Scaling theory of high elasticity

S. V. Panyukov

L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences, Moscow

(Submitted 7 March 1990)
Zh. Eksp. Teor. Fiz. **98**, 668–680 (August 1990)

A scaling theory of high elasticity of polymer networks synthesized both close to and far from the gel-formation threshold is developed. It is shown that disorder of the topological structure of the networks, which has not been taken into account previously, leads to an appreciable change of the scaling dependences in comparison with those in the case of a regular structure. The correlation functions of the network-density fluctuations are calculated, and it is shown that in structurally disordered networks the statistical density fluctuations considerably exceed the thermodynamic density fluctuations.

I. INTRODUCTION

Experimental data on the elastic characteristics of polymer networks (gels) are usually interpreted in terms of the classical theory of high elasticity.[1,2] However, the success of this typical mean-field theory does not in itself imply that the chains of the networks obey Gaussian statistics, which lies at the basis of this theory. As is well known, Gaussian statistics is characteristic only for networks prepared by the coalescence of a concentrated solution of chains when they are compressed or weakly stretched. Networks that have swollen in a good solvent are essentially non-Gaussian, and their description is possible only in terms of scaling theory.

The scaling theory developed by de Gennes[3] for polymer networks in a good solvent is based on the assumption that different chains of the network are completely separated spatially as a result of strong mutual repulsion of their monomer links. This assumption is known as Flory's gel theorem, according to which the equilibrium density of the links of the network is found from the condition for the threshold of overlap between dilute and semidilute solutions of its chains. According to this theorem, the properties of polymer networks in a good solvent are universal and do not depend on how the networks are prepared.[3]

The data from the experiments of Ref. 4 indicate the presence of a rather strong dependence

$$\partial \ln \bar{\rho}/\partial \ln \rho^{(0)} \approx 0.7-0.8$$

of the equilibrium density $\bar{\rho}$ of the links of the network on their average density $\rho^{(0)}$ while the network is being synthesized in a concentrated solution. The interpretation of the experimental data (see, e.g., Refs. 4–6) is made difficult by the presence of a large number of factors that influence the properties of the networks—the entanglement of the chains and their chemical nature, topological restrictions,[7] the quality of the solvent, etc. For an explanation of these data a number of phenomenological hypotheses have been put forward: Different ways of choosing the initial state have been proposed,[8,9] the concepts of physical knots[10] and of the interpenetration of parts of the network have been introduced,[11,12] etc.

In this situation a rigorous theoretical study of sharply defined "base" models is of fundamental significance. As examples of such models, we have considered polymer networks obtained under conditions of chemical equilibrium, with neglect of the effects of topological restrictions. The analysis has been performed using the renormalization-group method on the basis of the field-theoretical formalism developed in Ref. 13. It has been found that the results obtained can be clearly reproduced by means of the concept of "blobs."[3,14] The corresponding scaling theory is given in this article.

A preliminary rigorous analysis is necessary because polymer networks are a solid phase of matter (for a discussion and the corresponding order parameter, see the Conclusion in Ref. 14). Because of the presence of long-range order, the properties of a fragment of a network on scales large in comparison with the correlation length ξ differ substantially from the properties of a fragment of an isolated macromolecule of the same topological structure. This fact is not taken into account in the framework of the de Gennes approach (Ref. 3, p. 171) or in Refs. 12 and 15, which are devoted to a scaling description of polymer networks obtained near the gel-formation threshold.

The presence of long-range order in networks is also of fundamental significance for the description of the effects of topological restrictions. Here, we are concerned with the construction of the corresponding Ginzburg–Landau functional, dependent on an order parameter.[14] In Ref. 14 this was found for networks obtained under conditions of chemical equilibrium, by means of the standard Leontovich approach.[16] The condition used here that the fluctuations of the order parameter be small is fulfilled only in sufficiently concentrated systems. The concept of blobs has enabled us in this article to extend the results of Ref. 14 to the scaling region.

Real networks have a substantially disordered topological structure (see Fig. 1), but their chains are entangled with each other. Here we construct a scaling theory of such networks and show that Flory's gel theorem is correct only for regular networks, which are topologically equivalent to a regular lattice (see Fig. 2) and whose synthesis belongs more to the field of art.

We shall discuss briefly the basic ideas of the proposed theory.[17] As is well known, the elasticity of polymer networks has an entropic origin. The increase of entropy as a result of the presence of structural disorder in a network leads to a corresponding increase of the elastic stress π_{el} of its stretched chains. Under the action of this compressive force chains of the network strongly overlap with each other

0038-5646/90/080372-08$03.00

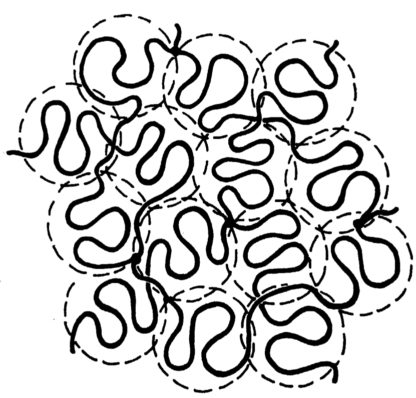

FIG. 1. Characteristic form of a structurally disordered network with $p \approx 1$, obtained by joining of chains in a semidilute solution $(\rho^{(0)} \gg \rho^{*(0)})$. Blobs (fragments of chains with $g \ll N$ links) are indicated by circles. On scales large in comparison with the blob size ξ the chains of the network are strongly entangled with each other.

and a regime of semidilute solution of the chains is realized. The equilibrium parameters of the networks are determined from the condition that the osmotic pressure $\pi_{\rm osm}$ of such a solution be equal to the stress $\pi_{\rm el}$ associated with the entropic elasticity of the chains. The calculation of the topological disorder depends essentially on how the polymer networks are synthesized and this causes the equilibrium parameters of the network to depend on the conditions of synthesis.

