

THEORETICAL MODELS AND MODEL THEORIES OF MICROBROWNIAN MOTION IN POLYMER NETWORKS

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Abstract - Viscoelastic theoretical models (TM) and model theories (MT) of microbrownian motion in polymer networks are considered. All dissipative effects in these models and theories are determined by the forces of mutual friction between contacting segments of the same chain or those of different chains. The intersegmental friction introduced in the TM and MT under consideration replaces the friction between given segment and surrounding medium (viscous matrix or solvent) usually used in most previous MT. According to Guth, Mark and James the finite value of the average volume of a cross-linked polymer is attained by the introduction of a effective internal pressure which prevents the collapse of a Gaussian network. For this class of TM local small-scale relaxation and diffusion properties are rather similar to the analogous properties of a network immersed in an external viscous medium. In the alternative case of long-time motions the introduction of mutual intersegmental friction markedly affects the properties and characteristic times of relaxation processes. Intersegmental friction leads to the cutting-off of the relaxation spectra on the side of large-scale "inter-cell" relaxation times.

INTRODUCTION

The TM and MT for two- or three-dimensional polymer networks actually taking into account the network structure were considered by many authors: Bueche, Takemura, Ham, Gotlib and Salikhov, Graessley, Ronca and Allegra (See e.g. monographs (1-3) and original papers (4-8)). The basic element of this networks was the well-known Kargin-Slonimskii-Rouse multisegmental bead-and-spring model (or a model of Gaussian subchains). In this type of TM the chains move on the background of a viscous external medium ("solvent") which is stationary or moves in the prescribed manner. In these TM the external viscous medium acts as a distinctive physical quantity or in other words as an independent dynamical variable. W.Kuhn and H.Kuhn and Cerf have introduced the internal viscosity (or internal intra-chain friction) caused by hindered internal rotation. This type of internal viscosity is a local dissipative effect depending only on short-range neighbour interactions in the polymeric chain.

Another important property of real polymer systems including cross-linked systems that should be taken into account in the theory is the existence of the finite volume of the polymer sample and the maintenance of its value during deformation for an incompressible rubber-like polymer. In a self-consistent molecular theory for a model of polymeric chains consisting of interacting units with a finite eigenvalue (e.g. Ref.9) this condition would be fulfilled automatically. However, in model (or phenomenological) viscoelastic theories it is necessary to use simplified methods of taking into account the resulting effects of finite volume. Only in this case is it possible to avoid excessive mathematical difficulties in dynamical theory insurmountable for complex multi-particle systems.

Following the approach of Guth, James and Mark (10,11) the finite value of the density of a polymer network can be ensured by an effective internal pressure expanding the network and preventing its collapse. In this case at small

relative deformations of a cross-linked polymer the vectors of mutual distances between the network elements vary about their average values not equal to zero. It should be recollected that in an "unstrained" network embedded in an external matrix (solution) the corresponding average values are equal to zero.

One can formulate some specific properties of TM for polymer networks embedded in an external viscous matrix. In these models two types of relaxation spectra exist, intra-cell and inter-cell relaxation spectra. The longest times of inter-cell relaxation spectra depend on the size of the polymer network. These times rise proportionally to the square of the network dimensions. Very high unrealistic contribution of longest intercell relaxation times to dynamic compliance appears. The one-dimensional relaxation spectra of dynamic compliance which appear at shear or uniaxial stretching are characterized by singularity at long times corresponding to those of the stretching or shear of the network as a whole.

It should be noted that in unstrained cross-linked systems without internal pressure the situation is slightly different. In this case if a small velocity gradient of the external medium exists (Ref. 6,12), dynamic effects are nonlinear in terms of the perturbations of normal coordinates even for the effects linear in terms of gradient. In a field of velocity gradient $Gx \exp(i\omega t)$ or $Gz \exp(i\omega t)$ terms x^2 or $-xz$ appear in the perturbed distribution function. The field perturbs the mean-square functions (x^2 or xz) rather than the average projections of the coordinates of units. In contrast to strained systems, "non-linear" (in the above sense) three-dimensional relaxation spectra with some weaker singularity at long relaxation times are manifested in viscoelastic functions (dynamic modulus or viscosity). However, in this case also relaxation times depending on the size of a network are exhibited in the relaxation properties of the network.

