

Statistics of polymers in random media

S. V. Panyukov

P. N. Lebedev Physics Institute, Moscow

(Submitted 11 November 1992)

Zh. Eksp. Teor. Fiz. **103**, 1287–1304 (April 1993)

A theory of localized states of linear and branched polymer macromolecules in a medium with “quenched” disorder is constructed. The conditions under which short chains are localized in one potential well are found, and the size distribution of such wells is obtained. It is shown that it is more energetically favorable for long chains to be distributed over several wells. The free energy and the sizes of macromolecules situated in a random medium in the presence of two-particle interaction between their links are calculated, as are the same quantities in the case of three-particle and long-range interactions. The reasons why these results differ from the results obtained previously in the framework of a variation approach are discussed. Characteristics of the disorder of polymer networks are calculated, and the dependence of the anisotropic deformation of macromolecules placed in them on the degree of stretching of the network is studied. The correlation functions of such macromolecules of a polymer solvent are also calculated, and it is shown that the results obtained are in agreement with the experimental data.

1. INTRODUCTION

The theory of polymers situated in random media^{1–8} has numerous applications. Polymer chains adsorbed on a rough surface constitute a typical two-dimensional situation. Polymer chains or porous media with chains inserted in them can serve as a physical realization of a three-dimensional system. Recently, various biological systems consisting of molecules interacting with impenetrable particles have also been studied intensively.

The simplest model of a polymer in a random medium is a Gaussian chain situated in a random lattice of impenetrable obstacles. Such a system was first studied in computer experiments,⁹ in which it was demonstrated that the size of a sufficiently long chain is asymptotically independent of its length. These results provided the impetus for a subsequent analytical examination of the influence of quenched impurities with a given concentration ν on the statistics of the polymer chain.¹⁰ It was shown that in space of dimensionality $d = 2$ or $d = 3$ a sufficiently long chain is localized over a scale $R_{\max} \sim \nu^{-1/(4-d)}$.

In Refs. 11 and 12 the influence of the interaction of the monomer links of the chain on the possibility of its localization in a medium with quenched impurities was studied. By means of variational estimates it was shown that impurities screen the two-particle interaction, leading to Gaussian statistics of the chains. With further increase of the concentration of impurities localization of the chains on the scale R_{\max} is predicted. In the case of three-particle interaction a compact state of the chain was obtained, with a density of monomer links that is independent of its length.¹² It was also stated that, in the presence of long-range interaction, an intermediate, “native” state of the chain should be formed.¹²

An approach substantially different from that of Refs. 10–12 was used in Ref. 13 to construct a theory of localized states of polymer chains. A more detailed examination of localized states of linear and branched polymer molecules is given in Secs. 2 and 3 of this article. On the basis of this approach, in Sec. 4 we find the average size of a chain in a random medium. The interest in this quantity is due to the fact that this is the quantity that was calculated in Refs. 11

and 12. The results that we obtain do not agree with the results of these papers. Therefore, first and foremost, the question of the applicability of the corresponding approaches arises.

In contrast to the variational estimates of Refs. 10–12, the method that we use is a regular expansion in a small parameter, which we find in Sec. 3. The reason for the differences under discussion is buried in the specific physical features of the problem under consideration. A large number of potential wells with a broad distribution of sizes cannot be simulated by a single-well potential in the framework of a variational approach.

From the experimental point of view, the most interesting realization of the systems under consideration here is provided by chains immersed in a polymer network. The theory of small-angle neutron scattering by these chains in such a polymer system was constructed in Refs. 5 and 6, and below we shall give a brief review of the corresponding experimental data.

In Refs. 14 and 15 a study was made of the influence of the degree of crosslinking X of the network (as judged from the degree of equilibrium swelling of the network) on the intensity of small-angle neutron scattering by free deuterated chains situated in the network. For small values of X the intensity turns out to be the same as in the case of a mixture of deuterated chains with uncrosslinked network chains of the same density. Under uniaxial deformation of the network the signal increases strongly in the direction parallel to the stretching, but remains unchanged in the perpendicular direction (see Fig. 1a).

In the case of intermediate values of X the scattering in the swollen state of the network is greater than that by a mixture of uncrosslinked chains. Upon stretching, the signal increases in the direction parallel to the stretching and decreases in the perpendicular direction, returning, with increase of the stretching, to its value for the mixture (Fig. 1b).

In the case of large values of X the scattering in the swollen state is considerably greater than the scattering by a mixture of uncrosslinked chains. In the direction parallel to the stretching the signal does not change with increase of the

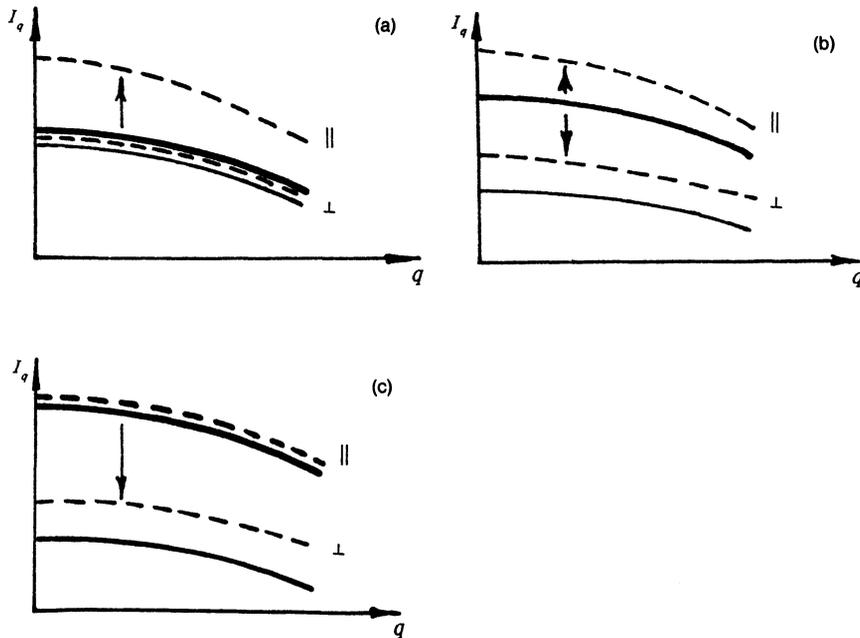


FIG. 1. Experimentally observed dependence^{14,15} of the intensity I_q of the scattering of neutrons by chains of a polymer solvent on the magnitude q of the wave vector. The solid curve is the signal from a mixture of solvent chains with uncrosslinked chains of the network. The thick solid curve is the signal from chains placed in a polymer network. The arrows show its variation under uniaxial stretching of the network, in the direction parallel to the stretching (\parallel) and in a direction perpendicular to the stretching (\perp). Figure (a) corresponds to a small degree X of crosslinking of the chains of the network, (b) corresponds to intermediate values of X , and (c) corresponds to large values of X .

stretching, while in the direction perpendicular to the stretching it decreases, but does not reach its value for the mixture (Fig. 1c).