The way the networks are prepared and the characteristics of the topological disorder are considered in detail in the second section of the article. In the third section the scaling dependence of the equilibrium and elastic characteristics of the networks on their structure and on the environment in which they are placed is obtained. In the fourth section, on the basis of the theory developed in Ref. 14, the correlation functions of the density fluctuations of polymer networks are calculated. These functions determine the intensities of the scattering of light, x rays, and neutrons by the structure of the polymer networks. In the Conclusion the principal results of the high-elasticity theory developed in this article are discussed.

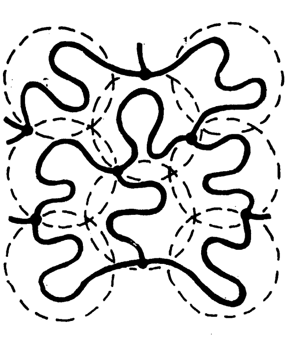

FIG. 2. Characteristic form of a network with a regular structure, obtained strictly on the threshold of overlap of the chain $(\rho^{(0)} \approx \rho^{*(0)})$. The chains of this network, which is obtained far from the gel-formation threshold $p \approx 1$, are spatially separated. The number of monomer links of a blob coincides with the number of links of one chain $(g \approx N)$.

2. POLYMER NETWORKS IN THE CONDITIONS OF SYNTHESIS

The physical properties of polymer networks depend on their topological structure and on the environment in which they are placed. In this section we describe the topological structure of the most common networks, obtained by the joining of linear chains, consisting of N monomer links, by their ends. Such joining can be attained, e.g., by introducing polyfunctional monomers into a concentrated or semidilute solution of polymer chains. An important characteristic of the topological structure of a network obtained in this way is the conversion $p > p_c$—the degree of completeness of the chemical reactions of the monomers being joined (p_c is the critical value of the conversion).

Near the gel-formation threshold $(\tau \equiv p/p_c - 1 \ll 1)$, both critically branched networks and macromolecules of finite sizes (a sol) are formed. These networks consist mainly of fragments linked to them by only one end. Such fragments do not make a contribution to the entropic elasticity of the network, which thus owes its origin entirely to the elasticity of the skeleton of the network. The latter is obtained by amputating the above-mentioned fragments from the network. In the case of networks obtained far from the gel-formation threshold $(p = 1)$ the skeleton of the network coincides with the network itself and sol macromolecules are absent.

It is usual to assume that the parameters N and τ completely characterize the scaling laws that are satisfied by polymer networks.[3] In the following section it is shown that knowledge of these quantities is insufficient for the description of networks, because of the presence of topological disorder. Below we shall determine the principal parameters characterizing such disorder. An important characteristic is the spatial scale $\xi^{(0)}$ of the disorder in the conditions of synthesis of the network. Over short distances $r < \xi^{(0)}$ different fragments of chains of the network are spatially separated, and, starting from the scale $\xi^{(0)}$, their mutual overlap becomes important. The quantity $\xi^{(0)}$ is found from the condition that the numbers of links within a sphere of radius $\xi^{(0)}$ that belong to neighboring and remote fragments of the chain [$g^{(0)}$ and $g'^{(0)} = \rho^{(0)}(\xi^{(0)})^3$, respectively, where $\rho^{(0)}$ is the average density of links] be equal.

Topological disorder in networks obtained far from the gel-formation threshold

In a sufficiently concentrated solution of chains $(\rho^{(0)} \gtrsim \rho^{**(0)})$ the density fluctuations are small and the scale $\xi^{(0)}$ is related to the parameter $g^{(0)}$ *by* $\xi^{(0)} = a(g^{(0)})^{1/2}$ for a Gaussian chain, where a is the length of a monomer link. By means of this relation and the condition $g^{(0)} = g'^{(0)}$ we find

$$g^{(0)}=a^{-6}(\rho^{(0)})^{-2}, \quad \rho^{(0)} \gg \rho^{**(0)}=B^{(0)}/a^6, \tag{1}$$

where $B^{(0)}$ is the second virial coefficients of the interaction of the monomer links. The lower bound $\rho^{**(0)}$ in (1) is obtained from the condition that for $\rho^{(0)} = \rho^{**(0)}$ the energy $E^{(0)}$ of the interaction of the links on the scale $\xi^{(0)}$ should be of the order of the temperature:

$$E^{(0)} \approx T^{(0)}(\xi^{(0)})^3 B^{(0)}(\rho^{(0)})^2 \sim T^{(0)}.$$

In a semidilute solution of chains $(\rho^{**(0)} \gtrsim \rho^{(0)} \gtrsim \rho^{*(0)})$ the quantities $\xi^{(0)}$ and $g^{(0)}$ are connected by the relation

$$\xi^{(0)}=a(B^{(0)}/a^3)^{2\nu-1}(g^{(0)})^\nu,\quad \nu\approx {}^3/_5, \tag{2}$$

which determines the size of an isolated chain with $g^{(0)}$ links.[1] With the aid of (2), from the condition $g'^{(0)}=g^{(0)}$ we obtain

$$g^{(0)}\approx a^{-3/2}(B^{(0)})^{-3/4}(\rho^{(0)})^{-5/4},\quad \rho^{**(0)}\gg\rho^{(0)}\gg\rho^{*(0)}, \tag{3}$$

where the quantity $\rho^{*(0)}=a^{-6/5}(B^{(0)})^{-3/5}N^{-4/5}$ is found from the condition $g^{(0)}=N$ for the threshold of overlap ($\rho^{(0)}=\rho^{*(0)}$) of the chains in the solution.

Our calculated parameter $g^{(0)}$ characterizes the extent of the topological disorder while the network is being synthesized. In the case $g^{(0)}\ll N$ its chains are strongly entangled with each other (see Fig. 1), while for $g^{(0)}\approx N$ such a network is topologically equivalent to a regular lattice (see Fig. 2).

