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STATISTICAL MODEL OF THE EXTENSION OF ELASTOMERS

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A model of a nematic elastomer in the form of a chain whose links are in one of the two possible states is suggested. For such a two-component system an exact expression of the configuration integral with unknown single-particle potentials of mean forces is obtained. Within the framework of the approximation of a self-coordinated field, physically justified approximations that allowed one to calculate the extension curves at different temperatures have been introduced for them.

Keywords: *nematic elastomer, configuration integral, potentials of mean forces, distribution function, orientational order, extension curve, plateau.*

Introduction. The construction of models of deformation of nematic elastomers is an urgent and complex problem in connection with the substantially nonlinear features of their behavior on stretching. In solving this problem, a statistical approach, within the framework of which an elastomer is represented as a chain formed by N one-dimensional elements with each being in one of the two states, has turned out to be very efficient.

In the first case the element has the length b_1, in the second, b_2. The forces **F**, identical in magnitude but oppositely directed, are applied to both ends of the elastomer. Let N_1 elements be in the first state and N_2 elements in the second, so that their total number is $N = N_1 + N_2$, with the chain length being equal to $L = N_1 b_1 + N_2 b_2$.

Statistical Description. The probability of finding a system located in an external homogeneous field of force **F** in one of the states characterized by numbers N_1 and N_2 has the form

$$W(N_1, N_2, q) = Q_N^{-1} \exp \left\{ -\beta \left(U(N_1, N_2, q) - N_1 \mathbf{F}\cdot\mathbf{b}_1 - N_2 \mathbf{F}\cdot\mathbf{b}_2 \right) \right\} . \tag{1}$$

The number of states that have the same values of N_1 and N_2 is equal to the number of means by which both states can be distributed among the N elements, i.e., is equal to $N!/(N_1!N_2!)$. In this connection, the normalized factor is defined by the formula

$$Q_N = \sum_{N_1=0}^{N} \frac{N!}{N_1!N_2!} \int dq \exp \left\{ -\beta \left[U(N_1, N_2, q) - N_1 \mathbf{F}\cdot\mathbf{b}_1 - N_2 \mathbf{F}\cdot\mathbf{b}_2 \right] \right\} , \tag{2}$$

and the average value of the chain length is equal to

$$\langle L \rangle = \frac{1}{\beta} \left(\frac{\partial \ln Q_N}{\partial F} \right)_{T,N} . \tag{3}$$

To calculate the integral in Eq. (2), we will avail ourselves of the scheme of description of multicomponent systems suggested in [1]: the model considered represents a two-species system. The configuration integral is determined conventionally:

$$Q(N_1, N_2) = \int_V d1 \ldots \int_V dN \exp(-\beta U) . \tag{4}$$

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The digits designate the generalized coordinates of the elements, and V designates the corresponding volume. We will enumerate the elements of the system so that the numbers 1 to N_1 correspond to particles of the 1st species, and from $N_1 + 1$ to $N_1 + N_2$ to those of the 2nd. Then the configuration integral (4) can be represented in the form (the Greek symbols designate the species of particles):

$$Q\,(N_1, N_2) = \prod_{\lambda} \prod_{i_\lambda} \int_V di_\lambda \exp\,(-\,\beta U)\,. \tag{5}$$

Now, we will introduce the distribution functions for such a system:

$$f_\mu\,(i) = \prod_{i_\mu \neq i} \int_V di_\mu \prod_{\lambda \neq \mu} \prod_{i_\lambda} \int_V di_\lambda \exp\,(-\,\beta U)\,, \tag{6}$$

$$f_{\mu\nu}\,(i, j) = \prod_{i_\mu \neq i} \int_V di_\mu \prod_{i_\nu \neq j} \int_V di_\nu \prod_{\lambda \neq \mu,\nu} \prod_{i_\lambda} \int_V di_\lambda \exp\,(-\,\beta U)\,. \tag{7}$$

