{(n)}(\mu(C), \vec{x}_1 \dots \vec{x}_n)$ —the irreducible vertex parts—are related to the irreducible correlation coefficients $G_{\alpha_1 \dots \alpha_n}^{(n)}(\mu(C), \vec{x}_1 \dots \vec{x}_n)$ of the fluctuations of the density $\rho_\alpha(\vec{x})$ by simple equations.¹

Substituting into (1) the dependence $\mu(C, \{\rho_\alpha(\vec{x})\})$ found from (5), we reexpand the functional F in powers of the functions

$$\varphi_\alpha(\vec{x}) = \psi_\alpha(\vec{x}) + \psi_\alpha^s, \quad \psi_\alpha^s = \rho_\alpha^s - \bar{\rho}_\alpha. \quad (8)$$

The coefficients $T_{\alpha_1 \dots \alpha_n}^{(n)}(\eta(C), \vec{x}_1 \dots \vec{x}_n)$ of this expansion are the same as $\Gamma_{\alpha_1 \dots \alpha_n}^{(n)}(\mu(C), \vec{x}_1 \dots \vec{x}_n)$ for low-molecular systems, since in this case we have $\psi_\alpha^s = 0$, and the $\mu(C)$ do not depend on $\{\rho_\alpha(\vec{x})\}$. A specific feature of polymer systems is that $\Gamma^{(n)}$ differs from $T^{(n)}$ for $n \geq 4$, because of the appearance of nonlocal contributions to the vertices $\Gamma^{(n)}$, which have been ignored in previous studies.^{3,4}

The most compact representation of the vertices $\Gamma^{(n)}$ is found by a diagram technique which is a modification of one which has been used previously in the description of nonuniform fluctuations in low-molecular systems.¹ To the notation intro-

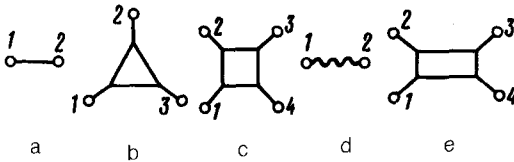


FIG. 1. Elements of the diagram technique: the n -point correlation functions $\tilde{G}_{\alpha_1 \dots \alpha_n}^{(n)}(\vec{q}_1 \dots \vec{q}_n)$ for (a) $n = 2$, (b) $n = 3$, and (c) $n = 4$. Also shown here are the function $G_{\alpha, \alpha}^{(2)}(0, 0)$ and the “brick” $G_{\alpha, \alpha, \alpha, \alpha}^{(4)}(\vec{q}_1, \vec{q}_2 | \vec{q}_3, \vec{q}_4)$.

$$\Gamma^{(4)} = \left\{ \square - \Sigma \left[\begin{array}{c} \text{Y} \\ \text{X} \end{array} \right] \right\} + \Sigma \left[\left[\begin{array}{c} \text{X} \\ \text{Y} \end{array} \right] - \square \right\} + \Gamma_{int}^{(4)}$$

FIG. 2. Diagram representation of the vertex $\Gamma^{(4)}$.

duced in Ref. 1 for the correlation functions $G^{(n)}$ (Fig. 1, a-c), we will add some additional diagrams for our modification of the technique. At $n = 4$, for example, these additional diagrams are the wavy line and the "brick" in Fig. 1, d and e. Corresponding to these diagram elements in an analysis of polymer systems in the momentum representation are the following expressions:

$$\tilde{G}_{\alpha_1 \dots \alpha_n}^{(n)}(\vec{q}_1 \dots \vec{q}_n) = \sum_C n(C) g_{\alpha_1 \dots \alpha_n}^{(n)}(C, \vec{q}_1 \dots \vec{q}_n), \quad (9)$$

$$\tilde{G}_{\alpha_1 \alpha_2 | \alpha_3 \alpha_4}^{(4)}(\vec{q}_1 \vec{q}_2 | \vec{q}_3 \vec{q}_4) = \sum_C n(C) g_{\alpha_1 \alpha_2}^{(2)}(C, \vec{q}_1 \vec{q}_2) g_{\alpha_3 \alpha_4}^{(2)}(C, \vec{q}_3 \vec{q}_4),$$

where $g_{\alpha_1 \dots \alpha_n}^{(n)}(C, \vec{q}_1 \dots \vec{q}_n)$ is the Fourier component of the n -point correlation function of the density of the units of molecule C (these units do not interact with each other). The correlation functions $G^{(n)}$ in (9) are equal to $G^{(n)}(\mu(C), \dots)$ for the particular choice $\mu(C) = \mu(C, \{\bar{\rho}_\alpha\})$.

Figure 2 shows a graphic representation of the vertex $\Gamma^{(4)}$ in this notation. The term $\Gamma_{int}^{(4)}$, which reflects the interaction of the units, is equal to the corresponding fourth derivative of the function $f^*(\rho_\alpha)$ in (6). As in Ref. 1, the symbols Σ mean a summation over all partitionings of the arguments into groups. The expression in braces (curly brackets) in Fig. 2 has the standard form¹ for $T^{(4)}$, while the other terms (which are generally not small in comparison with $T^{(4)}$) are associated with the nonlocal nature of the functional F . The first and second terms in square brackets arise because of the reexpansion of ψ'_α and $T^{(2)}$ [see (8)], respectively. They cancel each other out exactly in the case of low-molecular systems.

Nonlocal effects are particularly important in the derivation of a theory of periodic superstructures in heteropolymer systems. For melts of polyblock heteropolymers, for example, these effects lead⁸ to the formation of superstructures with a period which depends strongly $\sim (T_c - T)^{-1/2}$ on the proximity of the temperature T to the critical temperature T_c .

The approach proposed in this letter is evidently of general interest for the theory of real polymer systems, since it predicts phase diagrams qualitatively different from those found in an analysis of such systems without consideration of the nonlocal nature of the functional $F\{\rho_\alpha\}$.

One of us (S.I.K.) wishes to thank S. Edwards for useful discussions.

- ¹A. Z. Patashinskiĭ and V. G. Pokrovskiĭ, *Fluctuation Theory of Phase Transitions*, Pergamon, New York, 1979.
- ²S. A. Brazovskii, Zh. Eksp. Teor. Fiz. **68**, 175 (1975) [Sov. Phys. JETP **41**, 85 (1975)].
- ³I. Ya. Erukhimovich, NTsBI Preprint, Pushchino, 1985.
- ⁴A. V. Dobrynin and I. Ya. Erukhimovich, Vysokomol. Soedin. A **33**, 1100 (1991).
- ⁵L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon, New York, 1980.
- ⁶M. A. Leontovich, *Introduction to Thermodynamics. Statistical Physics*, Nauka, Moscow, 1983.
- ⁷I. M. Lifshits, A. Yu. Grosberg, and A. R. Khokhlov, Usp. Fiz. Nauk **127**, 353 (1979) [Sov. Phys. Usp. **22**, 123 (1979)].
- ⁸S. V. Panyukov and S. I. Kuchanov, Zh. Eksp. Teor. Fiz. **99**(2), 659 (1991) [Sov. Phys. JETP **72**, 368 (1991)].

Translated by D. Parsons