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THEORY OF THE RELAXATION SPECTRA OF CROSS-LINKED POLYMERS IN THE PRESENCE OF STRUCTURAL AND DYNAMIC HETEROGENEITY

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The spectra of relaxation times of polymer meshes in the presence of various types of structural and dynamic heterogeneity have been considered. The influence of the orientation ordering of elements of macromolecules between the mesh nodes on the intrachain spectrum has been investigated. Analysis of the interchain large-scale processes in polymer meshes containing rodlike inclusions has been carried out. It has been shown that the presence of structural and dynamic heterogeneity of the above types along with the previously considered domain structure of cross-linked polymers leads to a fine structure of the relaxation spectra of polymer meshes.

Introduction. Cross-linked polymers are, as a rule, inhomogeneous systems with different types of irregularities (of chemical or physical nature) that show up as various physical and mechanical relaxation properties of such systems (mechanical and dielectric relaxation, NMR and dynamic scattering of light, IR spectra, etc.). The structural and dynamic heterogeneity can influence both the intrachain small-scale relaxation processes corresponding to motions inside chains between mesh nodes and the relatively large-scale interchain relaxation characteristics.

Many theoretical studies of the relaxation properties of regular and irregular polymer meshes were made on the basis of dynamic models consisting of multisegment chains of "beads and springs" (Kargin–Slonimskii–Rauz model of the chain) as well as with the use of a "coarse-grained" model in which each chain between nodes is modeled by one spring and the friction factor of a mesh node corresponds to the total friction of the portions of the chains adjoining this node. Such a dynamic model was used in the literature [1–4] to describe large-scale, specifically meshy, interchain relaxation processes. In [1–4], the contributions of intra- and interchain relaxation processes leading to a dynamic heterogeneity of cross-linked polymers to the viscoelastic characteristics of two- and three-dimensional Gaussian meshes were compared.

One possible cause of the appearance of a dynamic heterogeneity of elastomers could also be the presence of domains differing in the cross-link density, molecular mass of chains between nodes, etc. In [5–7], it is shown that a "domain"-type heterogeneity leads to a change from the "power" to the "fractional-exponential" time dependence of the relaxation modulus. A cross-linked polymer is modeled [5–7] as an ensemble of noninteracting cross-linked domains of various sizes. These domains represent regular cubic meshworks of finite size made up of joined multisegment Gaussian chains and differ from one another in the number of meshes. To perform averaging over all domains, the exponential distribution function of the number of polymer segments in a domain is used [8–11]. It has been shown that the temporal behavior of the relaxation modulus of a cross-linked polymer with a "domain"-type inhomogeneity is defined by the fractional-exponential dependence [5–7] in contrast to regular meshes of infinite extent for which the theory predicts a power law of fall of the relaxation modulus. The manifestation of the fractional exponent in the relaxation properties of polymer systems is discussed in [12–17]. A "domain"-type heterogeneity also leads to a rapid decrease in the modulus in the range of low frequencies compared to this quantity for regular systems. This conclusion can be generalized to domains with other exponential-type distribution functions in the number of segments, i.e., to a fairly wide class of heterogeneous polymer meshes [7].

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Another cause of the dynamic heterogeneity observed in cross-linked polymers is the difference in relaxation properties between longitudinal and transverse (relative to the principal direction of the chain) elements of chains. This effect is especially appreciable in chains with a considerable torsional and flexural rigidity. Movements of the transverse elements of mesh chains were considered in [15, 16] on the basis of a dynamic model of a chain of plane elastically coupled rotators. In these works, Gotlib et al. have developed a theory of high-frequency, transverse, torsion-oscillation relaxation processes for heterogeneous polymer systems at exponential distributions of chains in the degree of polymerization, which can arise at both certain mechanisms of polarization and structural heterogeneity of domain-type polymers. They have investigated the autocorrelation function of the ordering parameter of an individual fragment of a chain averaged over all elements of this chain and over all chains of the system. The autocorrelation function of the ordering parameter of a heterogeneous polydisperse mesh is described by the fractional-exponential time dependences both in the range of small times t due to the intrachain torsional-vibrational motions and at large t due to the chain-length distributions between nodes. Such a behavior distinguishes the transverse torsion-oscillation relaxation processes from the longitudinal ones considered in [5–7] with the use of a model of Gaussian subchains. In the case of longitudinal relaxation processes in chains, fractional-exponential time dependences of the dipole relaxation and other physical quantities manifest themselves only in the range of large t due to the polydispersion of the mesh, and at small t power laws $\sim t^{-n}$ $(n > 0)$ take place due to the intrachain motions.