The comparison of results of the existing TM and MT of polymers in a highly elastic rubber-like state (including network systems) with the experimental data was performed in detail in many papers, e.g., in well-known monographs by Ferry, Bueche, Vinogradov and Malkin (1-3). This comparison shows an interesting peculiarity. Virtually all the main relationships of dynamical properties of cross-linked polymers (the shape of relaxation spectra, the dependence of relaxation times on the average molecular weight of the chain segment between neighbouring junctions, etc.) are fairly satisfactorily described by the single-chain theories (or single-chain approximations). In most theories at least in the first approximation, the correlations or coupling of motions of different chains really included in a common three dimensional network were not taken into consideration. Hence, we can say that polymer network models with external friction actually taking into account collective chain motions appear to be inadequate in some details (e.g. in interpreting the relationships of dynamic compliance in the long-time range). What is the reason for the apparent cutting-off of the network relaxation spectra and why is the one-chain approximation so fruitful? An attempt at the explanation of these paradoxical facts will be presented below on the basis of the theoretical models with a straightforward introduction of intersegmental (or inter-chain viscous friction).

One of the major problems of TM and MT of microbrownian motion both in linear and cross-linked polymer systems is the adequate description or modelling of volume intermolecular interactions exhibited during contacts between the segments of one chain or different chains which cannot be reduced to external friction. This problem is of particular importance for concentrated polymer systems when a mobile solvent is absent or is present in small amounts. However, in a concentrated polymer system the velocity of the effective medium in the vicinity of a given segment or chain should be a function of the positions and velocities of all other segments or chains. In other words there must be a definite correlation between the velocity of the medium near a given segment and the velocities of the particles which form this medium. We will consider the TM's of a cross-linked polymer that are a generalization of a model of "contact" viscous interaction between contacting units introduced recently by Gennes (13) in the theory of the internal viscosity of the macromolecules. In the class of TM in question it is assumed that the average value of the force of mutual friction of two segments is proportional to the probability of the formation of contacts and the difference between the velocities of the particles.

In the most general case we must consider several types of intersegmental and segment-solvent viscous friction.

1. Local short-range internal viscous friction (W. and H. Kuhn, Cerf).
 2. Intersegmental (but intrachain) friction (de Gennes).
 3. Intersegmental (and interchain) friction.
 4. "Conventional" external friction between segment and solvent.
- If the intermolecular contacts are long-lived compared to the times of dynamical processes under consideration they can be treated as permanent junctions. In the opposite case of short-lived contacts additional viscous friction arises. Thus we can emphasize that each TM of the network system should take into account the following main specific features of polymer network (a) Permanent junctions which lead to statistical (conformational) restrictions and dynamic coupling between chain motions. (b) Transient intersegmental interactions between the contacting segments which lead to intersegmental friction. (c) Steric repulsions which lead to a finite value of the network density described by the effective internal pressure. (d) Entanglements. The consideration of entanglements is a very important but special problem and is beyond the scope of our treatment.

THEORY

In a MT for a viscoelastic TM of a three-dimensional network polymer system with intersegmental viscous friction the equations of motion for segments that are not located at network junctions are presented in the most general form

$$\zeta \sum_{\{\beta\}, k, s} \rho(\{\alpha\}, j, p | \{\beta\}, k, s) (\dot{\vec{r}}_{\{\alpha\}, j, p} - \dot{\vec{r}}_{\{\beta\}, k, s}) + K (2\vec{r}_{\{\alpha\}, j, p} - \vec{r}_{\{\alpha\}, j, p-1} - \vec{r}_{\{\alpha\}, j, p+1}) = \mathcal{F}_{\text{Brown}}(\{\alpha\}, j, p) \quad (1)$$