As is well known,[3] in a semidilute solution linear chains with $N>g^{(0)}$ links can be regarded as Gaussian chains, consisting of $N/g^{(0)}$ noninteracting blobs of size $\xi^{(0)}$, each of which has $g^{(0)}$ monomer links. Therefore, the size of these chains is equal to

$$R^{(0)}\approx\xi^{(0)}(N/g^{(0)})^{1/2}. \tag{4}$$

An important topological characteristic of the network is the number N_e of links between two effective topological couplings of the chain. In a concentrated solution the chains are Gaussian and the parameter $N_e\approx 200$ (Ref. 18). In a semidilute solution, using the representation of a Gaussian chain of blobs, we find

$$N_e\approx 200 g^{(0)},\quad g^{(0)}\gg 1. \tag{5}$$

Topological disorder in networks obtained near the gel-formation threshold

We now consider critically branched networks with $\tau_G\lesssim\tau\lesssim 1$, where the Ginzburg number τ_G will be obtained below. On scales small in comparison with the size $R^{(0)}$ of a ring such networks have a "tree" structure. The number $L^{(0)}$ of links in a ring on this scale $R^{(0)}$ and the average density of links in the gel network are given by the expressions

$$\rho_g^{(0)}\approx\rho^{(0)}\tau,\quad L^{(0)}=N/\tau^2. \tag{6}$$

In accordance with the first of these, only a small fraction ($\sim\tau$) of the chains of the solution belong the structure of the network. The remaining chains take part in the formation of the tree macromolecules of the sol. Because of the absence of topological couplings with the polymer network such macromolecules can be eluted from it, and the network obtained is placed in an experimental environment that differs from the conditions for synthesis of the network.

The skeleton of the network under consideration consists of elastically active chains. The density of the links of the skeleton and the average number of links of its chains are given by the expressions

$$\rho_n^{(0)}\approx\rho^{(0)}\tau^2\approx\rho_g^{(0)}\tau,\quad l^{(0)}=N/\tau. \tag{7}$$

The size of an elastically active chain is determined by an expression analogous to (4):

$$R^{(0)}\approx\xi^{(0)}(l^{(0)}/g^{(0)})^{1/2}. \tag{8}$$

The characteristic scale $\xi_n^{(0)}=\xi^{(0)}/\tau^2$ of the entangling of such chains is determined from the conditions

$$\xi_n^{(0)}=\xi^{(0)}(g_n^{(0)}/g^{(0)})^{1/2},\quad g_n^{(0)}=\rho_n^{(0)}(\xi_n^{(0)})^3.$$

we note that it considerably exceeds the quantity $\xi^{(0)}$, which determines the scale of the entangling of all the macromolecules of the system, including the sol. Thus, as the gel-formation threshold is approached the topological disorder of the skeleton of the polymer network decreases:

$$g_n^{(0)}=g^{(0)}/\tau^4>g^{(0)}.$$

The analysis given above is valid only in the case $\xi_n^{(0)}<R^{(0)}$, to which corresponds $\tau>\tau_G=(g^{(0)}/N)^{1/3}$. In the case $\tau\approx\tau_G$ the skeleton of the network is close to a regular lattice: $g_n^{(0)}\approx l^{(0)}$. To elucidate the physical meaning of the parameter τ_G we estimate the density fluctuations of the links of the network on the scale $R^{(0)}$:

$$\delta\rho_g^{(0)}=L^{(0)}/(R^{(0)})^3\approx(\tau_G/\tau)^{1/2}\delta\rho_g^{(0)}. \tag{9}$$

According to (9) the quantity τ_G has the meaning of the Ginzburg number.[19]

In the case $\tau\lesssim\tau_G$ the relative density fluctuations on the scale $R^{(0)}$ are of order unity, i.e., $\delta\rho_g^{(0)}\approx\rho_g^{(0)}$, and this gives $L^{(0)}\approx\rho_g^{(0)}(R^{(0)})^3$. Such a network has a percolation structure,[20,13] and its parameters $\rho_g^{(0)}$ and $R^{(0)}$ are determined by the expressions

$$\rho_g^{(0)}\approx\rho^{(0)}\tau_G^{1-\beta}\tau^\beta,\quad R^{(0)}\approx\xi^{(0)}\tau_G^{\nu-2}\tau^{-\nu}, \tag{10}$$

where β and ν are the critical indices of percolation theory and the coefficients of proportionality are found from the condition for matching of (10) with the expressions (6) and (8) at $\tau=\tau_G$. By means of the relations (10) we find

$$L^{(0)}=N\tau_G^{-2+\nu D^{(0)}}\tau^{-\nu D^{(0)}},\quad D^{(0)}=(d+2-\eta)/2, \tag{11}$$

where $D^{(0)}$ is the fractal dimension of the percolation cluster and d is the dimensionality of space.

3. ELASTICITY OF STRUCTURALLY DISORDERED NETWORKS

We now study the properties of networks in a good solvent with given virial coefficients $B>0$ and $C>0$ describing the interaction of the monomer links. Important characteristics of such networks are the swelling coefficient α and expansion coefficient α_T of its chains:

$$\alpha=(V/V^{(0)})^{1/3}=(\rho_g^{(0)}/\rho)^{1/3},\quad \alpha_T=R^{(0)}/R, \tag{12}$$

where V is the volume of the network, $V^{(0)}$ is its volume in the conditions of synthesis, ρ is the density of the links of the network, and R is the length of its chains when they are in the unconnected state in the solvent under consideration.

Networks obtained far from the gel-formation threshold. In the classical theory of Flory the free energy of such a network is equal to the sum of an entropy and an energy contribution:

$$F={}^3/_2 QTV\nu\alpha_T^2\alpha^2+E(\rho),\quad Q\sim 1, \tag{13}$$

where T is the temperature, $\nu=\rho/n$ is the density of the chains, and it is assumed that the difference of α_T from unity is due entirely to the thermal expansion of the chains. Henceforth we shall neglect these effects, so that in the framework of the mean-field theory we have $\alpha_T=1$. For a small link density the virial expansion of the function $E(\rho)$ has the form

$$E(\rho)/V = TB\rho^2, \quad \rho \ll B/C. \tag{14}$$

The equilibrium value of the density of links of the network ($\rho = \bar{\rho}$) is found by minimizing the free energy (13), (14).

$$\bar{\rho} \approx B^{-3/5}(\rho^{(0)})^{2/5}N^{-3/5}, \quad \bar{\rho} \gg \rho^{**} = B/a^6. \tag{15}$$

The expressions (13)–(15) are valid only in the region where mean-field theory is applicable, which is determined by the inequality (15).