The first of these relations determines the unnormalized distribution function of the particles of species μ, and the second, particles of species μ and ν. All higher distributions are determined analogously. Equalities (6) and (7) show that the distribution functions of different orders are interrelated by integral relations of the type

$$f_\mu\,(i) = \int_V dj f_{\mu\nu}\,(i, j)\,, \ldots \tag{8}$$

irrespective of the species of particles over the coordinates of which integration is performed. Moreover, from Eqs. (5) and (6) it is seen that the configuration integral can be expressed only in terms of the single-particle function of arbitrary species:

$$Q\,(N_1, N_2) = \int_V di f_\mu\,(i)\,. \tag{9}$$

Having selected the corresponding nondimensionalizing factors, we will represent the selected functions in an exponential form. From Eq. (6) it follows that the function $f_\mu(i)$ has the dimensionality of volume of degree $N - 1$. Since the $(N - 1)$-fold integration in (6) consists of $N_\mu - 1$ integrations over the particles of species μ and N_λ integrations over all the remaining ones, we will select the indicated factor in the form $\left(Q_\mu^{N_\mu - 1} \prod_{\lambda ! \neq \mu} Q_\lambda^{N_\lambda} \right)^{-1}$, where the quantities Q_λ have the dimensionality of the volume. Then we may write

$$f_\mu\,(i) = Q_\mu^{-1} \prod_{\lambda} Q_\lambda^{N_\lambda} \exp\,[-\,\beta \varphi_\mu\,(i)]\,, \tag{10}$$

where

$$\exp\,[-\,\beta \varphi_\mu\,(i)] = \left(Q_\mu^{-1} \prod_{\sigma} Q_\sigma^{N_\sigma} \right)^{-1} \prod_{i_\mu \neq i} \int_V di_\mu \prod_{\lambda \neq \mu} \prod_{i_\lambda} \int_V di_\lambda \exp\,(-\,\beta U)\,. \tag{11}$$

The quantity $\varphi_\mu(i)$ has the meaning of the potential of the mean force acting on the given particle from the side of all the remaining ones. Having substituted (10) into (9), we obtain

$$Q(N_1, N_2) = Q_\mu^{-1} \prod_\lambda Q_\lambda^{N_\lambda} \int_V di \exp[-\beta\varphi_\mu(i)] . \tag{12}$$

Since the last expression must be valid for any value of μ, as Q_μ we must select the integral figuring in (12). Then

$$Q(N_1, N_2) = \prod_\lambda Q_\lambda^{N_\lambda} = \prod_\lambda \left\{ \int_V di \exp[-\beta\varphi_\lambda(i)] \right\}^{N_\lambda} . \tag{13}$$

As applied to the two-species system considered, in the external field the last expression acquires the form

$$Q(N_1, N_2) = Q_1^{N_1} Q_2^{N_2} . \tag{14}$$

In this case

$$Q_1 = \int_V dq \exp\left\{- \beta [\varphi_1(q) - \mathbf{F}\cdot\mathbf{b}_1]\right\} , \tag{15}$$

$$Q_2 = \int_V dq \exp\left\{- \beta [\varphi_2(q) - \mathbf{F}\cdot\mathbf{b}_2]\right\} . \tag{16}$$

Substituting (14) into (2), we have

$$Q_N = \sum_{N_1=0}^{N} \frac{N!}{N_1! N_2!} Q_1^{N_1} Q_2^{N_2} = (Q_1 + Q_2)^N . \tag{17}$$

The expression obtained is precise, but the problem is that the introduced potentials of mean forces are unknown. Their determination is connected with the solution of a chain of integral equations following from the relations of type (8) and, consequently, with the necessity of using this or another technique of closing this chain. The molecular theory of highly elastic orientationally ordered systems was developed in [2]. In the present work we adopt certain simplifying assumptions and physically justified considerations to seek for these quantities. As the first assumption we assume that all the elements of the elastomer are in self-consistent middle field of all the remaining ones. Next, we will consider that the first state is related to the orientation of the chain links and that its energy is defined by the formula

$$U_1 = -\frac{3}{2} ap \cos^2 \vartheta , \tag{18}$$

where ϑ is the angle between the axis of the element and force **F**; p is defined as the mean value of the second Legendre polynomial:

$$p = \langle P_2(\vartheta) \rangle = \left\langle \frac{1}{2} (3 \cos^2 \vartheta - 1) \right\rangle . \tag{19}$$