where $\vec{r}_{\{\alpha\}, j, p}$ is the radius vector of the p-th centre of viscous resistance (p-th segment in a Rouse-Kargin-Slonimskii model of Gaussian subchains), ζ is the coefficient of mutual intersegmental friction of two neighbouring segments and $\mathcal{F}_{\text{Brown}}$ is the random Brownian force. The value of the friction coefficient ζ is the function of the polymer concentration, the local conformational and kinetic microstructure of a polymer chain and barriers to internal rotation in rotational isomerization. Subscripts $\{\alpha\}$, j and p refer to the numbers of network cells, different chains in this cell and units in this chain, respectively. The values of $\rho(\{\alpha\}, j, p | \{\beta\}, k, s)$ determine the average local concentration of segment $(\{\beta\}, k, s)$ in the vicinity of segment $(\{\alpha\}, j, p)$. For a dense network the condition of the constancy of complete local concentration of all units near any segment of the chain is fulfilled, i.e. $\sum_{\{\beta\}, k, s} \rho(\{\alpha\}, j, p | \{\beta\}, k, s) = \text{const.}$

It should be noted that Eqs.(1) with constant coefficients independent of time $\rho(\{\alpha\}, j, p | \{\beta\}, k, s)$ are valid only in a certain space-time range of motions. In fact, if characteristic times of the smallest-scale local motions are less than the lifetime of contact $\tau_{jk} = \tau_{\text{contact}}$ between a given pair of kinetic segments, then, in the framework of this model the system is "frozen-in" in some irregular conformation. For the class of local motions with characteristic times $\tau_{jk} > \tau_{\text{rupture}}$ segmental motion is developed in the system and it is possible to introduce in the viscoelastic theory the forces of intersegmental friction. However, if the values of τ are not too high, the equilibrium distribution ρ_{jk} near each given unit will not yet be established during this time τ . The system remains dynamically heterogeneous even for an absolutely regular network. Strictly speaking, an explicit treatment of processes of breaking and restoration of any pair of contacts $(\{\alpha\}, j, p | \{\beta\}, k, s)$ should be carried out as in the theory of networks with reversibly broken junctions. Finally the condition of the fulfillment of Eq.1 for a given type of motions at a characteristic time τ reduces to the inequality

$$\tau > \tau_{\text{recombination}}(j, k) > \tau_{\text{rupture}}(j, k) \quad (2)$$

In a regular Gaussian network (e.g. a cubic or tetrahedric network) of a flexible-chain polymer containing N segments between the junctions the number of

chains included in an average volume occupied by a given chain is proportional to $N^{1/2}$. The number of cells $-n$ (along a given direction) the chains of which predominantly occupy the volume of a given chain is $N^{1/6}$. In other words at $N \sim 10^2 - 10^4$ the number n is not great and only those chain units in the cells of the network that are not very distant from each other should be included in inequality (2). This means that Eq.(1) is best applied to slow relatively large-scale modes of microbrownian motion with the characteristic size of the order of magnitude of the cell size or greater by a factor of $n \sim N^{1/6}$. The value of n determines the size of the effective volume of viscoelastic correlation (in cell units) that will be discussed below. At the same time, the use of Eq.(1) for small-scale motions also gives physically correct results averaged over dynamically heterogeneous parts of the network. Actually Eq.(1) can be used for a fairly wide range of motions with $\tau > \tau_{rupture}$ by the smoothed description of dynamic properties of the network.

At a given density of units in a polymer the value of $\rho(\{\alpha\}, j, \rho(\{\beta\}, k, s))$ depends on the number of units in the chain between junctions, N , and the functionality and topology of the network. The quantitative measure of the degree of average chain stretching by an internal pressure in a network of finite volume may be presented by parameter

$$\gamma = [\overline{\Delta x^2} / \langle h^2 \rangle] \sim N^{-1/3} \sim (1/n)^2 \quad (3)$$

This quantity γ is the ratio of the square of the average projection of a particular chain on the axis of the laboratory coordinate system $\overline{\Delta x^2}$ to the mean-square chain length $\langle h^2 \rangle$. For phantom Gaussian networks expanded by internal pressure the distribution of distances between each pair of units (or network junctions) remains a Gaussian distribution with respect to the average distance for a given pair. The dispersion of this distribution is independent of the average distance and remains the same as for an unstrained Gaussian network, in accordance with the results obtained by James and Guth, Ronca and Allegrò (Refs.10,11,8).