As will be shown below, in the fluctuation region the semidilute regime for the fluctuations of the chains of the network is realized:

$$\rho^{**} \gg \bar{\rho} \gg \rho^* \approx a^{-6/5}B^{-3/5}N^{-4/5}. \tag{16}$$

The basic idea of the scaling description is to go over from the monomer links to new structural units—blobs, each of which has size ξ and consists of g monomer links [see also (2) and (3)]:

$$\xi \approx a^{2/5}B^{1/5}g^{3/5}, \quad g \approx a^{-3/2}B^{-3/4}\rho^{-5/4}. \tag{17}$$

In fact the blobs are close-packed ($g \approx \rho\xi^3$) and have the same effective virial coefficient ($B_{\text{bl}} \approx \xi^3$) as hard spheres of radius ξ. Therefore, the interaction energy of blobs of density $\rho_{\text{bl}} = \rho/g$ is equal to

$$E(\rho)/V = TB_{\text{bl}}\rho_{\text{bl}}^2 \approx \rho T/g. \tag{18}$$

The elasticity of Gaussian chains of blobs can be described by means of the classical theory (13), where the function $E(\rho)$ is obtained in (18). Because the character of the swelling of unconnected chains in the conditions of their synthesis differs from that in the conditions of their use, the parameter $\alpha_T \neq 1$ (12), and the quantities appearing in it are determined by the expressions (4) and

$$R \approx \xi(N/g)^{1/2}. \tag{19}$$

The condition for the minimum of the free energy (13), (18) of the network with respect to the density ρ can be found by equating the osmotic pressure of a semidilute solution of chains to the stress associated with the entropic elasticity ($\pi_{\text{osm}} = \pi_{\text{el}}$), with

$$\pi_{\text{osm}} \approx T\rho/g, \qquad \pi_{\text{el}} \approx \nu T\alpha_T^2\alpha^2. \tag{20}$$

The difference of the quantities (20) is equal to the external pressure $p = \pi_{\text{el}} - \pi_{\text{osm}}$. For a small deformation of the network its elastic modulus K is determined by the expression

$$P = K(\alpha/\bar{\alpha} - 1), \quad \bar{\alpha} = (\rho^{(0)}/\bar{\rho})^{1/3}. \tag{21}$$

With the aid of the expressions (20), (17), and (4), (19) we find the equilibrium density of the links of the network

$$\bar{\rho} \approx a^{-6/5}B^{-3/5}(g^{(0)})^{-1/5}N^{-3/5} \tag{22}$$

and its elastic modulus (21)

$$K \approx \bar{\rho}T/g, \quad g \approx (g^{(0)})^{1/4}N^{3/4}. \tag{23}$$

The expression (22) makes it possible to convince oneself directly of the existence of the semidilute fluctuation regime (16).

Owing to topological coupling the maximum value of the number g of links of an untangled segment of a chain is bounded by the quantity N_e (5). In reality, it is somewhat smaller than N_e because of the finiteness of the osmotic pressure stretching the chains of the network. To find it we make use of the expression for the elastic stress of a network with strongly entangled chains, which is obtained by differentiation of the entropy S [the expressions (26) and (27) of Ref. 14]:

$$\pi_{\text{el}} \approx (\rho/N_e)\alpha_T\alpha, \quad N_e\alpha_T\alpha \lesssim N.$$

As a result, for networks with $g^{(0)} \gtrsim N_e^4/N^3$, in which the contribution of topological restrictions is important, we find the number of links of a blob:

$$g \approx N_e(g^{(0)}/N_e)^{1/7} \leqslant N_e. \tag{24}$$

Neglecting the weak power dependence (24) we have $g \approx N_e$, and for the parameters $\bar{\rho}$ and K for such networks we obtain from (17) the expressions

$$\bar{\rho} \approx \bar{a}^{6/5}B^{-3/5}N_e^{-4/5}, \quad K \approx \bar{\rho}T/N_e. \tag{25}$$

Networks obtained near the gel-formation threshold. We first consider critically branched networks in the framework of mean-field theory. In the case $1 \gtrsim \tau \gtrsim \tau_G$ a contribution to the entropic term is given only by the network skeleton, which consists of elastically active chains. The density ν of these chains and the density ρ_n of their links are determined by formulas that follow from (7):

$$\rho_n \approx \rho\tau, \quad \nu = \rho_n/l^{(0)} \approx \rho\tau^2/N. \tag{26}$$

Minimization of the expression (13) with allowance for (26) gives

$$\bar{\rho} \approx B^{-3/5}(\rho^{(0)})^{2/5}N^{-3/5}\tau^{8/5}, \quad B/C \gg \bar{\rho} \gg \rho^{**} = B/a^6. \tag{27}$$

Thus, as τ decreases the region of applicability of mean-field theory ($\rho \gtrsim \rho^{**}$) decreases.

We now consider the fluctuation region $\rho \lesssim \rho^{**}$. The decreases of the network density as $\tau \to 0$ [see, e.g., (27)] leads, according to (17), to an increase of the blob size ξ and of the number g of links in the blob. For $\tau \gtrsim 1$ the quantity $g \lesssim N$ (23). Therefore, there is a region $1 \gtrsim \tau \gtrsim \tau^*$ in which the blob has the structure of a linear chain. In this region, minimizing the network free energy(13), (18),and(26) with respect to ρ, with the aid of the expression $R \approx \xi(1^{(0)}/g)^{1/2}$ for the size of an elastically active chain, we find

$$\bar{\rho} \approx a^{-6/5}B^{-3/5}(g^{(0)})^{-1/5}\tau^{8/5}N^{-3/5}, \tag{28}$$

$$K \approx \bar{\rho}T/g, \quad g \approx (g^{(0)})^{1/4}N^{3/4}\tau^{-2}. \tag{29}$$

The parameter $\tau^* = (g^{(0)}/N)^{1/8}$ is found from the condition $g = N$ for $\tau = \tau^*$. Thus, the intermediate scaling regime (28), (29) can be observed only in the case of sufficiently long chains of the network and of strong topological disorder, when the parameter $\tau^* \ll 1$.