We will identify this energy with the potential of mean forces in the first state, i.e.,

$$\beta\varphi_1 = \beta U_1 = -\frac{3}{2} \beta ap \cos^2 \vartheta . \tag{20}$$

Then the function of distribution over orientations will take the form

$$f_1(\vartheta) = Q_1^{-1}\exp\left[\beta\left(\mathbf{F}\cdot\mathbf{b}_1 - \varphi_1\right)\right] = Q_1^{-1}\exp\left[\beta\left(Fb_0 + \frac{3}{2}ap\cos\vartheta\right)\cos\vartheta\right], \tag{21}$$

where $b_0 = \left|\mathbf{b}_1\right|$ is the length of the element in the undeformed state, and the constant Q_1 is defined by the relation

$$Q_1 = 2\pi b_0\int\limits_0^{\pi} d\vartheta\,\sin\vartheta\,\exp\left[\beta\left(Fb_0 + \frac{3}{2}ap\cos\vartheta\right)\cos\vartheta\right]. \tag{22}$$

Using (19) and (21), we obtain an equation to determine the parameter of the order

$$p = \pi b_0\int\limits_0^{\pi}\left(3\cos^2\vartheta - 1\right)f_1(\vartheta)\sin\vartheta\,d\vartheta$$

$$= \frac{\pi b_0}{Q_1}\int\limits_0^{\pi} d\vartheta\,\sin\vartheta\left(3\cos^2\vartheta - 1\right)\exp\left(\beta\left(Fb_0 + \frac{3}{2}ap\cos\vartheta\right)\cos\vartheta\right). \tag{23}$$

Next we will consider that the second state is determined by deformation (extension-compression) of the elastomer elements the energy of which in the linear approximation is defined by the relation

$$U_2 = \frac{c\left(b - b_0\right)^2}{2}, \tag{24}$$

where b is the length of an element in a deformed state. We assume that the middle force potential of this state is determined by the energy (24). Then the distribution function in this state has the form

$$f_2(b) = Q_2^{-1}\exp\left[\beta Fb - \frac{\beta c\left(b - b_0\right)^2}{2}\right], \tag{25}$$

where the normalizing factor is defined by the relation

$$Q_2 = 4\pi\int db\,\exp\left[\beta Fb - \frac{\beta c\left(b - b_0\right)^2}{2}\right]. \tag{26}$$

Due to the presence, in the introgroud function, of the exponentially decreasing factor, the integration limits in (26) may be considered infinite. On introducing the notation $\gamma = \beta Fb_0$, $\alpha = \frac{\beta c b_0^2}{2}$, and $\varepsilon = \frac{b - b_0}{b_0}$, expression (26) takes the form

$$Q_2 = 4\pi b_0\sqrt{\frac{\pi}{\alpha}}\exp\left[\gamma\left(1 + \frac{\gamma}{4\alpha}\right)\right]. \tag{27}$$

The parameter α was determined from the $b_0 = \sqrt{\langle b^2\rangle}$ condition at a zero tensile force, as a result of which $\alpha = \beta b_0^2/2$. Substitution of (17) into (3), using (22) and (27), yields

$$\langle L\rangle = \frac{N}{\beta}\,\frac{Q_1' + Q_2'}{Q_1 + Q_2}, \tag{28}$$

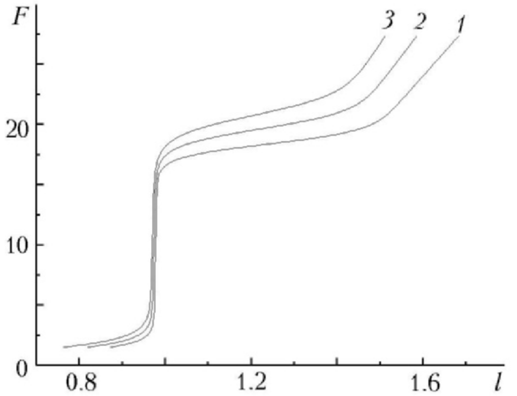

Fig. 1. Curves of the extension of elastomer: a) T = 300 K; 2) 350; 3) 400. F, N.