For units of the same sufficiently long chain or for neighbouring chains with a common junction

$$\rho(p, s) \sim q^{-3/2} G(q, N, \gamma) \quad (4A)$$

where q is the number of units separating two chosen units ($q = |p - s|$) in one chain or $q = p + s$ if p and s are counted from the same junction for adjoining chains). Here $G(q)$ is a weak function of q , N and the topology of the mutual position of a given pair of units. For units of chains belonging to cells located far from each other along the network, $\{\alpha\}$ ($\alpha_1, \alpha_2, \alpha_3$) and $\{\beta\}$ ($\beta_1, \beta_2, \beta_3$), the value of ρ weakly depends on the position of a unit in the chain and is mainly a function of the square of the average distance between a given pair of cells $\overline{R}_{\{\alpha\}, \{\beta\}}$

$$\overline{R}_{\{\alpha\}, \{\beta\}}^2 \sim (\alpha_1 - \beta_1)^2 + (\alpha_2 - \beta_2)^2 + (\alpha_3 - \beta_3)^2$$

$$\rho(\{\alpha\}, \{\beta\}) \sim \exp[-\overline{R}_{\{\alpha\}, \{\beta\}}^2 / 2\Delta] \quad (4B)$$

$$\Delta \sim \gamma^{-1} \sim N^{1/3}$$

wherein numbers d for a cubic lattice determine the number of the cell along a given j -th axis. The dispersion of the Gaussian distribution (4B) does not depend on $\overline{R}_{\{\alpha\}, \{\beta\}}$ (or on $\{\alpha\}$ and $\{\beta\}$) for distant cells. The quantity $\Delta \sim \gamma^{-1} \sim N^{1/3}$. The $\rho(R_{\alpha\beta})$ as a function of $R_{\alpha\beta}$ decreases exponentially with a characteristic scale of decrease $\sqrt{\Delta} \sim N^{1/6} = n$ equal to the size of the above mentioned volume of viscoelastic correlation.

The distributions of the values of ρ_{ps} are different for units with different distance from the network junction. This leads to dynamic heterogeneity of the chain. However, evaluations show that in cross-linked unswollen polymers with constant local density this dynamic heterogeneity is not high. In this case the properties of symmetry, the classification of normal modes and eigenvectors of Eq.(1) are close to those for regular spatial cross-linked systems consisting of homogeneous chains between the junctions (4-6). Eigenvectors and normal modes of regular cross-linked TM can be used as a first approximation. Each normal mode will be determined by inter- and intra-cell wave vectors. The inter-cell wave vector $\vec{\Theta}$ is given by three components $\Theta_1, \Theta_2, \Theta_3$ determining the phase shift between the displacements of neighbouring network junctions. The intra-cell wave number Ψ determines the phase shift between the displacements of neighbouring units (segments) of a given chain. For a cubic network model consisting of homogeneous chains in which all units are under the same dynamic conditions, normal modes, are given by (Ref.6)

$$\begin{aligned} x_p(d_1, d_2, d_3, j) = \sum_{\vec{\Theta}, \Psi} \exp [i(d_1\Theta_1 + d_2\Theta_2 + d_3\Theta_3)] \times \\ \times (A_j e^{i\Psi p} + B_j e^{-i\Psi p}) \times \exp(-\lambda[\vec{\Theta}, \Psi]t) \end{aligned} \quad (5)$$

where d_1, d_2, d_3 is the cell number, subscript j refers to the j -th chain of the cell, λ is the reciprocal relaxation time for a given mode ($\lambda = \tau^{-1}$) and constants A_j and B_j are found by solving the corresponding secular equation under certain boundary conditions in network junctions.