In the region $\tau^* \gtrsim \tau \gtrsim \tau_G$ each blob is a macromolecule having the structure of a random tree.[13] We denote by ξ and g, respectively, the size of such a branched blob and the number of its links, which are related to the average density of links of the network by the condition for close packing of the blobs: $g = \rho\xi^3$. Regarding these blobs as the new structural units, we can characterize the resulting network by the parameter $\tau_{\rm bl}$, analogous to the parameter τ that corresponds to choosing individual chains of the network as such structural units. In the new units the second of the relations (6) and (7) are rewritten in the form

$$L^{(0)}=g/\tau_{\rm bl}^2, \quad l=g/\tau_{\rm bl}, \tag{30}$$

where l is the number of links of an elastically active chain dressed in a "coat" of $\tau_{\rm bl}^{-1}$ blobs.

The quantity l is greater than $l^{(0)}$, since, in addition to the $l^{(0)}$ links of the elastically active chain, lattice fragments of size $\lesssim\xi$, attached to the chain by only one end, also make a contribution to l. Such fragments, contained in branched blobs, transmit elastic stress in the network because of the presence of correlations in the position of their links with links in the network skeleton. These correlations are due to the steric interaction of the links of the network. Thermal fluctuations destroy them on the scale ξ. Therefore, network fragments with a size greater than ξ do not affect its entropic elasticity $\pi_{\rm el}$ but make a decisive contribution to the osmotic pressure $\pi_{\rm osm}$.

Eliminating the parameter $\pi_{\rm bl}$ from the relations (30), for the size of an elastically active chain we find the expression

$$R=\xi(l/g)^{1/2}\approx\xi(L^{(0)}/g)^{1/4}. \tag{31}$$

Substituting the expressions (31) and (8) into (12) and into the equation $\pi_{\rm el}=\pi_{\rm osm}$ (20), with the aid of (26) we find for the number of monomer links of a blob the expression

$$g\approx(g^{(0)})^{2/5}N^{3/5}\tau^{-16/5}, \quad \tau^*\lesssim\tau\lesssim\tau_G. \tag{32}$$

We note that, according to (32), for $\tau=\tau_G=(g^{(0)}/N)^{1/3}$ we have $g=L^{(0)}$. Thus, the equilibrium density of the links of the network with $\tau=\tau_G$ is found from the condition for the threshold of overlap of its elastically active chains. The presence of this analog of Flory's gel theorem[1,3] is not surprising, since, as shown in the preceding section, the skeleton of such a network has a regular structure $g_n^{(0)}\approx l^{(0)}$.

The condition for applicability of Eqs. (30) is the presence of a large number ($\sim\tau_{\rm bl}^{-2}\gg1$) of blobs on the scale R (31). With the aid of (30) and (32) it is not difficult to convince oneself of the validity of this inequality for $\tau\gg\tau_G$, with $\tau_{\rm bl}\approx1$ for $\tau\approx\tau_G$.

To find the equilibrium density of the links of the network we must calculate how the size ξ of a branched blob depends on the number g (32) of its links. The correlations due to the presence of steric interactions of the links of the blob are taken into account most simply by means of Flory's approach.[1] For this we represent the free energy of a blob of size R in the form of a sum of an elastic contribution and an energy contribution:

$$F/T=R^2/R_0^2+Bg^2/R^3, \quad R_0^2=a^2N^{1/2}g^{1/2}, \tag{33}$$

where R_0 is the size of a branched macromolecule of g monomer links in the absence of interaction between them. The equilibrium value $R=\xi$ is found by minimizing the free energy of (33) with respect to R:

$$\xi=a^{2/5}B^{1/5}g^{1/2}N^{1/10}. \tag{34}$$

With the aid of the condition for close packing of the blobs ($\rho=g/\xi^3$) and (34), (32), for the equilibrium density of the links of the network we again find the expression (28), which is thus valid in the entire region $1\gtrsim\tau\gtrsim\tau_G$. However, the expression for the elastic modulus $K\approx\bar{\rho}T/g$, where g is determined in (32), differs from (29) because of the difference of the quantities g in (29) and (32).

As is well known,[3] the Flory approximation (33) for the calculation of the critical index ν gives the value $\nu=3/5$ for linear chains. However, in the case of branched macromolecules its accuracy is considerably worse. The more accurate scaling dependence (34) has the form[21]

$$\xi\approx a(B/a^3)^{2\nu-1}N^\nu(g/N)^{\nu_t}, \quad \nu\approx0{,}6, \quad \nu_t\approx0{,}45, \tag{35}$$

whence for the equilibrium density of the links we find the expression

$$\bar{\rho}\approx a^{-1{,}2}B^{-0{,}6}N^{-0{,}66}(g^{(0)})^{-0{,}14}\tau^{1{,}1}. \tag{36}$$

To conclude this section we consider the swelling of percolation networks ($\tau\ll\tau_G$). The equilibrium value of the density of their links is equal to

$$\bar{\rho}\approx L^{(0)}/\xi^3\approx a^{-6/5}B^{-3/5}N^{-3/10}(L^{(0)})^{-1/2}, \tag{37}$$

where for an estimate of the quantity ξ we have made use of the Flory approximation (33), (34) with the parameter $g=L^{(0)}$ determined in (11). The more accurate value $D\approx2.2$ for the fractal dimension of a percolation cluster[21] differs insignificantly from the result $D=2$ (34) of the Flory approximation. The elastic modulus of the network is given by the scaling expression

$$K\approx T/\xi^3\approx a^{-6/5}B^{-3/5}N^{-3/10}(L^{(0)})^{-3/2}. \tag{38}$$

We note that by virtue of the inequality $\tau\ll\tau_G=(g^{(0)}/N)^{1/3}$ the percolation regime (37), (38) can be observed, in fact, only in networks obtained in a solution of chains near the threshold of their overlap at $\rho^{(0)}\approx\rho^{*(0)}$ (3). Because of topological coupling of sufficiently large macromolecules of the sol with the polymer network, the sol cannot be completely eluted and introduces an extra contribution to the density of the network in addition to (37). Allowance for this effect requires a more detailed description of the effects of the topological coupling and lies beyond the scope of this article.

