Inhomogeneities as consequences of a stretching of polymer networks

S. V. Panyukov
P. N. Lebedev Physics Institute, Russian Academy of Sciences, 117924 Moscow, Russia

(Submitted 19 May 1993)
Pis'ma Zh. Eksp. Teor. Fiz. **58**, No. 2, 114–118 (25 July 1993)

A replica method is used to calculate the orientational distribution function of the chains of polymer networks subjected to a given stretching or swelling.

The enormous success of the classical theory of high elasticity[1,2] gave rise to the widespread belief that the stretching of the chains of a polymer network is affine, with proportional changes in the dimensions of the sample. If there are no inhomogeneities during the synthesis, the density distribution in such a network remains uniform even after an affine extension. Recent neutron experiments[3] have cast doubt on the affinity hypothesis. In order to explain these experiments, it has been necessary to invoke a network model consisting of clusters with an elevated density of cross-links and "holes" between them. When a network is stretched, the clusters move away from each other in an affine fashion, undergoing no changes in size or shape.

Because of ambiguities in interpretation, these neutron experiments have succeeded not so well in shedding light on the physical picture of the stretching of networks as in hardening the positions of the various researchers, some of whom attribute the observed effects to ordinary thermodynamic fluctuations of the density of spatially homogeneous networks.[4] The presence of inhomogeneities is of general theoretical interest, and it is also a question of fundamental importance to the industrial synthesis of polymer materials with given elastic and strength properties. The probability for the rupture of a chain of l units of size a can be characterized by the degree of stretching of the chain, $h_\mu = R_\mu^2/2a^2l$, where R_μ is the distance between the ends of the chain (between its cross-links with other chains of the network) along the coordinate axes, $\mu = x,y,z$.

In this letter we calculate the orientation distribution function

$$w_1(h_\mu) = \left\langle \prod_\mu \delta(h_\mu - R_\mu^2/2a^2l) \right\rangle \tag{1}$$

of Gaussian chains of phantom networks produced through an instantaneous cross-linking (vulcanization)of linear chains in a spatially homogeneous "initial" system. The average in (1) is taken in accordance with a Gibbs measure, over all the chains of the network. The random nature of the formation of cross-links means that these chains differ in their length l. Distribution function (1) also describes NMR data. To determine the modulus of the loss of elastomers,[5] this function should be averaged over the distribution function $f(l) = \bar{l}^{-1} \exp(-l/\bar{l})$, of the numbers of units (l) of the elementary chains of the network.

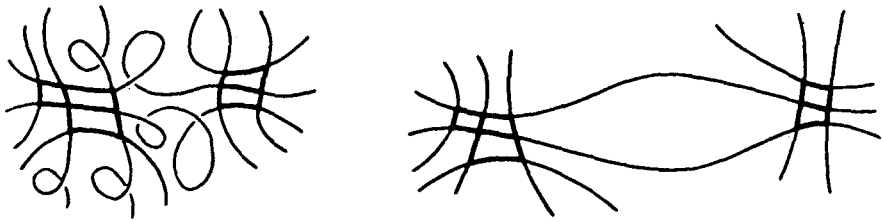

FIG. 1. Randomly cross-linked polymer networks in the initial system under the synthesis conditions (a) and in the final stretched system under the experimental conditions (b). The heavy lines represent short chains which are parts of weakly deformed clusters.

The expression we have derived for a network which is stretched (with respect to the synthesis conditions) by factors λ_μ along the axes $\mu=x,y,z$, i.e.,

$$w_l(h_\mu)=\int_0^\infty d\sigma P(\sigma)\prod_\mu\left(\frac{\alpha_\mu}{\pi h_\mu}\right)^{1/2}\exp(-\alpha_\mu h_\mu), \tag{2}$$

$$\alpha_\mu=(\sigma+a^2l)/(\sigma+a^2l\lambda_\mu^2), \quad \int_0^\infty d\sigma P(\sigma)=1,$$

supports the qualitative network model proposed in Ref. 3. The function $P(\sigma)$ represents the probability distribution of clusters with respect to their mean square size $\sigma=\langle R_{\rm cl}^2\rangle$. Short chains of size $a^2l\ll\sigma$ are part of such clusters, and they are not deformed when the network is stretched, according to (2). Fairly long chains with $a^2l>\sigma$ in the gaps between clusters undergo an affine deformation. As Fig. 1 shows, the density distribution, which is homogeneous under synthesis conditions, becomes very inhomogeneous when the network is stretched.