For long chains it is often convenient to pass from a discrete to a continuous chain model (see Ref.5,6). The substitution of the solution in the form of Eq.(5) into Eq.(1) makes it possible to obtain to a first approximation the expressions for the λ eigenvalues and relaxation times τ for various types of motion. The use of boundary conditions at network junctions leads to the establishment of a definite relationship between Ψ and $\{\Theta_1, \Theta_2, \Theta_3\}$. Thus, for a cubic lattice the relationship between Ψ and Θ is given by (5,6)

$$\Psi = (2\pi k / N) + (1/N) \arccos \left[\frac{1}{3} (\cos \Theta_1 + \cos \Theta_2 + \cos \Theta_3) \right] \quad (6)$$

where $k = 0, \dots, N/2$ and Θ_j are the wave numbers for inter-cell motions. Apart from normal modes (6) a double degenerate set of intra-cell motions exists

$$\Psi' = \pi k / N + 1 \quad (k = 1, \dots, N)$$

For these types of motions network junctions do not move.

As a result of the above substitutions approximate expressions for relaxation times $\tau(\Psi)$ are obtained

$$\lambda(\Psi) = \tau^{-1}(\Psi) = \frac{2K(1 - \cos \Psi)}{\zeta \langle \rho(\vec{\Theta}, \Psi) \rangle} \quad (7)$$

where $\zeta \langle \rho(\Psi, \vec{\Theta}) \rangle$ is the eigen-value of the dissipative function of the system for a given normal mode averaged over the position of the segment in a dynamically heterogeneous chain. In other words

$$\zeta \langle \rho(\Psi, \vec{\Theta}) \rangle \sim \vec{U} R \vec{U}^* \quad (8)$$

where \vec{U} are the eigenvectors (Eq.5) and R is the matrix of the dissipative function of the system when only intersegmental friction exists. The ana-

lysis of fairly cumbersome expressions for $\tau(\Psi)$ is based on certain assumptions valid either for small-scale motions the scale of which is much smaller than the chain size between junctions or for slow large-scale motions the scale of which greatly exceeds this size. Naturally, for the motions the scale of which coincides with the distance between junctions only qualitative evaluation of properties can be obtained.

RESULTS AND DISCUSSION

Spectrum of relaxation times

In the TM investigated two ranges of relaxation behaviour appear for the processes and times of microbrownian motion.

1) The range of predominantly intra-cell small-scale motions for which the value of k (from Eq.(6)) is much greater than unity and the main contribution to Ψ is that of the intra-cell term $2\pi k/N$. For these normal modes the phase shifts of segments of other chains are mutually compensated with respect to a particular segment of a given chain (phase randomization). This compensation is carried out both by the summation of contributions of segments of one of the chains with which this chain interacts and by the summation of contributions of different chains with their phase factors $\exp[i\bar{\theta}(\alpha-\beta)]$. The fractions of contacts with chains "foreign" to a given segment are much greater by about an order of magnitude or even more) than those of contacts between the segments of a given chain. This follows from both the theoretical evaluations of the relative contribution ρ_{ijk} of the segments of the same chain to the local concentration near a given segment (Ref.14) and an analysis of ESR experimental data for concentrated solution of spin-labeled polymers (Ref.15(a)) and of intrachain quenching in macromolecules with luminescent markers (Ref.15(b)).

The randomization of viscous interactions of a given segment with the contacting segments of a given chain occurs to a lesser extent than in the interaction with the segments of other chains. However, the relative contribution of intra-chain interactions to $\zeta \langle \rho(\Psi) \rangle$ is small and at low Ψ it is of the order of magnitude of $\Psi^{3/2}$ (Ref.(13)). On the whole, it may be said that for small-scale motions the relaxation behaviour of the chain (i.e. the dependence of $1/\tau(\Psi)$) is (to within the values of $\sim \sin N\Psi/N\Psi$) such a behaviour as though the chain were located in a viscous matrix with external friction. This friction is determined on the average only by the velocity of the particular segment and is independent of the relative velocities of motion of different segments. We also suggest that for macromolecules immersed in concentrated polymer network the intrachain short-range internal viscosity (of Kuhn-Cerf type) is low.