One possible cause of the appearance of a dynamic heterogeneity and a fine structure of the relaxation spectra in polymer meshes could also be the orientation ordering of chain elements arising from the interactions of liquid-crystal (LC) type elements of chains. Interactions of such a type are especially strong in nematic elastomers and influence their equilibrium properties [18–22]. An orientation order of fragments of mesh chains can also appear due to the ordering of rodlike particles embedded into the mesh and capable of forming the LC state [23]. An investigation of the fine structure of the relaxation spectrum of the mesh in the presence of an orientation order has been made by us recently [24, 25]. We considered the local dynamics of the mesh at fixed boundaries where ordering occurs due to the orientation of the chain elements in the intermolecular field with a fixed position of the boundaries of a nondeformed mesh clamped between two rigid plates. The present paper also considers the influence of an extension of a mesh with free boundaries along the order axis (director) on the form of the relaxation spectrum and discusses the effects caused by the structural heterogeneity of the mesh (the length distribution of chains, the presence of domains with a different value of the local order, etc.).

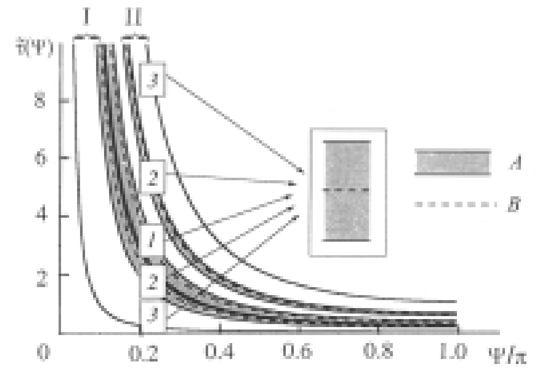
Fine Structure of the Relaxation Spectrum and Heterogeneity of the Local Dynamics of the Mesh in the Presence of an Orientation Order. To describe the mesh structure of a cross-linked polymer, the "*three-chain*" model proposed in [18] is used. The mobility of macromolecular links is described by means of the model of a free-linked chain consisting of either rigid rodlike elements or quasi-elastic (Gaussian) subchains with a fixed rms length [26, 27]. The latter model assumes that when an orientation order is established in a system, the mean-square projections of the chain elements on the axis of the Cartesian system of coordinates change; however, the sum of the squares of these projections remains constant. The respective change in the elastic constants of the elements describes the change in the reactions of the constraint forces (and the corresponding Lagrange factors [28, 29]) acting on the rigid fragments of chains.

In the model under consideration, the relaxation times τ_ξ are determined by the factors $\zeta_\xi(\Psi)$ and K_ξ [30]:

$$\tau_\xi (\Psi) = \zeta_\xi (\Psi) \frac{1}{2K_\xi [1 - \cos \Psi]} . \tag{1}$$

In relation (1), the index $\xi = x, y, z$ numbers three directions of the Cartesian system of coordinates along which the relaxation of the projections of the chain elements b_ξ is considered.

The "dynamic" factor $\zeta_\xi(\Psi)$ is associated with the dissipative effects: friction of elements against the environment and the overcoming of the molecular LC-field barrier during rotation of the chain elements. Its influence on the relaxation properties of non-cross-linked linear polymers was considered in [27, 28]. The calculation of $\zeta_\xi(\Psi)$ for polymer meshes is a special problem which was qualitatively discussed in [24, 25]. In the present work, the above relaxation time $\tau_\xi(\Psi)/\zeta_\xi(\Psi)$ dependent on the contribution of K_ξ to (1) has been calculated.