The puzzling features described here find a natural explanation in terms of the theory we propose, which takes into account the distortion of the shape of the potential wells as a consequence of the deformation of the random medium—the polymer network.

2. THE OPTIMAL-FLUCTUATION METHOD

a) General theory

In this section we construct the theory of the localized states of Gaussian noninteracting polymer chains consisting of l lines of length a . The random Gaussian field $u(\mathbf{x})$ acting on the links of the chains in d -dimensional space is characterized by the correlators

$$\overline{u(\mathbf{x})} = 0, \quad \overline{u(\mathbf{x})u(\mathbf{x}')} = v(\mathbf{x} - \mathbf{x}'), \quad (1)$$

where the bar denotes averaging over the random realizations of the field $u(\mathbf{x})$. The probability measure of the distribution of such a field has the form

$$W\{u(\mathbf{x})\} = \text{const} \exp[-S\{u(\mathbf{x})\}],$$

$$S\{u(\mathbf{x})\} = 1/2 \int d\mathbf{x} \int d\mathbf{x}' B(\mathbf{x} - \mathbf{x}') u(\mathbf{x}) u(\mathbf{x}'), \quad (2)$$

where the kernel $B(\mathbf{x})$ is related directly to the correlation function (1):

$$\int d\mathbf{x}'' B(\mathbf{x} - \mathbf{x}'') v(\mathbf{x}'' - \mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}'). \quad (3)$$

In a weakly fluctuating localized state the free energy of such a chain with a given density $c(\mathbf{x})$ of links is determined by the Lifshits expression¹⁶

$$F_0\{c\} = T \int d\mathbf{x} \left\{ \frac{a^2}{2d} [\nabla c^{1/2}(\mathbf{x})]^2 + u(\mathbf{x})c(\mathbf{x}) \right\}, \quad \int d\mathbf{x} c(\mathbf{x}) = l. \quad (4)$$

The equilibrium value of the density $c(\mathbf{x})$ is found from the condition for the minimum of the functional (4). We shall

take the normalization condition (4) into account by introducing a Lagrange multiplier μ . The minimization of the functional (4) leads to an equation of the Schrödinger type for the function $\psi(\mathbf{x}) = c^{1/2}(\mathbf{x})$, with eigenvalues $\varepsilon\{u\} = \mu$:

$$\left[-\frac{a^2}{2d} \nabla^2 + u(\mathbf{x}) \right] \psi(\mathbf{x}) = \varepsilon\{u\} \psi(\mathbf{x}), \quad (5)$$

and the free energy (4) of the chain takes the form

$$F_0 = T \varepsilon\{u\}. \quad (6)$$

The minimum of F_0 (6) is reached when $\varepsilon = \varepsilon_0$ is the smallest eigenvalue of Eq. (3), corresponding to the eigenfunction $\psi = \psi_0$.

The key to the solution of the problem under consideration is provided by going over from the random field $u(\mathbf{x})$ to an abbreviated description of the disorder in terms of the variable $\varepsilon_0\{u\}$, which is given implicitly by Eq. (5). Typical realizations of the potential $u(\mathbf{x})$ have the form of rather deep potential wells, randomly distributed in the sample. The probability of finding a well with a given value $\varepsilon = \varepsilon_0\{u\}$ is given by the expression

$$p(\varepsilon) \equiv \frac{1}{V} \overline{\delta(\varepsilon - \varepsilon_0\{u\})} = \frac{1}{V} \int Du(\mathbf{x}) W\{u\} \delta(\varepsilon - \varepsilon_0\{u\}), \quad (7)$$

where V is the volume of the system.

In the framework of the optimal-fluctuation method¹⁷ the problem of calculating $p(\varepsilon) \sim e^{-S}$ with exponential accuracy reduces to that of the determination of the minimum of the functional $S\{u\}$ (2) under the condition

$$\varepsilon = \varepsilon_0\{u\}, \quad \varepsilon_0\{u\} = \min_{\psi_0} \int d\mathbf{x} \left[\frac{a^2}{2d} (\nabla \psi_0)^2 + u \psi_0^2 \right] / \int d\mathbf{x} \psi_0^2. \quad (8)$$

Taking this condition into account with the aid of a Lagrange multiplier λ , from the condition for the minimum of the functional $S\{u\}$ with respect to $u(\mathbf{x})$ we find an expression for the optimal fluctuation of the field $u(\mathbf{x})$ in terms of the function $\psi_0(\mathbf{x})$:

$$u(\mathbf{x}) = -\lambda \int d\mathbf{x}' v(\mathbf{x} - \mathbf{x}') \psi_0^2(\mathbf{x}') / \int d\mathbf{x}' \psi_0^2(\mathbf{x}'). \quad (9)$$

Substituting the expression (9) into the equality (8) to determine the parameter λ , we represent the exponent S on the optimum fluctuation in the form

$$S = \min_{\psi_0} \left\{ \int d\mathbf{x} \left[\frac{a^2}{2d} (\nabla \psi_0)^2 - \varepsilon \psi_0^2 \right] \right\}^2 / 2 \\ \times \int d\mathbf{x} \int d\mathbf{x}' v(\mathbf{x} - \mathbf{x}') \psi_0^2(\mathbf{x}) \psi_0^2(\mathbf{x}'). \quad (10)$$

b) Various type of disorder

The explicit form of the function $S(\varepsilon)$ depends on the relative magnitudes of the localization length R and the characteristic correlation length r_c of the correlation function (l). In the case $R \ll r_c$, by expanding the correlator (l) in powers of \mathbf{x} up to the quadratic terms:

$$v(\mathbf{x}) = v(0)(1 - x^2/2r_c^2), \quad (11)$$

from the condition for the minimum of the functional (10) we find

$$\psi_0(\mathbf{x}) = \exp(-x^2/2R^2), \quad R = (ar_c)^{1/2} |\varepsilon|^{-1/4}. \quad (12)$$