To find distribution functions (1), we introduce their generating function

$$W_t(k_\mu)=\left\langle\sum\exp\left(-tl+i\sum_\mu k_\mu h_\mu\right)\right\rangle=-\frac{1}{T}\frac{dF(\epsilon)}{d\epsilon}\Big|_{\epsilon=0}, \tag{3}$$

where the sum is over all the chains of the network, and T is the temperature. We are denoting by $F(\epsilon)$ the free energy of the network, in which each chain is characterized by the distribution function (G^ϵ) of distances between its ends:

$$G_l^\epsilon(\mathbf{R})\equiv G^0+\epsilon G'$$

$$=(2\pi a^2l)^{-3/2}\exp(-R^2/2a^2l)\left[1+\epsilon\exp\left(-tl+i\sum_\mu k_\mu R_\mu^2/2a^2l\right)\right]. \tag{4}$$

The chemical structure of a vulcanized network is characterized by a set of numbers $\mathbf{s}=\{s_i^j\}$, which determine the indices s_i^j of the units of the cross-links of chains i and j. In the case of equilibrium cross-linking, the probability for a given set $\mathbf{s}$ is proportional to the partition function of the system under the synthesis conditions, $Z^0(\mathbf{s})$:

$$p(\mathbf{s})=\frac{z^N}{N!}\frac{w^{N_c}}{N_c!}Z^0(\mathbf{s})/\sum_{NN_c}\int d\mathbf{s}\,\frac{z^N}{N!}\frac{w^{N_c}}{N_c!}Z^0(\mathbf{s}), \tag{5}$$

where z and w are the activities of the monomer units and cross-links, and $N$and N_c are their numbers. Taking the average of the free energy of the network with probability (5), we find

$$F(\epsilon)\equiv -T\sum_{NN_c}\int d\mathbf{s}p(\mathbf{s})\ln Z^{\epsilon}(\mathbf{s})=\frac{dF_m(\epsilon)}{dm}\Big|_{m=0}, \tag{6}$$

$$\exp[-F_m(\epsilon)/T]=\sum_{NN_c}\int d\mathbf{s}\,\frac{z^N}{N!}\frac{w^{N_c}}{N_c!}Z^0(\mathbf{s})[Z^{\epsilon}(\mathbf{s})]^m. \tag{7}$$

To simplify the calculations we ignore the interaction of the units of the polymer chains. For integer values of m, each chain then makes a contribution to (7) which is equal to the product of the corresponding correlation functions (4) of replicas $k=0,1,\ldots,m$, averaged over the chain length l:

$$G_m(\mathbf{X})=\int_0^l dlf(l)G_l^0(\mathbf{x}^0)G_l^{\epsilon}(\mathbf{x}^1)\ldots G_l^{\epsilon}(\mathbf{x}^m),\quad f(l)=z^l. \tag{8}$$

Expression (7) is the series of a perturbation theory in the parameter w of the functional integral:

$$\exp[-F_m(\epsilon)/T]=\int D\varphi\exp\left\{-\int dX\left[\frac{1}{2}\varphi G_m^{-1}\varphi-\frac{w}{4}\varphi^4\right]\right\}. \tag{9}$$

Here the components of the vector $\mathbf{X}$ are the set of coordinates of all replicas, $(\mathbf{x}^0,\mathbf{x}^1,\ldots,\mathbf{x}^m)$. Incorporating the interaction in each of them reduces to adding the interaction energies of the units in (9) and renormalizing the average chain length $\bar{l}=|\ln z|^{-1}$ in (8). These renormalizations are unimportant in the calculation of functions (3).

When fluctuations of the field $\varphi(\mathbf{X})$ are ignored, the integral in (9) can be evaluated by the method of steepest descent. In the case $\epsilon=0$ there is a self-similar solution of the saddle-point equations with a spontaneously broken translational symmetry:[6]

$$\varphi(\mathbf{X})=(w\bar{l})^{-1/2}\chi[(\mathbf{X}^{\perp})^2/2a^2\bar{l}]. \tag{10}$$

This solution depends on only those components $(\mathbf{X}^{\perp})$ of the vector $\mathbf{X}$ which are perpendicular to the directions

$$\mathbf{E}_x=(\mathrm{e}_x,0,0),\quad \mathbf{E}_y=(0,\mathrm{e}_y,0),\quad \mathbf{E}_z=(0,0,\mathrm{e}_z),$$

$$\mathrm{e}_{\mu}=(l,\lambda_{\mu},\ldots,\lambda_{\mu})/(1+m\lambda_{\mu}^2)^{1/2}. \tag{11}$$

The dimensionless function $\chi(t)$ in (10) is the solution of the following equation in the limit $m\to 0$:

$$t\chi''(t)=\chi(t)-\chi^3(t),\quad \chi(0)=1,\quad \chi(t\to\infty)\propto t^{1/4}\exp(-2t^{1/2}). \tag{12}$$