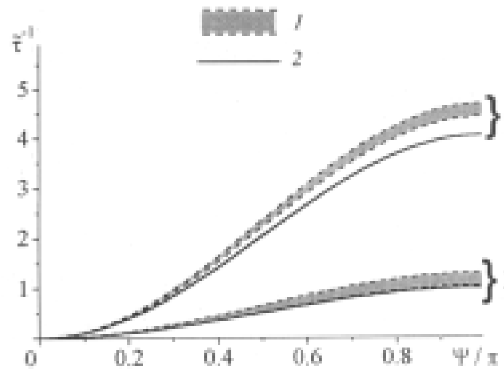


Fig. 1. Reduced relaxation times $\tilde{\tau}(\Psi) \equiv \tau(\Psi)[2K_0/\zeta(\Psi)]$ as a function of the wave number Ψ for a mesh with fixed boundaries at various values of the degree of order: 1) $S = 0$; 2) 0.28; 3) 0.7; *A*, model of a chain of rigid elements; *B*, model of Gaussian subchains with a fixed rms length of an element; I) $\tau_\perp$; II) $\tau_\parallel$; $\gamma = 0.5$. Ψ/π, rad.

Fig. 2. Inverse reduced relaxation times $\tilde{\tau}^{-1}(\Psi) \equiv \zeta(\Psi)/[2\tau(\Psi)K_0]$ as a function of the wave number Ψ for a mesh with free boundaries (1) and a mesh with fixed boundaries (2). Model of Gaussian subchains with a fixed rms length of an element: I) $\tau_\perp$; II) $\tau_\parallel$; $\gamma = 0.3$; $S = 0.5$.

The "statistical" factor K_ξ describes the contribution of the effective elasticity of chains and is determined by the rms fluctuations of projections of the elements of chains stretched in various directions relative to the director:

$$\frac{K_0}{K_\xi} = 3\,\frac{\langle b_\xi^2 \rangle - \langle b_\xi \rangle^2}{l^2}\,, \quad K_0 = 3kT/l^2\,. \tag{2}$$

The present paper is devoted to the investigation of the dependence of the statistical factor K_ξ on the order parameter $S = [3\ \langle \cos^2 \vartheta \rangle - 1]/2$ and the degree of stretching of the chains between the mesh nodes. The degree of stretching of chains in a mesh is characterized by the dimensionless parameter $\gamma \equiv h_0/Nl$, where Nl is the contour length of chains between nodes and h_0 is the distance between the ends of equally stretched chains in the "three-chain" netlike model for a nondeformed mesh.

The presence of an orientational order leads to the appearance of two branches of the relaxation spectrum of the polymer mesh corresponding to the relaxation times of projections of chain elements along ($\tau_\parallel$) and transverse to ($\tau_\perp$) the director.

For a mesh at fixed boundaries where ordering occurs due to the reorientation of the chain elements in the intermolecular field at a fixed position of the boundaries of the nondeformed mesh clamped between two rigid plates, the model of Gaussian subchains gives the following expressions for the statistical factor of relaxation times $\tau_\parallel$ and $\tau_\perp$:

$$\frac{K_0}{K_\parallel} = 1 - \gamma^2 + 2S\,, \quad \frac{K_0}{K_\perp} = 1 - \gamma^2 - S\,. \tag{3}$$

From relations (1) and (3) it is seen that with increasing degree of order the given relaxation times $\tau_\parallel/\zeta_\parallel$ increase due to the statistical factor and $\tau_\perp/\zeta_\perp$ decrease. The relaxation times of the mesh turn out to be shorter than for the non-cross-linked polymer ($\gamma = 0$). An increase in the degree of stretching of chains and in the cross-link density leads to a decrease in the values of $\tau_\parallel/\zeta_\parallel$ and $\tau_\perp/\zeta_\perp$ for both chains.