(2) The second range of relaxation behaviour is that of large-scale inter-cell relaxation processes the scale of which is larger than the cell size. For these processes the change in the displacement phase in the same chain is not great and the units of several chains adjoining one junction may be considered as one subparticle with the mutual friction coefficient ζN . These subparticles form a quasi-elastic large-grain phantom network the junctions of which interact with the nearest neighbours at an elasticity constant $K_{\text{eff}} \sim (k/N)$. The viscous interaction between the particles is determined by $\zeta_{\text{eff}} \sim N\zeta$. In this case the low-frequency behaviour of the simplified TM of polymer network is described by the motion of a coarse-grain network. The dissipative properties of this network are determined by the mutual "interchain" friction of its junctions. The $\rho(\alpha, \beta)$ coefficients for this model network, i.e., for relatively slow large-scale motions of a real network, are expressed in the form of Eq.(4). Characteristic relaxation times are determined by wave vectors Θ only and reduce to

$$\frac{1}{\tau(\Theta)} = \frac{2K_{\text{eff}}(3 - \cos \Theta_1 - \cos \Theta_2 - \cos \Theta_3)}{\zeta_{\text{eff}} \{1 - \exp[-\eta(\Theta_1^2 + \Theta_2^2 + \Theta_3^2)]\}} \quad (9)$$

where the η parameter is equal to $\text{const.} \gamma^{-1}$, i.e. $\eta \sim N^{1/3}$.

It follows from Eq.(9) that in the range of slow large-scale motions the existence of mutual intersegmental, or (which is more precise for these motions) "interchain" friction, greatly affects the dispersion dependence $\tau(\Theta)$ and the shape of relaxation spectra for various viscoelastic functions.

The relaxation spectrum is found to be cut off at some maximum time, τ_{\max}

$$\tau_{\max} = \tau_{\text{eff}} N^{4/3} \sim (\zeta/K) N^{2,33} \quad (10)$$

where $\tau_{\text{eff}} \cong (\zeta_{\text{eff}}/K_{\text{eff}}) \sim (\zeta/K) N^2$

Here τ_{\max} is the characteristic relaxation time for the finite viscoelastic correlation volume. For slow large-scale motions when the scale of motion becomes greater than the characteristic length of viscoelastic correlation the above TM behaves like a set of Kelvin-Foight elements. In this limiting case only the effective internal friction between neighbouring subunits appears.

Diffusion properties and viscoelastic relaxation functions of TM with intersegmental and interchain friction

It follows from the foregoing discussion that it is most important to take into account intersegmental friction in the consideration of the effects caused by slow inter-cell motions the scales of which are comparable to or exceed the size of the network cells or the characteristic length of viscoelastic correlation. Thus, the relationships of diffusion motion in the absence of external fields, e.g. for the mean-square displacement of a network junction differ from those for a cubic network immersed in an external viscous matrix (Ref.8) for $t \geq \tau_{\max}$. In particular, these differences will be shown by the properties of the structural factor at dynamic scattering of neutrons for low values of wave vector and high values of time. For a network with intersegmental friction, just as for that with external friction, the mean-square displacement of a junction tends to a finite value with increasing time but now the value of $|\langle \delta r^2 \rangle_{\infty} - \langle \delta r^2 \rangle_{(t)}|$ decreases as a function of time much faster (according to the exponential law) than for a three-dimensional (cubic or tetrahedral) network "floating" in solution. In the latter case the value of $|\langle \delta r^2 \rangle_{\infty} - \langle \delta r^2 \rangle_{(t)}|$ decreases according to the power law $t^{-1/2}$. The corresponding differences also become apparent in the long-time behaviour of the structural factor e.g. for non-coherent neutron scattering. It can be noted that long-time diffusion behaviour of the above TM depending on the cut-off of the relaxation spectra is very similar to that of the tree-like network considered by Ronca (Ref.16).

The discussion of a model of cross-linked systems with mutual intersegmental friction can also be used for infinite tree-like networks without rings. It should be noted that the theoretical analysis carried out by Ronca (16) should be supplemented by the consideration of long times corresponding to the stretching from the ends of long tree-like parts of the network. Unlike the times of the relaxation spectrum considered in Ref.16, these times will depend on the size and molecular weight of the network as a whole. Moreover, it should be taken into account that, generally speaking, steric limitations prevent the formation of large isotropic steric branched systems.

A strong exponential dependence of the expectation time of great fluctuations of size (or volume) of a network cell on the fluctuation amplitude is also an interesting feature of cross-linked polymer structures.

