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# The Local and Collective Mobility in Polymer Chains and Networks with Included Rigid Particles Elastically Connected with the Network

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**Summary:** The theory of molecular mobility of a polymer network with included rod-like particles is developed. The case is considered when the length of rods is comparable or greater than the average distance between neighboring cross-links of the primary network. The long-scale dynamics of the network is described by means of a regular cubic "coarse-grained" model. The junctions of this model describe the great network fragments (domains) the sizes of which are near to the average distance between neighboring rods.The quasi-elastic interactions between rods and network fragments lead to a broad relaxation spectrum for included rods as compared with free rods which are characterized by a single relaxation time of rotational diffusion. The frequency dependence of the dielectric loss factor of included rods is calculated for rods with permanent dipole moments directed parallel to the long axes of the rods chaotically distributed in the network. The frequency dependence of dynamic modulus of a polymer network with included rods is obtained. The increment in the dynamic modulus of the relatively short network motions (smaller than the distance between rods) also is taken into account. The broad relaxation spectrum of included rods leads to appearance of several maximums on the frequency dependences of both the dielectric loss factor and dynamical modulus.

**Keywords:** dielectric and mechanical relaxation; polymer networks; relaxation spectra; rods in a network

## Introduction

In the last years, polymer network gels containing rod-like particles were synthesized and experimentally investigated [1–5]. The ability of gels with included rods to change drastically and reversibly their volume in response to variation of the external stimulus (temperature, pH etc.) widens the area of practical application of hydrogels as functional materials (e.g. sensors, actuators, carriers for controlled drug release, membranes with regulated permeability etc.).

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The long enough rigid rods in these systems are not covalently attached to the network but they are effectively retained inside the gel and cannot diffuse up to long distance from their average positions [5]. The rods can be quasi-elastically involved into long-scale network motions (due to topological entanglements) and therefore should move together with network fragments. This effect has been described in ref. [6–8] Recently, the authors considered the effects of rods on the dynamics of a polymer network due to orientational nematic-like interactions between network fragments and included rods [9].

The present work considers the dielectric and mechanical relaxation properties of a polymer network with included long rods taking into account the effects of involving of rods into long-scale network motions (due to topological entanglements). The relaxation spectra are calculated using renormalized ''coarse-grained'' network model. The dielectric relaxation of included rods with permanent dipole moments directed parallel to the long axes but distributed chaotically in the space is considered. The mechanical relaxation properties (dynamical modulus) of a polymer network with included rods are also investigated. The effects of the existence of average volume of a swollen gel and average chain stretching between network junctions which were not considered in ref.[6,7] are taken into account.

## Model of a Polymer Network with Included Rods and Main Equations

The present work deals with the dynamics of long rods the length of which, $l$, is greater than the average distance between neighboring cross-links of the gel, $h_0$: $l >> h_0$ (as in systems synthesized and investigated in refs. [1–5] – see Figure 1). The visco-elastic properties of the network are characterized by the friction coefficient of network junctions $\zeta_{N0}$ and by elasticity constant, $K_{N0}$, characterizing the entropic elasticity of network strands (Figure 1). It is proposed that the distribution of end-to-end distances of network strands is Gaussian and $K_{N0} \cong 3kT/h_0^2$. We propose also the simplest case when the average distance between junctions is equal to the mean square length of the chain between junctions. The included rods (dumbbell models) are characterised by the length $l$ and by the friction coefficient of rod ends, $\zeta$, which is assumed to be proportional to the rod length: $\zeta = \zeta_0(l/h_0)$. Here $\zeta_0$ is the friction coefficient of a rod with length $l = h_0$. We shall consider the case when the average distance between neighbouring rods, $h$, has the same order of magnitude as $l$.

The effects of network motions on the dynamics of included rods (due to topological entanglements) are described here by means of a ''coarse-grained'' network model (Figure 2).

The validity of using ''coarse-grained'' models for describing the long-scale dynamics of polymer network systems are justified in refs. [10–12].

The ''primary'' polymer network (Figure 1) is divided into cubic cells (domains) the sizes of which, $h$, are equal to the average distance between the neighbouring rod-like particles [6,7]. In this case elasticity constant $K_N$ of a subchain of the model characterises the effective elasticity acting between neighbouring domains, and the friction coefficient of the domain $\zeta_N$ (Figure 2) may be described by equations:

$$\zeta_N = \zeta_{N0} \cdot (h/h_0)^3 = \zeta_{N0} \cdot n^3 \quad (1)$$

$$K_N = K_{N0} \cdot (h/h_0) = K_{N0} \cdot n \quad (2)$$

where $n = h/h_0$. The Eq. (1) presents the total friction of the cubical domain with $n^3$ junctions of the primary network

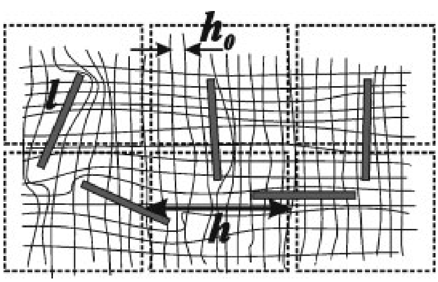


*Figure 1.*
A polymer network with long included rod-like particles.