Substituting the expression (12) into (10), with exponential accuracy we find for the concentration of wells with a given size $R \ll r_c$ the results $c(R) \sim e^{-S(R)}$, where¹⁸

$$S(R) = \varepsilon^2/2v(0) = (ar_c)^4/2v(0)R^8 \gg 1. \quad (13)$$

The most interesting case is that when the localization length R is large in comparison with the correlation length r_c of the disorder. In this case the correlator $v(\mathbf{x})$ can be represented in the form

$$v(\mathbf{x}) = v\delta(\mathbf{x}), \quad v = \int d\mathbf{x} v(\mathbf{x}), \quad (14)$$

and the function $\psi_0(\mathbf{x})$ is equal to

$$\psi_0(\mathbf{x}) = \chi(x^2/R^2), \quad R = a|\varepsilon|^{-1/2}. \quad (15)$$

The dimensionless function $\chi(t)$ is found by solving the equation

$$\chi' + \frac{2t}{d} \chi'' = \chi - \chi^3, \quad \chi(t \rightarrow \infty) \rightarrow 0. \quad (16)$$

It was found in Ref. 19 by numerical solution of Eq. (16). Substituting the expression (15) into (10), we obtain

$$S(R) = A_d a^d |\varepsilon|^{2-d/2} / v = A_d (R_{max}/R)^{4-d}, \quad (17)$$

$$r_c \ll R \ll R_{max} = (a^4/v)^{1/(4-d)}, \quad A_2 = 2,95, \quad A_3 = 2,57.$$

We now find the distribution function of the potential wells with respect to their sizes R . According to the definition (7) of the probability $p(\varepsilon)$, the concentration of wells with size smaller than or equal to R is given by the expression

$$c(R) = \int \frac{d\varepsilon p(\varepsilon)}{a^2/R^2} \approx R^{-d} [S(R)]^{(d-1)/2} e^{-S(R)}, \quad R \ll R_{max}, \quad (18)$$

where we have also made use of the expression obtained in Ref. 20 for the pre-exponential factor in $p(\varepsilon)$.

In terms of the variable R (15) the free energy (6) of the chain is equal to

$$F_0(R) = -T a^2 l / R^2. \quad (19)$$

Therefore, the condition $|F_0| \gg T$ for the existence of the solution under consideration can be represented in the form $l \gg l_{min} = (R/a)^2$. Sufficiently short chains with $l \ll l_{min}$ have Gaussian size $R = al^{1/2}$.

c) Localization of branched polymers

To conclude this section we shall consider the localized state of a randomly branched molecule that has a fixed structure of the tree type and consists of n elementary chains. The average number N of links of such a chain is related to the degree l of polymerization of the molecule by the obvious relation $N = l/n$. To find the free energy of this branched polymer localized in a potential well of size R , we must subtract from the expression (19) the contribution of the translational entropy of its elementary chains:

$$F_{br}(R) = F_0(R) - T \Delta S_{tr}(R), \quad (20) \\ \Delta S_{tr}(R) = -n \ln [R^3 / (aN^{1/2})^3].$$

The logarithmic term in (20) describes the change of entropy of an elementary chain when it is localized from the free state, in which is occupied volume $(aN^{1/2})^3$, down to the volume R^3 .

The relation (20) was first obtained by us in the framework of the replica formalism,²¹ but, because of the transparency of its physical meaning, there is no need to give a rigorous derivation of it here.

3. FREE ENERGY OF A POLYMER CHAIN

a) Localization of a chain in one potential well

The Gaussian-chain model considered in the previous section is convenient for computer calculations, but is better regarded as a touchstone for a more realistic theory that should take the interaction of the monomer links of the chain into account. In the presence of two-particle interaction the free energy of the polymer is equal to

$$F\{c\} = F_0\{c\} + F_{int}\{c\}, \quad F_{int}\{c\} = \frac{1}{2} w_2 T \int d\mathbf{x} c^2(\mathbf{x}), \quad (21)$$

where w_2 is the second virial coefficient. Following the method of Ref. 22, we expand the desired solution that minimizes the free-energy functional (21) in the eigenfunctions of Eq. (3):

$$\varphi(\mathbf{x}) \equiv c^{1/2}(\mathbf{x}) = \sum_{k=0}^{\infty} c_k \psi_k(\mathbf{x}). \quad (22)$$

The coefficients c_k are found by substituting the expansion (22) into the functional (21) and minimizing the resulting expression with respect to the c_k . Below, we show that in the localized region it is sufficient to confine ourselves to taking into account the single term with $k=0$. In this approximation we find for the coefficient c_0 the expression

$$c_0^2 = \left(1 - \frac{d}{4}\right) \frac{|\varepsilon| - \mu}{|\varepsilon| w_2}, \quad |\varepsilon| > \mu. \quad (23)$$

The Lagrange multiplier μ is found by substituting the solution obtained for $\varphi(\mathbf{x})$ into the second equality (4):

$$\mu = |\varepsilon| - B_d w_2 l a^{-d} |\varepsilon|^{d/2}, \quad B_d^{-1} = 2A_d(1 - d/4)^2. \quad (24)$$

With allowance for (23) and (24) the free energy (21) of a polymer localized on a scale $R = a|\varepsilon|^{-1/2}$ takes the form

$$F(R) = F_0(R) + F_{int}(R), \quad F_{int}(R) = TB_d w_2 l^2 / 2R^d, \quad (25)$$

where the function $F_0(R)$ is defined by the expression (19).

The conditions $F < 0$ and $|F| \gg T$ for the existence of such a solution can be represented in the form

$$a^2 w_2^{-1} R^{d-2} = l_{max} > l > l_{min} = (R/a)^2. \quad (26)$$

The inequality $R \ll (a^4/w_2)^{1/(4-d)}$ [which follows from (26)], together with $R < R_{max} = (a^4/v)^{1/(4-d)}$ (17), determines the maximum localization length for the polymer.