Substituting solution (10) into (9), we find, in first order in ϵ,

$$F_m(\epsilon)-F_m(0)=-\frac{\epsilon T}{2}\sum_{k=1}^{m}\int d\mathbf{X}\varphi G_m^{-1}G'^k G_m^{-1}\varphi=-\frac{\epsilon T}{2w^2}\sum_{k=1}^{m}\int d\mathbf{X}\varphi^3 G'^k\varphi^3. \tag{13}$$

We used saddle-point condition (9) in deriving the second equality here. The fraction G'^k is taken from (4) with $\mathbf{R}=\mathbf{x}^k$. The integral in (13) can be evaluated by going over to the Fourier representation. The Fourier component of the function $\varphi^3(\mathbf{X})$ in (10) is $(w\bar{l})^{-3/2}\kappa(q)$ in the limit $m\to 0$, where

$$\kappa(q)=1-aq(2\bar{l}))^{1/2}\int_0^\infty dx\chi^3(x)J_1[aqx(2\bar{l})^{1/2}], \tag{14}$$

and $J_1(x)$ is the Bessel function. We also introduce the function $P(\sigma)$, by means of a Laplace transformation:

$$\int_0^\infty d\sigma P(\sigma)e^{-\sigma q^2}=\kappa^2(q). \tag{15}$$

The sum in (13) reduces to a multiplication by m. According to (6), the coefficient of the factor $-\epsilon mT$ is thus the same as the generating function we are seeking, (3). Taking inverse Fourier transforms in t and Fourier transforms in k in (3), we finally find expression (2).

There is an important quantitative distinction between the results of a rigorous calculation and those of the qualitative model of Ref. 3. It was assumed in Ref. 3 that the clusters have dimensions large in comparison with the typical size of a unit cell of the network, $a\bar{l}^{1/2}$. Actually, the number of such clusters is exponentially small:

$$P(\sigma)=\frac{\text{const}}{a^2\bar{l}}\left(\frac{a^2\bar{l}}{\sigma}\right)^{1/3}\exp\left[-\frac{3}{2}9^{2/3}\left(\frac{\sigma}{a^2\bar{l}}\right)^{1/3}\right]. \tag{16}$$

To find the asymptotic form of (16), we consider $\kappa(q)$ as an analytic function of the complex variable $z=q^2$. Its imaginary part at $z<0$ in the limit $|z|\to 0$ is found by evaluating the integral in (14) by the method of steepest descent with the help of the asymptotic limit ($t\to\infty$) of the function $\chi(t)$ in (12). Comparing the result of the calculations with the corresponding saddle-point value of integral (15), we find (16). With $\sigma=0$, the function $P(\sigma)$ reaches a maximum $P(0)=9[\chi'(0)]^2/2a^2\bar{l}$, which is found from Eqs. (14) and (15) in the limit $z\to\infty$. Differentiating these equations with respect to z at $z=0$, we find the mean square size of a cluster:

$$\langle R_{\text{cl}}^2\rangle\equiv\int_0^\infty d\sigma\sigma P(\sigma)=2a^2\bar{l}\int_0^\infty dxx\chi^3(x)\approx 0,\ 2a^2\bar{l}. \tag{17}$$

Most of the clusters are thus small in comparison with the typical size of a cell of the network.

We have thus shown that the stretching of randomly cross-linked networks leads, through a deviation from affinity, to the appearance of large spatial inhomogeneities in the networks. At the same time, the elasticity of such networks is described well[6] by the classical theory of high elasticity, based on the affinity hypothesis. The macro-

scopic elasticity thus does not reflect the rather complex nature of the stretching of a polymer. The reason is that the analysis assumes Gaussian networks, whose free energy can be expressed in terms of exclusively the first moment $\langle h_\mu \rangle$ of distribution (1), which is a linear function of λ_μ^2 according to (2). For large deformations, $\lambda_\mu > \bar{l}^{1/2}$, the higher moments of this distribution become important, and the elastic characteristics of the grid depend on its microstructure. Spatial inhomogeneities also arise[7] during the stretching of networks with only slight cross-linking, with $\bar{l} > N_e \sim 200$. In this case, topological constraints must be taken into account.

I wish to thank T. N. Khazanovich for useful discussions.

[1] H. M. James and E. Guth, J. Chem. Phys. **2**, 455 (1973).
[2] P. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, New York, 1971).
[3] J. Bastide, L. Leibler, and J. Proat, Macromolecules **23**, 1821 (1990).
[4] Y. Rabin and R. Bruinsma, Europhys. Lett. **20**, 79 (1992).
[5] I. P. Borodin and T. N. Khazanovich, Polymer **27**, 1044 (1986).
[6] S. V. Panyukov, JETP Lett. **55**, 608 (1992).
[7] S. V. Panyukov, Zh. Eksp. Teor. Fiz. **96**, 604 (1989) [Sov. Phys. JETP **69**, 342 (1989)].

Translated by D. Parsons