4. DENSITY FLUCTUATIONS IN POLYMER NETWORKS

In disordered systems there are two types of averaging—Gibbsian and configurational. We determine the local average density $\langle\rho(\mathbf{x})\rangle$ of the links of the network with the aid of the usual Gibbsian thermodynamic averaging of its microscopic density $\rho(\mathbf{x})$. The quantity $\langle\rho(\mathbf{x})\rangle$ is a random function of the coordinates. Such statistical density fluctuations are usually disregarded in the theory of polymer systems. However, as will be shown below, in the scaling region statistical fluctuations $d\rho(\mathbf{x})$ of the density of the links of the network are considerably greater than their thermodynamic fluctuations $\delta\rho(\mathbf{x})$:

$$\delta\rho(\mathbf{x})=\rho(\mathbf{x})-\langle\rho(\mathbf{x})\rangle, \quad d\rho(\mathbf{x})=\langle\rho(\mathbf{x})\rangle-\langle\overline{\rho(\mathbf{x})}\rangle. \tag{39}$$

Important characteristics of the density fluctuations are their correlation functions

$$g(\mathbf{x},\mathbf{x}')=\langle\delta\rho(\mathbf{x})\delta\rho\mathbf{x}')\rangle, \quad G(\mathbf{x}-\mathbf{x}')=\overline{d\rho(\mathbf{x})d\rho(\mathbf{x}')}. \tag{40}$$

The bar in (39) and (40) denotes averaging over the configuration (the different topological structures of the network), the probability of each of which is determined by the conditions of synthesis.

The replica method[13,14] makes it possible to perform the averaging over the configurations before the calculation of the thermodynamic averages. For this we consider a system incorporating the network under the conditions of synthesis and m identical replicas of the network under the conditions of use. We shall label these subsystems by the indices $k = 0$ and $k = 1,...,m$, respectively. After the configurational averaging has been performed an effective interaction that has the character of attraction appears between these subsystems.

Under the conditions of synthesis, by virtue of the translational symmetry of the system, the monomer links are delocalized. The effective attraction localizes the position of the links of the network near certain average positions of the links. This physical picture corresponds to the solid phase of the polymer. The restriction of the conformational set of the system under consideration, with specified average densities $\rho^{(k)}(\mathbf{x})$ by virtue of the localization of its links, is described by an entropy functional $S_m\{\rho^{(k)}\}$. Henceforth, we shall consider only long-wavelength density fluctuations in each of the replicas $k = 0,1,...,m$, with scales large in comparison with the respective correlation lengths $\xi^{(k)}$. Such fluctuations can be described by means of the blob concept that was discussed above. Choosing these blobs as the new structural units, to find the functional $S_m\{\rho^{(k)}\}$ we can make use of the mean-field approach developed in Ref. 14.

We give a brief account of this approach as applied to the system under consideration. We denote by

$$P^{(0)},\ T^{(0)}\ \text{и}\ P^{(k)}=P,\ T^{(k)}=T,\quad k=1,\dots,m \tag{41}$$

the pressure and temperature under the conditions of synthesis and when the network is in use, respectively. Then the thermodynamic potential of the system can be represented in the form

$$\Phi_m\{\rho^{(k)}\}/T=\sum_{k=0}^{m}[E^{(k)}\{\rho^{(k)}\}+P^{(k)}V^{(k)}]/T^{(k)}-S_m\{\rho^{(k)}\}. \tag{42}$$

Here $E^{(k)}\{\rho^{(k)}\}$ is the energy of the steric interactions of the blobs in the kth replica [see (18)]:

$$E^{(k)}\{\rho^{(k)}\}=T^{(k)}\int d\mathbf{x}^{(k)}\rho^{(k)}(\mathbf{x}^{(k)})/g^{(k)}(\mathbf{x}^{(k)}),\quad g^{(k)}=\rho^{(k)}(\xi^{(k)})^3. \tag{43}$$

The integration in (43) is performed over the volume $V^{(k)}$ of this replica, and $g^{(k)}(\mathbf{x})$ is the number of monomer links of a blob and depends on the local average density $\rho^{(k)}(\mathbf{x})$ of the links.

Under the conditions (41) the equilibrium values $\bar{\rho}^{(0)}$ and $\bar{\rho}^{(k)}=\bar{\rho}^{(0)}/\alpha^3$ $(k=1,...,m)$ of the densities are determined from the condition for the minimum of the functional Φ_m (42). Therefore, its expansion in powers of the density fluctuations $\Delta\rho^{(k)}$ starts from the quadratic terms:

$$\Delta\overline{\Phi}_m\{\rho^{(k)}\}=\frac{T}{2}\sum_{k,k'}\int d\overline{\mathbf{x}}^{(k)}\,d\overline{\mathbf{x}}'^{(k')}(\mathrm{G}^{-1})^{kk'}(\overline{\mathbf{x}}^{(k)},\overline{\mathbf{x}}'^{(k')})\times\Delta\rho^{(k)}(\overline{\mathbf{x}}^{(k)})\Delta\rho^{(k')}(\overline{\mathbf{x}}'^{(k')}), \tag{44}$$

where the integration is over the volumes $\overline{V}^{(k)}$ of the undeformed network and the matrix $\mathbf{G}^{-1}$ is the inverse of the matrix of the correlation functions of the density fluctuations of the replicas:

$$\mathbf{G}^{kk'}(\mathbf{x}^{(k)},\mathbf{x}'^{(k')})=\langle\Delta\rho^{(k)}(\mathbf{x}^{(k)})\Delta\rho^{(k')}(\mathbf{x}'^{(k')})\rangle. \tag{45}$$

As shown in Ref. 14, the elements of the matrix (45) in the limit $m\to 0$ determine the correlation functions (40) of interest to us:

$$\begin{aligned}&\mathbf{G}^{11}(\mathbf{x}-\mathbf{x}')=\overline{\mathbf{g}}(\mathbf{x}-\mathbf{x}')+\mathbf{G}(\mathbf{x}-\mathbf{x}'),\\&\mathbf{G}^{12}(\mathbf{x}-\mathbf{x}')=\mathbf{G}(\mathbf{x}-\mathbf{x}'),\end{aligned} \tag{46}$$

where $\overline{\mathbf{g}}$ is obtained by configurational averaging of the function $\mathbf{g}$ (40).