We now discuss the possibility of neglecting the higher harmonics in the expansion (22). The coefficients c_k ($k \neq 0$) of this expansion can be taken into account in perturbation theory. Taking into account that $\varepsilon_k - \varepsilon \sim |\varepsilon|$ for $k \neq 0$, for the small parameter of perturbation theory it is not difficult to obtain the estimate

$$1 - \mu/|\varepsilon| \approx l/l_{max}, \quad (27)$$

where we have made use of the expression (24) for the parameter μ . Thus, the expressions (25) and (19) fully determine the free energy of a chain for which the number l of links lies in the interval (26). Chains with $l < l_{min}$ have Gaussian statistics (the free energy $|F| \approx T$, and the size $R = al^{1/2}$).

b) Localization of a chain in several potential wells

We consider now the behavior of long chains with $l \gg l_{max}$ in space of dimensionality $d = 3$. In the case of weak disorder ($v < w_2$), potential wells with size $R < a^4/w_2$ are exponentially rare [see (18)]. Since the loss of energy of the chain outside the wells substantially exceeds the energy gain (25) in the wells, the tension of the chain pulls it from the potential wells. In the case of strong disorder ($v \gg w_2$), such chains consist of a large number of localized blobs, the most probable size of which is R_{max} (see Fig. 2). According to (18), the deeper potential wells with size $R \ll R_{max}$ are exponentially rare, and unimportant in the study of the statistics of long chains. With neglect of the contribution of such wells the average number g_1 of links of the globular blobs is found by minimizing the free energy of the chain

$$\frac{F_l}{T} = \frac{l}{g_1 + g_2} \left[-\frac{a^2 g_1}{R_{max}^2} + 1,56 \frac{w_2 g_1^2}{R_{max}^3} + \frac{L^2}{a^2 g_2} + \frac{a^2 g_2}{D^2} \right] \quad (28)$$

with respect to g_1 and the number g_2 of links of the chain fragment between neighboring wells, the average distance between which is $L = c^{-1/3} (R_{max})$ (18). Such a fragment is situated in an effective tube of diameter $D \approx R_{max}$, created by the random field $u(x)$. Since for $w_2 \ll v$ the interaction of the links within a tube is unimportant, the free energy of this fragment is the sum of the energy of stretching of the chain along the tube ($TL^2/a^2 g_2$) and the energy of its compression in the perpendicular direction ($Ta^2 g_2/D^2$). Minimization of the expression (28) with respect to g_1 and g_2 gives

$$g_1 \approx \kappa^{1/2} a^6 / w_2^{1/2} v^{3/2}, \quad g_2 \approx LD/a^2 \ll g_1, \quad (29)$$

where the dimensionless parameter $\kappa = L/D \gg 1$. The quan-

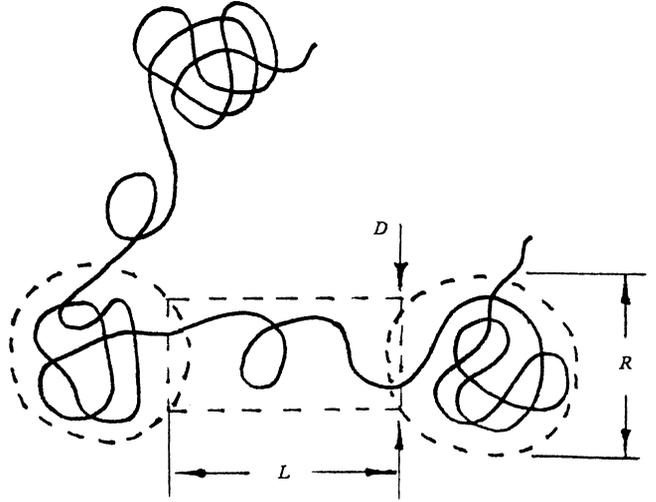


FIG. 2. Typical conformation of a chain with $l \gg l_{max}$ links in a random medium. The fragment of the chain between neighboring potential wells of size $R \approx R_{max}$ is situated in an effective tube of diameter $D \approx R_{max}$ and length $L = \kappa D$.

tity $g_1 < l_{max}$ for $v > \kappa w_2$, as a consequence of the above-indicated effect of partial expulsion of the chain from the potential wells. Thus, the perturbation-theory parameter g_1/l_{max} (27) is indeed small. The results (29) also make it possible to convince oneself that the interaction of the monomer links inside a tube is small. In fact, the corresponding perturbation-theory parameter¹⁶

$$z = w_2 g_1^{1/2} / a^3 \approx \kappa^{1/2} w_2 / v \ll 1 \quad (30)$$

is small for $v > \kappa w_2$. This condition also guarantees fulfillment of the inequality $F_l < 0$.

4. AVERAGE SIZE OF A POLYMER CHAIN

To find the size of a chain in the localized state we must distinguish the cases of unpinned chains and the chains with one fixed end. Chains with a fixed end are localized in the nearest potential well with size $\sim R_{max}$. It is this case which is realized in the numerical experiments of Ref. 9. Free chains find the sparsely located [see (18)] but deeper energy minima with $R \ll R_{max}$.

The probability that a chain is localized in a well with a given size R is proportional to $\exp[-F(R)/T]$. The concentration $c(R)$ of such wells was calculated in (18). Thus, the mean square size of a chain in a localized state is given by the expression

$$\overline{R^2} = \int dR c'(R) e^{-F(R)/T} R^2 / \int dR c'(R) e^{-F(R)/T}. \quad (31)$$

a) Three-particle interaction (the θ -conditions)

In the absence of two-particle interaction between the links the dependence $F_0(R)$ is given by (19) and the main contribution to the integrals (31) is made by small values of R . In this compact state we must take into account the three-particle interaction of the chain links that is described by the third virial coefficient w_3 . In analogy with the derivation of Eq. (25) for the free energy of such a chain for $d = 3$ it is not difficult to obtain the expression

$$F(R)/T = -a^2 l / R^2 + w_3 l^3 / R^6. \quad (32)$$

Calculating the integrals in (31) and (32) by the method of steepest descent, we find

$$\overline{R^2} \approx \frac{w_3^{1/2} l}{a}, \quad \frac{a^3 w_3^{1/2}}{v^2} = l_{\min} < l < l_{\max} = \frac{a^9}{w_3^{1/2} v^2}. \quad (33)$$

Chains with $l > l_{\max}$ are distributed over l/g potential wells of size $R_{\max} \approx a^4/v$. For the number g of monomer links of these wells, in analogy with (29) we can obtain the expression

$$g \approx a^8/w_3^{1/3} v^2 < l_{\max}. \quad (34)$$

Regarding such blobs as the structural units of the chain, we easily find the average size of the chain:

$$\overline{R^2} \approx R_{\max}^2 l/g \approx w_3^{1/3} l, \quad l > l_{\max}. \quad (35)$$

Thus, in the localized state the chain is more compact than a Gaussian chain in the absence of disorder, but its size has the same scaling dependence $\overline{R^2} \sim l$. The results (33) and (35) obviously cannot be obtained in the framework of the variational approach of Refs. 10–12, which does not take account of the presence of the large number of potential wells with a broad distribution (18) of sizes.

b) Two-particle interaction

We now find the average size of a chain with excluded volume in the case when it is localized in one potential well. Substituting into (31) the expression (25) obtained above for $F(R)$ and calculating the integral over R by the method of steepest descent, we find for $d = 3$ and $v > w_2$

$$\overline{R^2} = w_2^2 l^2/a^4, \quad l < l_{\max} \approx a^6/w_2^2. \quad (36)$$

Equation (36) demonstrates the difference between statistical (quenched) averaging and the ordinary Gibbs (annealed) average. In the latter case the dependence $R \sim l$ implies that the chain is stretched out into a string. In reality, it finds sparsely located potential wells with size (36), which have, on the average, the shape of a sphere.