The rms fluctuations of projections of the chain elements entering into the right-hand side of (2) and influencing the relaxation times of the ordered mesh have also been calculated with the use of the model of free-linked chains consisting of rigid rodlike elements. The calculation procedure is described in detail in [31]. For the model of Gaussian subchains, the statistical factor of relaxation times is independent of the stretching direction of the chain to the order axis and is described by relation (3) for each of the three chains in a net mesh. For the model of a chain consisting of rigid elements, the rms fluctuations of projections of segments along the selected axis turn out to be different for the chains stretched in different directions to this axis. In this case, for an ordered mesh consisting of chains with rigid elements, a fine structure of the spectrum inside each of the two branches corresponding to the relaxation times $\tau_{\parallel}$ and $\tau_{\perp}$ arises.

For sparsely cross-linked meshes ($\gamma < 0.1$) throughout the domain of change in the degree of order the boundaries of "continuous" spectrum lines for the model of the chain consisting of rigid elements are close to one another and to the "discrete" lines for the model of Gaussian subchains. This result substantiates the possibility of describing the dynamics of rigid rodlike fragments of Gaussian mesh chains by a simpler model of Gaussian subchains with a fixed rms length of an element. For non-Gaussian meshes with strongly stretched chains ($\gamma > 0.1$), it is necessary to take into account the spectrum line splitting due to the rigidity of the chain elements (Fig. 1).

Additional dynamic heterogeneity can also arise because of the structural inhomogeneity of the mesh in the presence of the length distribution of macromolecules and the different degree of stretching of chains between nodes. The latter can be caused not only by the structure heterogeneity, but also by the extension of the regular mesh with free boundaries along the director. In this case, the chains stretched along the order axis extend and those stretched perpendicular to this axis contract (provided the volume for elastomers is constant). Since the relaxation times of each chain depend on the degree of its stretching, an additional splitting of the relaxation spectrum lines $\tau_{\parallel}$ and $\tau_{\perp}$ of the extended mesh arises because of the different stretching of the chains between the nodes (Fig. 2). The cross-linked polymer extension along the order axis also leads to a decrease in $\tau_{\parallel}$ and $\tau_{\perp}$ for the mesh with free boundaries as compared to $\tau_{\parallel}$ and $\tau_{\perp}$ for the crossed-linked polymer with fixed boundaries (Fig. 2).

Another cause of the appearance of a fine structure of the ordered mesh relaxation spectrum could be the presence of domains with a different value of the local degree of order, each of which will be characterized by its own set of relaxation times (1) and (3).

Model Theory of the Relaxation Spectrum of Cross-Linked Gel with Embedded Rodlike Molecules. To describe the dynamic properties of cross-linked polymers and gels containing hard rod-like particles, we use the simplified viscoelastic rough model of [4] (Fig. 3). In so doing, we restrict ourselves to the consideration of the case where the characteristic scale of the model meshwork (mesh dimensions) has the same order as the mean distance between the centers of mass of rigid rods.

Rods are characterized by the length l and parameters determined by the value of translational and rotational friction in an effectively viscous medium against whose background a compound motion of the mesh with embedded rods occurs.

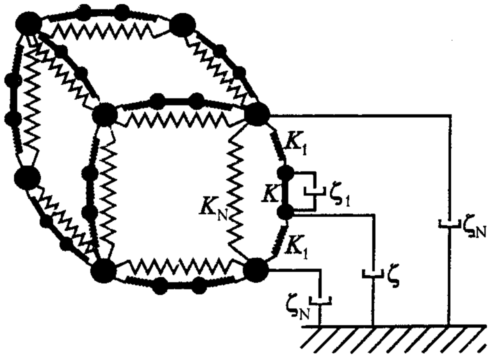
The elastic properties of macromolecules between the cross-linked polymer nodes are given by a Gaussian potential with an elastic constant K_{N}. From the point of view of the rough viscoelastic dynamic model the friction is assumed to be concentrated in the mesh nodes and is characterized by the friction factor ζ_{N} (Fig. 3).