We also give the expressions for the thermodynamic potentials of the network under the condition of its synthesis and use:

$$\Phi^{(0)}=\Phi_0\{\bar{\rho}^{(0)}\},\quad \Phi=\frac{d}{dm}\Phi_m\{\bar{\rho}^{(k)}\}|_{m=0}. \tag{47}$$

In Ref. 14 an explicit expression was obtained for the entropy S_m of a network synthesized far from the gel-formation threshold:

$$\begin{aligned}S_m\{\rho^{(k)}\}/\overline{V}&=-\prod_{k=0}^{m}(\alpha_T^{(k)})^{-3}\Big[\sum_{k=0}^{m}(\alpha_T^{(k)}\lambda^{(k)})^2\Big]^{3/2}f(v)+v\nu N,\\ f(v)&=Q\nu\exp(Nv/Q),\end{aligned} \tag{48}$$

where $Q = 1 - 2/f$, f is the functionality of the linking monomer, $\lambda^{(k)}=(V^{(k)}/\overline{V}^{(0)})^{1/3}$ is the coefficient of linear expansion of the network in the kth replica, and the field v should be found from the condition for the maximum of the right-hand side of the first equality (48). Eliminating this field from (48), we find

$$S_m\{\rho^{(k)}\}=Q\nu\overline{V}\Big[3\sum_{k=0}^{m}\ln\alpha_T^{(k)}-\frac{3}{2}\ln\sum_{k=0}^{m}(\alpha_T^{(k)}\lambda^{(k)})^2-1\Big]. \tag{49}$$

The quantities $\alpha_T^{(k)}$ and $\lambda^{(k)}$ in the right-hand side of (49) must be expressed in terms of the density $\rho^{(k)}$ of the links with the aid of the relation (43) and

$$\alpha_T^{(k)}=\frac{R^{(k)}}{\overline{R}^{(0)}},\quad R^{(k)}=\xi^{(k)}\Big(\frac{N}{g^{(k)}}\Big)^{1/2},\quad \xi^{(k)}\approx a^{2/5}(B^{(k)})^{1/5}(g^{(k)})^{3/5}. \tag{50}$$

The physical meaning of these relations was discussed in Sec. 3.

Substitution of (49), (43) into (42) reproduces the expressions (13), (18) for the free energy of the network. We now expand Φ_m (42) in powers of the density fluctuations

$$u^{(k)}\equiv\Delta\rho^{(k)}/\bar{\rho}^{(k)}=-\Delta V^{(k)}/\overline{V}^{(k)},\quad \Delta V^{(k)}=V^{(k)}-\overline{V}^{(k)}. \tag{51}$$

As a result of the calculations given in the Appendix we obtain

$$\Delta\Phi_m\approx\frac{T\overline{V}}{2}\Big[\frac{\bar{\rho}}{g}\sum_{k=1}^{m}(u^{(k)})^2-\frac{\bar{\rho}}{g^{(0)}}\Big(\sum_{k=1}^{m}u^{(k)}\Big)^2\Big]. \tag{52}$$

Inverting the matrix of the quadratic form (52), for the

Fourier components of the correlators (46) corresponding to wave vector $\mathbf{q} = 0$ we find the expression

$$\mathbf{g}_{\mathbf{q}=0} \approx \bar{\rho} T g, \qquad \mathbf{G}_{\mathbf{q}=0}/\mathbf{g}_{\mathbf{q}=0} \approx g/g^{(0)} = (N/g^{(0)})^{3/4}. \tag{53}$$

Thus, in structurally disordered networks with $g^{(0)} \ll N$ the statistical density fluctuations are considerably greater than the thermodynamic density fluctuations.

5. CONCLUSION

Thus, in the scaling region it is not possible to understand the elastic properties of polymer networks without taking the interaction of their chains into account. The magnitude of this interaction depends on the degree of entanglement of the chains under the conditions of synthesis, which is described by the parameter $g^{(0)}$. The experimental data are often expressed in terms of the ratio

$$\rho^{(0)}/\rho^{*(0)} = (N/g^{(0)})^{4/5}.$$

Flory's gel theorem[1] holds only for networks that are synthesized strictly on the threshold of overlap (with $\rho^{(0)} \approx \rho^{*(0)}$) and have an almost regular topological structure. The strongly disordered networks obtained in semidilute solution ($\rho^{**(0)} \gg \rho^{(0)} \gg \rho^{*(0)}$) swell considerably more weakly. The interaction of the chains of such networks leads to the formation of a semidilute fluctuation regime ($\rho \gg \rho^*$).

It is interesting to note that in the scaling region ($\rho \lesssim \rho^{**}$) the equilibrium density of networks obtained in a concentrated solution of chains ($\rho^{(0)} \gtrsim \rho^{**(0)}$) is determined by the same formulas as in the region ($\rho \gg \rho^{**}$) where the mean-field approximation is applicable [see, e.g., (22), (1), and (15) in the case $p \sim 1$, and (28), (3), and (27) in the case $\tau = p/p_c - 1 \ll 1$]. This fact explains the success of the classical theory[1] in the description of the region of developed density fluctuations. This accidental agreement obtains only for the equilibrium density $\bar{\rho}$ of the links of the network when the Flory-approximation value is used for the critical index ν. The elastic characteristics of polymer networks are substantially different in these theories: The mean-field theory yields an overestimate of K. We note that the quantity K is more sensitive to the presence of topological disorder than the equilibrium density $\bar{\rho}$ of the network.