In the case of weak disorder ($v < w_2$) there is no extremal point and the size of the chain is determined by the contribution of the delocalized states [which were not included in the definition (31)]:

$$\overline{R^2} = a^{4/5} w_2^{2/5} l^{6/5}, \quad v < w_2. \quad (37)$$

In this case the localized states make only an exponentially small contribution to the average (37).

As shown in the preceding section, for $v > \kappa w_2$ sufficiently long chains with $l \gg l_{\max}$ consist of l/g_1 localized blobs of size R_{\max} . It is not difficult to show that configurations in which the polymer chain visits a given potential well several times are not favored: The energy losses amount to κT for each ring. Therefore, the size of the chain is determined by the formula

$$\overline{R^2} = R_{\max}^2 (l/g_1)^{6/5} \approx a^{4/5} w_2^{2/5} l^{6/5}, \quad l \gg l_{\max}, \quad (38)$$

which describes a random walk without self-intersections, each step of which is equal to $L \approx R_{\max}$. In (38) the parameter $\hat{w}_2 = w_2^{3/2} v^{-1/2} < w_2$. Thus, on scales large compared with R_{\max} , impurities effectively screen the interaction of the monomer links of the chain, but do not change the scaling dependence $\overline{R^2} \sim l^{6/5}$.

c) Long-range interaction

To conclude this section we shall consider the influence of long-range interaction of the Coulomb type, with potential $Tw/|x|$, on the statistics of a chain situated in a disordered medium. The free energy of such a chain, localized in a well of size R , is equal to

$$F(R)/T = -a^2 l/R^2 + w l^2/R. \quad (39)$$

The principal contribution to the integral (31) is made by small values of R , at which the contribution of the long-range interaction is small in comparison with the contribution of ordinary short-range interactions. Therefore, the quantity $\overline{R^2}$ is given by the expression (36). However, the condition $v > w_2$ for the existence of a saddle-point solution changes, and, with allowance for the long-range interaction, takes the form

$$v^{-1} + w l^2/a^4 < w_2^{-1}. \quad (40)$$

Besides the inequality (36), this condition also imposes a restriction on the maximum number l_{\max} of links of a chain localized in one potential well.

We now consider long chains (with $l \gg l_{\max}$ links) that cannot be localized in one well. The free energy of such a chain is determined by an expression analogous to (28):

$$\frac{F_l}{T} = \frac{l}{g_1 + g_2} \left[-\frac{a^2 g_1}{R_{\max}^2} + C \frac{w g_1^2}{R_{\max}} + \frac{L^2}{a^2 g_2} + \frac{a^2 g_2}{D^2} \right]. \quad (41)$$

In contrast to (28), the term $\sim w$ in (41) takes into account not only the interaction of the links within one well but also the long-range interaction of the links in different wells. This interaction leads to renormalization [in comparison with the one-well case (39)] of the numerical coefficient C multiplying w . Since the quantity C depends in an essential way on the characteristic conformations of the chain, we shall find this coefficient at the end of the calculations.

The expression (41) has a minimum with respect to the variables g_1 and g_2 :

$$g_1 \approx \kappa^{1/2} a^2 / C^{1/2} w^{1/2} v^{1/2}, \quad g_2 \approx LD/a^2 < g_1 \quad (42)$$

in the case of sufficiently strong disorder

$$v > v_c \approx (\kappa C a^8 w)^{1/3}. \quad (43)$$

In the case of weak disorder ($v < v_c$) the tension of the chains pulls them completely out of the potential wells. With neglect of disorder effects, the size of such chains for $v < v_c$ is equal to²³

$$\overline{R^2} = a^{4/3} w^{2/3} l^2, \quad l > (a/w)^{2/3}. \quad (44)$$

Since the potential energy per localized blob for $v > v_c$ is of the order of

$$T w g_1^2 / R_{\max} \sim \kappa T > T,$$

on scales large in comparison with the size R_{\max} of a blob the chain is stretched out into a string under the action of the long-range interaction, and its size is equal to

$$\overline{R^2} \approx L^2 (l/g_1)^2 \approx C \kappa a^4 w v^{-1} l^2, \quad l > g_1. \quad (45)$$

Summing the contributions of the interactions between the l/g_1 potential wells threaded onto such a string, for the pa-

parameter C we find the expression

$$C = 1 + 2\alpha^{-1} \ln(l/g_1). \quad (46)$$

The logarithmic term in (46) leads to "ultra-stretching out" of the chain in comparison with the case (44). This effect is due to the partial pulling out of the links of the chain [see (39)] from the potential wells under the action of the long-range interaction.

d) Connection with the variational approach

The results obtained in this section differ substantially from the results of the variational approach.¹² In order to understand the physical reason for this difference, we shall compare the problem considered here with the problem (studied in Ref. 22) of the condensation of a Bose field in a random potential. In this problem the chemical potential μ is fixed and the condensate fills all the energy wells with $\varepsilon < \mu$. The free energy of such a system is equal to the sum of the contributions of the different wells, and, therefore, is a self-averaged quantity:

$$F = \bar{F} = V \int_{\varepsilon < \mu} dc(R) F(R).$$

The polymer analog of this problem is a system of chains that are in chemical equilibrium with respect to the formation and breaking of their bonds.

In the problem of the behavior of an isolated chain the length l of the chain is fixed and, for $l < l_{\max}$, the chain can occupy only one energy well. The quantum analog of this problem is a system with a continuous spectrum of energy levels $F(R)$ and with $Vdc(R)$ states in the interval dR . The partition function of such a system is given by the expression

$$Z = V \int dc(R) e^{-F(R)/T}.$$

Thus, in this problem what is averaged over the sizes R of the wells is not the free energy but the partition function. Therefore, the formal use of the method of replicas¹⁰⁻¹² in a problem in which only a small fraction of the disorder configurations is accessible leads to erroneous results. This distinctive feature of polymer systems is due to the fact that the number l of particles in them is finite ($l < l_{\max}$). In the limit $l \rightarrow \infty$ the chain visits a large number of wells and its free energy becomes a self-averaging quantity. Therefore, to determine it we can use the standard method of replicas. The principal contribution in this limit is made by many-well configurations, allowance for which lies beyond the scope of the single-well variational approach proposed in Refs. 10-12.