The rigid rod dynamics is modeled by means of a "rigid, on average," quasi-elastic element (dumb-bell), for which the Lagrange factor in the motion equations is replaced by the mean values (mean constraint) so that the rms element length equal to l remains. As for the model of the chain from "rigid, on average," elements, the mean value of the Lagrange factor determines the elastic constant K of the quasi-elastic element.

The rigid rod friction on the environment is assumed to be concentrated on the elastic dumb-bell ends and is given by the friction factor ζ of the viscous drag center on each end of the dumb-bell. We also introduce internal friction ζ_1 of the dumb-bell, which is determined from the condition of equality of the ratio between the translational and rotational diffusion coefficients of the rigid dumb-bell and of the viscoelastic dumb-bell with a fixed, on average, length [28]. In our case, $\zeta_1 = \zeta/4$ [28].

The gel–rod interaction is described by the effective elastic potential that fixes the rods to the gel, prevents translational and orientational mobility of the rod, and is characterized by the constant K_1 (Fig. 3).

For the model of the three-dimensional mesh with embedded rods under consideration, the rms length of the elastic element modeling the rod can be calculated as a function of K, K_1, and K_{N}. From the condition of equality of the rms length to a given length of the rigid rod the value of the effective constant (mean constraint) K is calculated as a function of K_1, K_{N}, and l. The relationship between K_1, K_{N}, and l is defined by the equation



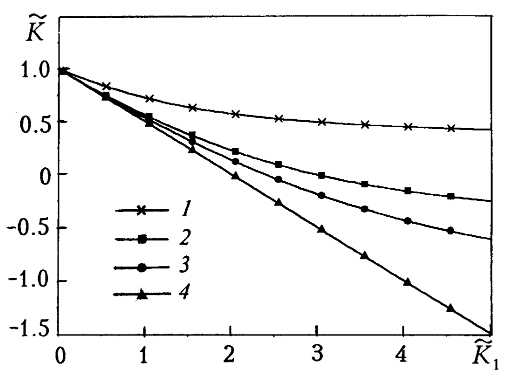


Fig. 3. Cell of the three-dimensional regular cubic model of a mesh with embedded rods.

Fig. 4. Reduced elastic constant $\tilde{K} \equiv K/[3kT/l^2]$ as a function of $\tilde{K} \equiv K_1/[3kT/l^2]$ at K_N = 0 (1); $K_N/[3kT/l^2]$ = 1 (2); 2 (3); and 100 (4).

$$K + \left[\frac{2}{K_1} + \frac{1}{3K_N + 2KK_1/(K_1 + 2K)} \right]^{-1} = \frac{3kT}{l^2} . \tag{4}$$

For illustration, Fig. 4 shows the dependences of K on K_1 for various K_N. At fairly large K_1 and K_N the value of K can become negative, which, from the point of view of the model, corresponds to the negative constraint reaction to the rod contraction.

The equations of motion for the rigid rod ends permit relating their displacements and velocities to the displacements and velocities of the nodes bordering with the rod. Therefore, the dynamical problem is reduced to the solution of the system of equations of motion for the mesh nodes. This system (when projected onto the x-axis) can be given in the form

$$\zeta_N \dot{x}_{\alpha,\beta,\gamma} + K_N \left[6x_{\alpha,\beta,\gamma} - x_{\alpha+1,\beta,\gamma} - x_{\alpha-1,\beta,\gamma} - x_{\alpha,\beta+1,\gamma} - x_{\alpha,\beta-1,\gamma} - x_{\alpha,\beta,\gamma+1} - x_{\alpha,\beta,\gamma-1}\right] +$$

$$+ K_1 \left[6\,(a-b)\, x_{\alpha,\beta,\gamma} - a\,(x_{\alpha+1,\beta,\gamma} + x_{\alpha-1,\beta,\gamma} + x_{\alpha,\beta+1,\gamma} + x_{\alpha,\beta-1,\gamma} + x_{\alpha,\beta,\gamma+1} + x_{\alpha,\beta,\gamma-1})\right] = 0 , \tag{5}$$