We have shown that in the fluctuation region in polymer networks the thermodynamic fluctuations usually taken into account are small in comparison with its statistical (spatial) fluctuations. The latter are due to fluctuations of the topological structure of the network[14] and give direct information about its degree of disorder. The correlation function of these fluctuations can be measured in experiments on scattering by small wave vectors $q \ll \xi^{-1}$. The opposite case $q \gg \xi^{-1}$ is not of interest, since on small scale $\sim q^{-1} \ll \xi$ there is no contribution from fluctuations of the topological structure ($\mathbf{G} = 0$) and the correlator $\mathbf{g}$ (40) of the thermodynamic fluctuations has the same form as in a semidilute solution of unconnected chains.

The theory we have proposed makes it possible to describe all fluctuation regimes of networks obtained by joining linear chains by their ends and to find the regions of applicability of these regimes. With an appropriate choice of the parameters the theory also describes other types of networks. For example, in the case of networks obtained by radiation-induced joining of chains or by polycondensation of bifunctional and f-functional monomers the quantity N is equal to the average number of links between two transverse couplings. The case $N = 1$ describes networks obtained by polycondensation of only f-functional monomers.

APPENDIX

We shall obtain the expression (52) for the thermodynamic potential. For this we expand the entropy (49), (50) in powers of the parameters $u^{(k)}$ (51):

$$\begin{aligned} S_m = -Q\nu\bar{V}\Big\{ & u^{(0)} + (1-\delta+\delta\alpha^2\alpha_T^2)\sum_{k=1}^{m} u^{(k)} + \Big[(1-\delta)^2 \\ & - \frac{2}{3}\delta^2\alpha^2\alpha_T^2\Big] u^{(0)} \sum_{k=1}^{m} u^{(k)} \\ & + \frac{1}{2}\Big[(1-\delta)^2 - \frac{2}{3}\delta^2\alpha^4\alpha_T^4\Big]\Big(\sum_{k=1}^{m} u^{(k)}\Big)^2 - \frac{1}{2}(u^{(0)})^2 \\ & - \frac{1}{2}\Big[(1-\delta)(2-\delta) + \delta\Big(1 - \frac{2}{3}\delta\Big)\alpha^2\alpha_T^2\Big]\sum_{k=1}^{m}(u^{(k)})^2\Big\}, \end{aligned} \tag{A.1}$$

where $\delta = 1/2(3\nu - 1)$. In the mean-field theory $\nu = 1/2$ and $\delta = 1$. In this case the expression (A.1) for the entropy goes over into the expression obtained in Ref. 14. In the scaling region $\nu = 3/5$ and $\delta = 5/8$. The expansion of the energy term (43) has the form

$$E^{(k)} = (\bar{\rho}\bar{V}T^{(k)}/g^{(k)})[1 - 2\delta u^{(k)} + \delta(1+2\delta)(u^{(k)})^2]. \tag{A.2}$$

We substitute (A.1) and (A.2) into (42). The terms linear in $u^{(k)}$ cancel by virtue of the equilibrium conditions $\pi_{\rm el} = \pi_{\rm osm}$ (20). To obtain the functional (52), which depends only on the deformation tensor $u^{(k)}$ ($k = 1,...,m$) under the conditions of use, we minimize the previously obtained quadratic formula (44) with respect to $u^{(0)}$. The functional written out in (52) corresponds to the limiting case of structurally disordered networks with

$$\alpha^2\alpha_T^2 \approx (N/g^{(0)})^{1/4} \gg 1. \tag{A.3}$$

[1] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1967).

[2] H. M. James and E. Guth, J. Chem. Phys. **11**, 455 (1943).

[3] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979) [Russ. Transl., Mir, Moscow, 1982].

[4] S. Candau, A. Peters, and J. Herz, Polymer **22**, 1504 (1981).

[5] R. W. Richards and N. S. Davidson, Macromolecules **19**, 1381 (1986).

[6] J. Bastide and L. Leibler, Macromolecules **21**, 2647 (1988).

[7] S. F. Edwards and T. A. Vilgis, Rep. Prog. Phys. **51**, 243 (1988).

[8] P. J. Flory, J. Chem. Phys. **18**, 108 (1950).

[9] A. R. Khokhlov, Polymer **21**, 376 (1980).

[10] V. I. Irzhak, B. A. Rozenberg, and N. S. Enikolopyan, *Network Polymers* [in Russian] (Nauka, Moscow, 1979).

[11] J. Bastide, C. Picot, and S. Candau, J. Macromol. Sci. Phys. **19**, 13 (1981).

[12] M. Daoud, E. Bouchaud, and G. Jannink, Macromolecules **19**, 1955 (1986).

[13] S. V. Panyukov, Zh. Eksp. Teor. Fiz. **94**, No. 5, 116 (1988) [Sov. Phys. JETP **67**, 930 (1988)].

[14] S. V. Panyukov, Zh. Eksp. Teor. Fiz. **96**, 604 (1989) [Sov. Phys. JETP **69**, 342 (1989)].

[15] A. Johner and M. Daoud, J. Phys. (Paris) **50**, 2147 (1989).
[16] M. A. Leontovich, *Introduction to Thermodynamics* [in Russian] (Gostekhizdat, Moscow, 1952), Sec. 3.
[17] S. V. Panyukhov, Pis'ma Zh. Eksp. Teor. Fiz. **51**, 223 (1990) [JETP Lett. **51**, 253 (1990)].
[18] S. M. Aharoni, Macromolecules **16**, 1722 (1983).
[19] P. G. deGennes, J. Phys. (Paris) **38**, L335 (1977).
[20] T. C. Lubensky and J. Isaacson, Phys. Rev. Lett. **41**, 829 (1978); (erratum) **42**, 410 (1979).
[21] S. V. Panyukov, Vysokomol. Soedin. **31**, No. 10, 758 (1989).

Translated by P. J. Shepherd