5. THERMODYNAMICS OF CHAINS IN A POLYMER NETWORK

In our study of the phenomenon of localization of chains immersed in a polymer network we shall confine ourselves to the consideration of networks obtained under conditions of equilibrium with respect to the formation and breaking of the chemical crosslinks between their chains. The conditions in which real experiments are performed^{14,15,24} can differ substantially from those in the idealized model that we have used. Nevertheless, as will be shown in this and the next section, even this very simple model makes it possible to give an adequate description of the

changes that have been observed in a conformational set of chains of a polymer solvent in modern neutron experiments.^{14,15,24}

In the approximation of incompressibility the density $\rho(\mathbf{x})$ of the links of the network and the density $c(\mathbf{x})$ of the links of the chains are related to each other by the condition $\rho(\mathbf{x}) + c(\mathbf{x}) = \rho_{\text{tot}} = \text{const}$. This condition is also the most interesting from the point of view of the experiments of Refs. 14 and 15, in which a semidilute fluctuational regime is realized. Expressing the lengths of the chains and the density of their links in units of blobs,²⁵ each of which consists of $g \approx (\rho_{\text{tot}} a^3)^{-5/4}$ monomer links, in this case too we arrive at an incompressible system. The free energy of such a system is composed of the entropy contributions of the network and the polymer chains. We shall not study the first of these in more detail.

a) Relationship between physical and chemical networks

In statistical physics we consider two types of disordered systems—those with mobile (annealed) disorder and those with frozen (quenched) disorder. In correspondence with this classification we consider two types of polymer networks—physical and chemical. The topological (chemical) structure of physical networks is annealed, and the formation and breaking of the chemical crosslinks between the chains of such a network is described by the condition of chemical equilibrium. The topological structure Γ of chemical networks is fixed by the conditions of the synthesis. The physical properties of the two types of networks are substantially different: Physical networks are liquid, whereas chemical networks are solid. At the same time, as will be shown below, the characteristics of these networks turn out to be closely related to each other.

We shall denote by $S^{ph}\{\rho\}$ and $S^{ch}\{\rho, \lambda\}$ the entropies of a physical and a chemical network, respectively, with a given density $\rho(\mathbf{x})$ of links:

$$S^{ph} = \ln \Omega, \quad S^{ch} = \ln \Omega_{\Gamma}, \quad \Omega = \sum_{\Gamma} \Omega_{\Gamma}. \quad (47)$$

Here, Ω_{Γ} is the volume of the configuration-space region occupied by a network with topology Γ and density distribution $\rho(x)$. The quantities λ_{μ} in (47) are equal to the coefficients of expansion of the network along the axes $\mu = x, y, z$ relative to the network in the conditions of synthesis. Since a physical network is a liquid, the functional S^{ph} depends on the coefficients λ_{μ} only through the combination $\lambda_x \lambda_y \lambda_z$.

As a consequence of defects of the topological structure of a chemical network the entropy of the network reaches a maximum on a spatially nonuniform density distribution $n(\mathbf{x})$, which depends only on the topology Γ of the network. Expanding the entropy functional (47) in powers of the corresponding densities up to terms of second order, we obtain

$$S^{ph}\{\rho\} = \text{const} - \frac{V}{2} \int \frac{dq}{(2\pi)^3} \chi_q^{ph}(\lambda) \rho_q \rho_{-q}, \quad (48)$$

$$S^{ch}\{\rho, \lambda\} = \text{const} - \frac{V}{2} \int \frac{dq}{(2\pi)^3} [t_q(\lambda) n_q n_{-q} + \chi_q^{ch}(\lambda) (\rho_q - n_q)(\rho_{-q} - n_{-q})]. \quad (49)$$

Substituting the expressions (48) and (49) into (47) and going over, in the last of Eqs. (47), from the summation over

Γ to integration over the distribution $n(\mathbf{x})$, we find a relationship between the parameters of physical and chemical networks:

$$[\kappa_q^{ph}(\lambda)]^{-1} = [\kappa_q^{ch}(\lambda)]^{-1} + [t_q(\lambda)]^{-1}. \quad (50)$$

The function κ has been calculated in Refs. 26 and 27 by the replica method for networks obtained by equilibrium crosslinking of long chains. In the long-wavelength limit $q \rightarrow 0$ they have the form

$$\kappa_q^{ph}(\lambda) = -1/\rho N, \quad \kappa_q^{ch}(\lambda) = 3(\lambda q)^2/2q^2\rho N. \quad (51)$$

Here, N is the average length of a chain between neighboring crosslinks. Here and below, the notation λq is used for the vector with components $\lambda_\mu q_\mu$.

b) Characteristics of the disorder of polymer networks

Substituting the expression (50) obtained above for the parameter t into (49) and adding the contribution of the entropy of the free chains, we obtain for the free energy of a polymer system the expression

$$\begin{aligned} \frac{F_\Gamma\{c, \lambda\}}{TV} = & \int \frac{dq}{(2\pi)^3} \\ & \times \left[\frac{1}{2} \left(\kappa_q^{ch}(\lambda) + \frac{1}{S_q(\lambda)} \right) c_q c_{-q} + u_q c_{-q} + \frac{n_q n_{-q}}{2B_q} \right], \end{aligned} \quad (52)$$

where we have used the incompressibility condition $\rho_q = -c_q$, and $S_q(\lambda)$ is the form factor of the system of free chains:

$$S_q(\lambda) = c(l^{-1} + a^2 q^2/12)^{-1}, \quad c = c^{(0)}/\lambda_x \lambda_y \lambda_z. \quad (53)$$

Here and below, the superscript (0) indicates that the corresponding quantity pertains to the conditions of synthesis.

The quantities u_q and B_q appearing in (52) have the form

$$u_q = \kappa_q^{ch}(\lambda) n_q, \quad B_q(\lambda) = \frac{1}{\kappa_q^{ch}(\lambda)} \left[1 - \frac{\kappa_q^{ph}(\lambda)}{\kappa_q^{ch}(\lambda)} \right]. \quad (54)$$

Comparing the expressions (4) and (52) we find that u_q has the meaning of a Fourier component of the random field acting on the monomer links of the free chains.