where indices α, β, and γ denote the mesh node numbers in three mutually perpendicular directions and the coefficients a and b are given in terms of elastic and viscous characteristics of the mesh elements:

$$a = \frac{K_1\,(K - \lambda\zeta_1)}{(K_1 - \lambda\zeta)\,(K_1 + 2K - \lambda\,(\zeta + 2\zeta_1))} ; \quad b = \frac{\lambda\zeta\,(K_1 + 2K - \lambda\,(\zeta + 2\zeta_1))}{(K_1 - \lambda\zeta)\,(K_1 + 2K - \lambda\,(\zeta + 2\zeta_1))} . \tag{6}$$

Here $\lambda = 1/\tau$ denotes the inverse relaxation times for the mesh with embedded hard particles. The solution of Eq. (5) is represented, as usual, in the form [1]

$$x_{\alpha,\beta,\gamma}(t) = \sum_{\theta_1,\theta_2,\theta_3} q\,(\theta_1, \theta_2, \theta_3)\, \exp\left[i\,(\theta_1\alpha + \theta_2\beta + \theta_3\gamma) - \lambda t\right] , \tag{7}$$

where λ denotes the eigenvalues of system (5) (cf. [1, 2, 4]).

The system of equations obtained for $x_{\alpha,\beta,\gamma}(t)$ leads to a cubic equation for the eigenvalues $\lambda = 1/\tau(\theta_1, \theta_2, \theta_3)$, where $\tau(\theta_1, \theta_2, \theta_3)$ are relaxation times depending on the node displacements. For each set of θ_1, θ_2, θ_3, three λ values are obtained, which reflects the presence of three branches of the collective relaxation spectrum (τ_1, τ_2, and τ_3 in Fig. 5). Besides this solution, there appear two doubly degenerate solutions corresponding to the motion of rods at fixed angles of the mesh (τ_4 and τ_5 in Fig. 5). To each branch there corresponds translational and orientational motion of rods in the net meshes. Thus, the number of relaxation spectrum branches arising in the system under consideration

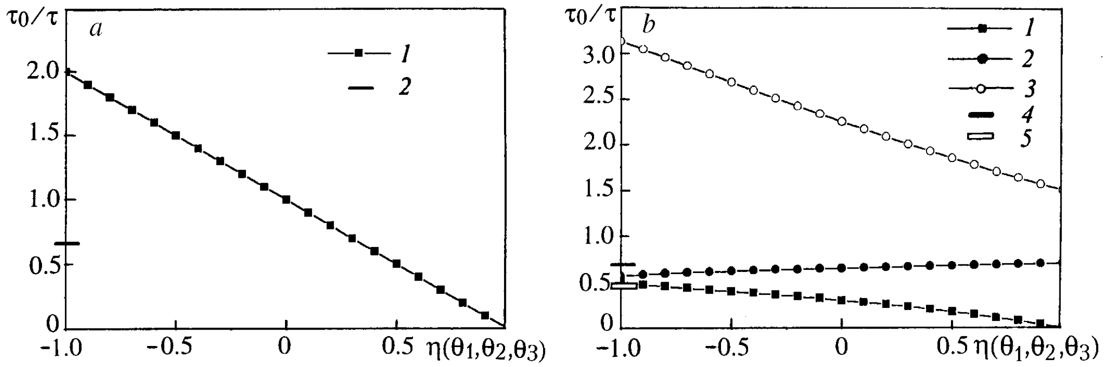


Fig. 5. Inverse relaxation times τ as a function of η for a cross-linked gel with embedded rodlike particles: a) $K_1 = 0$, $K_N = 3kT/l^2$ [1) τ_1; 2) $\tau_2 = \tau_3 = \tau_4$]; b) $K_1 = K_N = 3kT/l^2$ [1) τ_1; 2) τ_2; 3) τ_3; 4) τ_4; 5) τ_5].