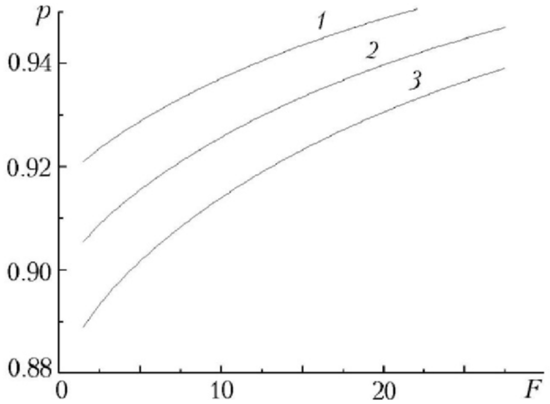

Fig. 2. Dependence of the order parameters on the tensile stress and temperature. Designations 1–3 are the same as in Fig. 1. F, N.

$$Q_1' = 2\pi\beta b_0^2 \int_0^{\pi} d\vartheta \sin\vartheta \cos\vartheta \exp\left[\left(\gamma + \frac{3}{2} ap \cos\vartheta\right)\cos\vartheta\right], \tag{29}$$

$$Q_2' = 4\pi\sqrt{\frac{\pi}{\alpha}}\,\beta b_0^2\left(1+\frac{\gamma}{2\alpha}\right)\exp\left[\gamma\left(1+\frac{\gamma}{4\alpha}\right)\right]. \tag{30}$$

Here the prime denotes the derivative over the magnitude of the tensile force F.

Having substituted (22), (27), (29), and (30) into (28), we can calculate dependence of the relative average length per element $l = \langle L \rangle / N b_0$ on the tensile force F. Calculations were carried out at $b_0 = 10^{-9}$ m and a = 13.62 J for different temperatures T. Figure 1 presents the results of these calculations. The curve that corresponds to the room temperature is in a quite satisfactory agreement with the experimental data of [3] (see also [4]). Five dimensionless units on the axis F correspond to the value 0.002 in the indicated work, where stress is used rather than force. As the temperature rises, the height of the plateau increases and its width decreases. Figure 2 presents the dependences of the order parameter on the tensile stress at different temperatures, from which the disorientating influence of the increase of the latter is seen.

Conclusions. Based on the statistical theory, the nonlinear extension of nematic elastomers with allowance for the orientational ordering of their links is described, and the temperature dependence of the effect considered has been revealed.

NOTATION

a, energy parameter, J; b_0, length of undeformed link, m; b_1, b_2, length of links in the first and second states, m; c, rigidity coefficient, J/m^2; $\mathbf{F}$, force; F, force modulus, N; $\mathbf{F}\cdot\mathbf{b}$, scalar product; $f_\mu(i)$, one-particle distribution function of particles of species μ; $f_{\mu\nu}(i, j)$, two-particle function of distribution of species μ and ν; i, j, numbers of particles; l, relative mean length of a link; L, length of a chain, m; N_μ, number of particles of species μ; N, total number of particles; N_1, N_2, numbers of particles in the first and second states; p, order parameter; P_2, second Legendre polynomial; q, generalized coordinate; Q_N, configuration integral of the system; Q_1, Q_2, configuration integrals of first and second species; Q_1', Q_2', derivatives of torsional stress; T, absolute temperature, K; U, potential energy of the system, J; U_1, U_2, potential energies of the first and second states, J; V, volume, m^3; W, probability; α, γ, dimensionless quantities; β, reciprocal energy, 1/J; ε, relative elongation; $\varphi_1(q)$, $\varphi_2(q)$, single-particle potentials of mean forces, J; μ, ν, λ, numbers of species; ϑ, angle; $\langle\,\rangle$, average value.

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