Henceforth we shall consider networks obtained under conditions of chemical equilibrium. The probability of synthesis of such a network with a given topological structure Γ is proportional to its partition function:

$$W_\Gamma = \text{const} \int D\rho \exp(-F_\Gamma\{\rho, 1\}/T^{(0)}). \quad (55)$$

Substituting the expression (52) and (55) and calculating the Gaussian integrals, for the probability distribution of the density $n^{(0)}(\mathbf{x})$ of spatial nonuniformities of the network in the conditions of synthesis we find the expression

$$\begin{aligned} W\{n^{(0)}\} = & \text{const} \cdot \exp \left(-\frac{V^{(0)}}{2} \int \frac{dq}{(2\pi)^3} v_q^{-1} n_q^{(0)} n_{-q}^{(0)} \right), \\ v_q = & A_q^2 G_q^{(0)} + B_q(1), \quad A_q = 1 - \kappa_q^{ph}(1)/\kappa_q^{ch}(1). \end{aligned} \quad (56)$$

The function $G_q^{(0)}$ in (56) has the meaning of the correlation

function of fluctuations of the density of the links of the free chains:

$$G_q^{(0)} = S_q(1)/(1 + \kappa_q^{ch}(1)S_q(1)). \quad (57)$$

The relationship between the distributions $n(\mathbf{x})$ and $n^{(0)}(\mathbf{x})$ can be found if we note that large-scale nonuniformities are deformed affinely with the network:

$$n(\mathbf{x}) = n^{(0)}(\lambda^{-1}\mathbf{x})/\lambda_x \lambda_y \lambda_z. \quad (58)$$

Here we again use the notation $\lambda^{-1}\mathbf{x}$ that we have adopted for the vector with components $\lambda_\mu^{-1}x_\mu$. Performing the average of the random field (54), (58) with the probability (56), we find the correlation function of the disorder:

$$v_q = \overline{u_q u_{-q}} = [\kappa_q^{ch}(\lambda)]^2 v_{\lambda q} / \lambda_x \lambda_y \lambda_z. \quad (59)$$

6. ORIENTATIONAL ORDER OF CHAINS IN DEFORMED NETWORKS

a) Isolated chains

The mechanism of the deformation of polymer chains under stretching of the medium is conveniently studied first for the example of an isolated chain localized in one potential well. To describe the change of its dimensions R_μ under the action of an anisotropic stretching $\lambda_\mu = \lambda(1 + \varepsilon_\mu)$ of the network we substitute into the functional (10) the variational function

$$\psi_0(\mathbf{x}) = \chi \left(\sum_\mu x_\mu^2 / R_\mu^2 \right). \quad (60)$$

Minimizing the resulting expression with respect to R_μ , in first order in the parameters ε_μ we find $R_\mu = R(1 - 2\varepsilon_\mu/5)$, where the size R of the undeformed chain is defined in (15). Thus, in the localized state the chain contracts in the direction of stretching of the network and is stretched in the direction of contraction of the network.

b) Polymer solvent

We now find the correlation function of the fluctuations of the density of the links of a polymer solvent that consists of free chains placed in a network:

$$\begin{aligned} I(\mathbf{x} - \mathbf{x}') \equiv & \overline{\langle \Delta c(\mathbf{x}) \Delta c(\mathbf{x}') \rangle} = \int Dn^{(0)} W\{n^{(0)}\} \\ & \times \left[\int Dc \Delta c(\mathbf{x}) \Delta c(\mathbf{x}') \exp(-F_\Gamma\{c, \lambda\}/T) \right] \\ & \int Dc \exp(-F_\Gamma\{c, \lambda\}/T). \end{aligned} \quad (61)$$

We substitute into (61) the expression (56) for the probability and the expression (52) for the free energy. The Gaussian integrals in (61) are calculated by going over to the Fourier representation:

$$\begin{aligned} I_q = & G_q + C_q, \quad G_q = S_q(\lambda)/(1 + \kappa_q^{ch}(\lambda)S_q(\lambda)), \\ C_q = & [\kappa_q^{ch}(\lambda)G_q]^2 v_{\lambda q} / \lambda_x \lambda_y \lambda_z. \end{aligned} \quad (62)$$

Here, G_q has the meaning of the correlation function of thermodynamic (temporal) fluctuations of the density of monomer links, and C_q is the correlation function of statistical (spatial) fluctuations of the density. The magnitude of the latter fluctuations can also be found from the condition for

the minimum of the free energy (52) with respect to c_q :

$$c_q = -\kappa_q^{ch}(\lambda) G_q n_q, \quad C_q = \overline{c_q c_{-q}}. \quad (63)$$

The quantity I_q (62) that we have calculated is proportional to the intensity of the small-angle scattering of neutrons by deuterated chains. Substituting into (62) the expression (56) for ν_q and making use of the expression (51) for the functions κ , we find that, depending on the relative magnitudes of λ (the degree of swelling of the lattice) and the parameter $X = cl/\rho N < 1$, three basic regions must be distinguished:

a) The case $\lambda < X^{-1/4}$ can be realized for small X . Under uniaxial stretching of such networks the intensity I_q (62) of scattering by free chains behaves in accordance with Fig. 1a.

b) The case $X^{-1/4} < \lambda < X^{-1/2}$ occurs for intermediate values of X . The dependence of the intensity I_q on the degree of uniaxial extension of the network is found in accordance with Fig. 1b.

c) The Case $\lambda > X^{-1/2}$ is realized for sufficiently large X . The intensity I_q depends on the degree of extension of the network in accordance with Fig. 1c.

c) Partially deuterated chains

In Ref. 15 the case in which only a fraction Φ of the free chains is deuterated was studied. We denote the density of their links by c_q^d . The entropy of the free chains of such a system is equal to

$$-\frac{V}{2} \int \frac{dq}{(2\pi)^3} \frac{1}{S_q(\lambda)} \left[\frac{c_q^d c_{-q}^d}{\Phi} + \frac{(c_q - c_q^d)(c_{-q} - c_{-q}^d)}{1 - \Phi} \right]. \quad (64)$$

Substituting the expression (64) into the free energy (52) in place of the corresponding contribution of the linear chains, we find without difficulty the following expression:

$$\overline{c_q^d c_{-q}^d} = \Phi(1 - \Phi) S_q(\lambda) + \Phi^2 I_q \quad (65)$$

for the correlation function of the fluctuations of the density of the deuterated chains. Thus, with decrease of the fraction Φ of such chains the signal (65) becomes isotropic, in agreement with the experimental data.¹⁵

Thus, we have shown that allowance for the spatial nonuniformities of polymer networks makes it possible to understand the unusual data of Refs. 14 and 15 on the small-angle neutron scattering.