totals seven: three of them correspond to collective modes of motions and four — to independent motions of rods. The low-frequency collective branch (for an infinite mesh) stretches from the minimum relaxation time, which in the general case is a composite function of K, K_1, K_N, ζ, and ζ_N, to infinitely large times when $\theta \to 0$ (for infinitely extended meshes) asymptotically dependent on the parameter characterizing the phase shift in the three-dimensional lattice $\theta^2 = \theta_1^2 + \theta_2^2 + \theta_3^2$:

$$\frac{1}{\tau(\theta)} \cong \frac{K_N + K_1 K/(K_1 + 2K)}{6\zeta + \zeta_N}\,\theta^2 \quad \text{at } \theta \to 0 . \tag{8}$$

To this branch there corresponds the displacement of the nodes, with their adjacent ends of six rods, from the nodes of the neighboring meshes.

The times of the other two collective branches corresponding to the translational and rotational motions of rods correlated with the motion of nodes always vary within finite limits whose values depend on the values of K, K_1, K_N, ζ, and ζ_N. In the case where $K_1 \to 0$ in the absence of the gel–rigid-rod interaction, only low-frequency collective motions of the mesh and one independent rotational relaxation time of the rod $1/\tau = (K_1 + 1K)/(\zeta + 2\zeta_1)$ remain. As an example, Fig. 5 compares the results of the calculations of the inverse relaxation times τ_0/τ as a function of parameters $\eta \equiv (\cos\theta_1 + \cos\theta_2 + \cos\theta_3)/3$ for the cases where $K_1 = 0$ and $K_1 = K_N$ at equal given values of l and ζ/ζ_N.

In developing the theory further, it also is necessary to take into account (especially for the case of small rods of size of the order of the statistical chain segment) the participation of the rod in small-scale intrachain motions. Another refinement of the theory should be associated with the account for the fixed volume of the elastomer and the presence of additional stretching of chains between nodes, which inevitably speaks about the value of K.

CONCLUSIONS

The obtained expressions for the relaxation times of oriented cross-linked polymers as well as for meshes and gels with embedded rigid rods will make it possible to calculate such relaxation characteristics of these systems as dynamic modulus and viscosity, dynamic correlation functions that appear as a dielectric relaxation, NMR, dynamic scattering of light, etc.

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NOTATION

t, current time; τ, relaxation time; ζ_ξ, dynamic factor of relaxation times; K_ξ, statistical factor of relaxation times; Ψ, wave number (phase shift between motions of neighboring elements); b_ξ, vector **b** component connecting chain-segment ends; K_0, elastic constant of the Gaussian chain element in the absence of orientational order; k, Boltzmann constant; T, absolute temperature; l, rms length of the Gaussian chain element; S, order parameter; θ, angle between the chain-segment direction and the director; N, number of segments in the chain; $\tau_{\parallel}$ and $\tau_{\perp}$, relaxation times of chain-element projections along the director and transverse to it, respectively; $K_{\parallel}$ and $K_{\perp}$, statistical factors of relaxation times $\tau_{\parallel}$ and $\tau_{\perp}$, respectively; K_{N}, elastic constant of mesh chain elements; ζ_{N}, friction factor of the mesh node; K, elastic constant of the quasi-elastic element imitating a hard rodlike particle embedded in the mesh; ζ, friction factor of the viscous drag center at the end of the dumb-bell imitating a hard rodlike particle embedded in the mesh; ζ_1, internal friction factor of the viscous drag centers at the ends of the dumb-bell imitating a hard rodlike particle embedded in the mesh; K_1, elastic constant of the "effective" potential fixing rods to the mesh; K, K_1, reduced elastic constants; x, coordinate of the mesh node on the $0x$ axis; $\dot{x}$, time derivative; q, normal coordinate; θ_1, θ_2, and θ_3, phase shifts between displacements of adjacent mesh nodes along the $0x$, $0y$, and $0z$ axes, respectively; θ, wave vector modulus ($\theta^2 = \theta_1^2 + \theta_2^2 + \theta_3^2$); $\tau_0 = \zeta l^2/6kT$, rotational diffusion time of an isolated quasi-elastic dumb-bell modeling a rigid rod. Subscript: N, mesh.

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