The greatest differences between the dynamic properties of cross-linked TM exhibiting intersegmental friction and "expanded" by internal pressure and those of TM immersed in the external viscous matrix become apparent in the long-time behaviour both when the network is deformed uniaxially by the forces applied to sample boundaries and in simple shear deformation (Ref.17). It should be noted that for the simplest cubic TM consisting of quasi-elastic Gaussian chains both types of deformation are characterized by the identical relaxation spectrum (calculated in the simplest manner for dynamic compliance). This is due to the fact that for Gaussian TM of finite volume with linearized equations of motion, i.e. in the linear range of the stress-strain plot, the change in the direction of the system of external forces does not change the equations of motion and the forms of boundary conditions. As already mentioned, in both cases a one-dimensional relaxation spectrum appears. The shape of the relaxation spectrum $\hat{M}(i\omega)$ for low-frequency motions is of a typically one-dimensional type. For complex compliance the value of $\hat{M}(i\omega)$ reduces to

$$\hat{M}(i\omega) = C \sum_{(\theta_i)} \cos^2 \frac{\theta_i}{2} \times \frac{1}{i\omega + \tau^{-1}(\theta_i)} \quad (11)$$

where ω is the frequency of the external field and the summation is carried out over all the values of the wave number Θ_1 . If the external forces are applied to a cross-linked TM as is shown in Fig.1, then, at uniaxial stretching the motions with $\Theta_1 \neq 0$ will appear and $\Theta_2 = \Theta_3 = 0$ whereas at shear deformation motions with Θ_3 not equal to zero will develop and $\Theta_1 = \Theta_2 = 0$.

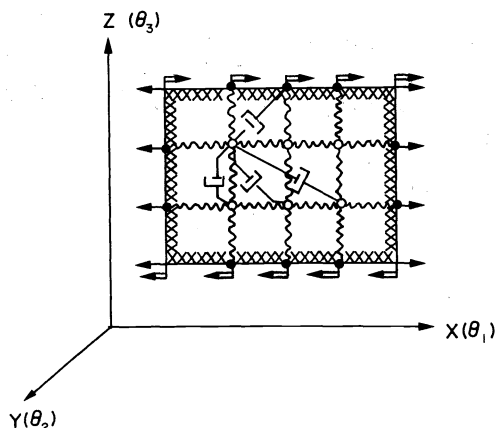


Fig. 1. Schematic of uniaxial $\leftarrow \rightarrow$ and shear $\swarrow \searrow$ deformations of polymer network.

In the TM class in question the relaxation spectrum for compliance is found to be limited consists virtually of the one-dimensional relaxation spectrum of a single chain (for high-frequency contribution) immersed in a viscous matrix usually described in the literature (1-3,12,17) and the cut off low-frequency relaxation spectrum.

The "high-frequency" part (although this division is tentative) ranges from $\tau_{\min} \sim (K/\zeta)$ to $\tau_{\text{eff}} \sim (K/\zeta)N^2$ and the low-frequency contribution ranges from $\tau_{\text{eff}} \sim (K/\zeta)N^2$ to $\tau_{\max} \sim (K/\zeta)N^{2.33}$. It should be remembered that if the uniaxial stretching of a network immersed in a viscous medium is considered, the "one-dimensional" type of deformation would lead to the appearance of unrealistic values of τ_{\max} proportional to the square of the complete number of chains along a given network direction. The relaxation behaviour of the polymer network with intersegmental friction is completely determined by the relaxation properties of the finite volume of viscoelastic correlation in the polymer. The long-range correlations, motions and times are cut-off. This fact explains the above-mentioned paradoxical result regarding the approximate validity of "one-chain" models for long-time relaxation properties.

In conclusion it should be noted that in the framework of the TM and MT considered here it is also possible to take into account qualitatively mutual steric and topological limitations to chain motion. These limitations have been reflected in the concept of the "motion along a tube" developed by Edwards (18), de Gennes (19) and other authors. To utilize this concept one can use a modified dissipative function taking into account the limitations to collective large-scale chain motions caused by the presence of other chains. At the same time this approach permits the retention of the advantages of viscoelastic models.

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