7. PRINCIPAL CONCLUSIONS

In this paper we have constructed a statistical theory of polymers situated in a random medium. The quantum analog of this problem is the well known problem of the localization of an electron in a random external field. This analogy has enabled us to carry over methods developed in the theory of solids to the description of a polymer system. The results obtained differ substantially from the results obtained previously in the framework of the variational approach of Refs. 11 and 12, which is found to be inadequate to the physical picture of the localization.

We have shown that the localization of sufficiently short chains with $l < l_{\max}$ links occurs in randomly positioned regions with sizes $R < R_{\max}$. Chains that are fixed at

one end are localized in the nearest region with the size R_{\max} . Free chains are localized in sparsely located but deeper energy wells. Because of the presence of the repulsive interaction, it is energetically more favorable to distribute chains with $l > l_{\max}$ over several wells.

An important application of the theory developed here is to a system of linear chains placed in a polymer network. We have shown that the correlation function ν characterizing the disorder in such a random medium can be expressed directly in terms of correlation functions of the polymer networks. The latter have been found previously in Refs. 26 and 27. In the case of isotropic stretching of the network by a factor of λ we obtained $\nu = 5\lambda^2 w_2/3$. Thus, the relation between the effective interaction parameter w_2 and the disorder ν can be changed by stretching the network, thereby scanning in a single sample all the localization regimes predicted above. In this sense polymer networks are an ideal object for the study of localization of polymers.

The physical picture of the localization of isolated chains differs substantially from the picture of the ordering of the overlapping chains of a polymer solvent. In the former case improbable fluctuations of the random field correspond to localized states, while in the latter case only typical values of this field are important.

We have shown that isolated chains that are localized in one potential well are ordered in a direction perpendicular to the direction of stretching of the elementary chains of the network during uniaxial stretching of the network, this effect being anomalously strong: $\Delta R/R \approx -\Delta\lambda/\lambda$. At the same time, according to the expression (65) for $\Phi \rightarrow 0$, the individual chains of a polymer solvent experience practically no orientational ordering. The experimentally observed anisotropy of the scattering is due to the collective effect of the interaction of the totality of these chains with nonuniformities of the polymer network. We have shown that the theory proposed by us for the anisotropic scattering is in good agreement with the experimental data discussed in the Introduction.

The author expresses his gratitude to J. Bastide and F. Boue for the opportunity to become acquainted with the experimental data of Ref. 15 and for discussion of some the results of the present paper.

¹B. Derrida, Phys. Rep. **103**, 29 (1984).

²A. B. Harris, Z. Phys. B **49**, 347 (1983).

³M. Kardar, G. Parisi, and Y.-C. Zhang, Phys. Rev. Lett. **56**, 889 (1986).

⁴M. Kardar, and Y.-C. Zhang, Phys. Rev. Lett. **58**, 2087 (1987).

⁵A. K. Roy and B. K. Chakrabarti, Z. Phys. B **55**, 131 (1984).

⁶B. Duplantier and H. Saleur, Phys. Rev. Lett. **59**, 539 (1987).

⁷A. R. Khokhlov and S. K. Nechaev, Phys. Lett. **112A**, 156 (1985).

⁸D. K. Klimov and A. R. Khokhlov, Vysokomol. Soedin. Ser. A **33**, 1921 (1991).

⁹A. Baumgärtner and M. Muthukumar, J. Chem. Phys. **87**, 3082 (1987).

¹⁰S. F. Edwards and M. Muthukumar, J. Chem. Phys. **89**, 2435 (1988).

¹¹S. F. Edwards and Y. Chen, J. Phys. A **21**, 2963 (1988).

¹²M. Muthukumar, J. Chem. Phys. **90**, 4594 (1989).

¹³S. V. Panyukov, Pis'ma Zh. Eksp. Teor. Fiz. **56**, 60 (1992) [JETP Lett. **56**, 61 (1992)].

¹⁴F. Hovasse-Zielinski, Thesis, Paris (1991).

¹⁵F. Zielinski, M. Buzier, C. Lartigue *et al.*, Preprint, Paris (1992).

¹⁶I. M. Lifshits, A. Yu. Grosberg, and A. R. Khokhlov, Usp. Fiz. Nauk **127**, 353 (1979) [Sov. Phys. Usp. **22**, 123 (1979)].

¹⁷I. M. Lifshits, Usp. Fiz. Nauk **83**, 617 (1964) [Sov. Phys. Usp. **7**, 549 (1965)].

¹⁸B. I. Shklovskii and A. L. Éfros, Zh. Eksp. Teor. Fiz. **58**, 657 (1970) [Sov. Phys. JETP **31**, 351 (1970)].

¹⁹I. M. Lifshits, S. A. Gredeskul, and L. A. Pastur, *Introduction to the*

- Theory of Disordered Systems* (Wiley, New York, 1988) [Russ. original, Nauka, Moscow, 1982].
- ²⁰J. L. Cardy, *J. Phys. C* **11**, L321 (1978).
- ²¹S. V. Panyukov, *Zh. Eksp. Teor. Fiz.* **96**, 604 (1989) [*Sov. Phys. JETP* **69**, 342 (1989)].
- ²²L. B. Ioffe and A. I. Larkin, *Zh. Eksp. Teor. Fiz.* **81**, 707 (1981) [*Sov. Phys. JETP* **54**, 378 (1981)].
- ²³A. Yu. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* [in Russian] (Nauka, Moscow, 1989), p. 211.
- ²⁴J. Bastide, F. Boue, and M. Buzier, *Springer Proc. Phys.* **29**, 112 (1987).
- ²⁵P. G. de Gennes, *Scaling Concepts in the Physics of Polymers* (Cornell University Press, Ithaca, New York, 1979) [Russ. transl., Mir, Moscow, 1982].
- ²⁶S. V. Panyukov, *Pis'ma Zh. Eksp. Teor. Fiz.* **55**, 584 (1992) [*JETP Lett.* **55**, (1992)].
- ²⁷S. V. Panyukov, *Zh. Eksp. Teor. Fiz.* **102**, 648 (1992) [*Sov. Phys. JETP* **85**, (1992)].

Translated by P. J. Shepherd