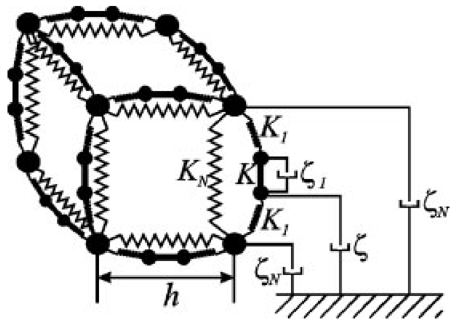


*Figure 2.*
The cell of 3-dimensional regular cubic network model with included rods.

 

($n$- junctions in every direction) and $K_N$ (Eq. 2) presents the average elasticity between two neighbouring domains. The value $K_N$ is proportional to average elasticity of one network "line" element containing $n$ springs in line multiplied on $n^2$ parallel lines of springs. The value of $n^2$ is the number of lines on the surface element of domains. It can be shown that for long-range normal modes (longer than $nh_0$) the relaxation times of the initial network and those of the "renormalized course-grained" network of domains are equal. In the dielectric relaxation for long enough rods only the relaxation of the "renormalized" network is active. It is possible to show that the mean-square fluctuations of a junction in coarse-grained model with $K_N = K_{N0}(h/h_0)$ (Equation (2)) are equal to those for center of domains at $n = h/h_0 >> 1$.

The use of this coarse-grained "renormalized" network model is based on an assumption that for the dynamics of long rods ($l >> h_0$) it is possible to neglect the network modes with characteristic scales smaller than the length of a rod and take into account only the contributions of the modes of the scale greater than $l$. The effects of topological entanglements of rods in a polymer network (when rods move together with network fragments) are taken into account by elastic potential that prevents the translational displacements of the rods on the distances greater than the average distance between rods and hinders the rotational mobility of the rods. In the coarse-grained model (Figure 2) this potential acts between the rod ends and the centers of network domains and is characterized by the elasticity constant $K_1$. The quasi-elastic potential of such type may be caused by the entropic and other forces in network strands when they are stretched and carried away by the moving rods.

The dynamics of the rigid rod may be also described by effective quasi-elastic element with internal friction that was shown in [13–17]. The elasticity constant $K$, is equal to the average value of the Lagrange multiplier of the rod so that the mean-square length of the elastic segment stays equal to the length of the rod $l$[14–17]. The coefficient of the internal friction of the elastic fragment, $\zeta_1$, is fixed so that the translational and orientational relaxation times for the single elastic fragment modelling the rod remain equal to the corresponding times for the single rigid dumbbell: $\zeta_1 = \zeta/4$ [13–17].

The equations of motion in the network model to be used represent a system of 7 linear differential equations corresponding to 7 degrees of freedom in the network cell:

$$\begin{cases} \zeta_N \dot{\vec{r}}_{\vec{\Omega}} + K_N \left[ 6\vec{r}_{\vec{\Omega}} - \sum\limits_n \left\{ \vec{r}_{\vec{\Omega}+\vec{e}_n} + \vec{r}_{\vec{\Omega}-\vec{e}_n} \right\} \right] \\ \quad + K_1 \left[ 6\vec{r}_{\vec{\Omega}} - \sum\limits_n \left\{ \vec{r}^{(1)}_{\vec{\Omega},n} + \vec{r}^{(2)}_{\vec{\Omega}-\vec{e}_n,n} \right\} \right] = \vec{F}^{(Br)}_{\vec{\Omega}} \\ \zeta \dot{\vec{r}}^{(1)}_{\vec{\Omega},n} + \zeta_1 \left[ \dot{\vec{r}}^{(1)}_{\vec{\Omega},n} - \dot{\vec{r}}^{(2)}_{\vec{\Omega},n} \right] + K_1 \left[ \vec{r}^{(1)}_{\vec{\Omega},n} - \vec{r}_{\vec{\Omega}} \right] \\ \quad + K \left[ \vec{r}^{(1)}_{\vec{\Omega},n} - \vec{r}^{(2)}_{\vec{\Omega},n} \right] = \vec{F}^{(Br)}_{\vec{\Omega},n,1}, \quad n = 1,2,3 \\ \zeta \dot{\vec{r}}^{(2)}_{\vec{\Omega},n} + \zeta_1 \left[ \dot{\vec{r}}^{(2)}_{\vec{\Omega},n} - \dot{\vec{r}}^{(1)}_{\vec{\Omega},n} \right] + K_1 \left[ \vec{r}^{(2)}_{\vec{\Omega},n} - \vec{r}_{\vec{\Omega}+\vec{e}_n} \right] \\ \quad + K \left[ \vec{r}^{(2)}_{\vec{\Omega},n} - \vec{r}^{(1)}_{\vec{\Omega},n} \right] = \vec{F}^{(Br)}_{\vec{\Omega},n,2}, \quad n = 1,2,3 \end{cases} \tag{3}$$

Here the index $n$ numbers three chains in a network cell, the index $\vec{\Omega} = (\Omega_x, \Omega_y, \Omega_z)$ numbers the cells in three-dimensional network: $\Omega_n = .., -1, 0, 1, .., \vec{e}_n$ is the unit vector directed along the $n$-axis; $\vec{r}_{\vec{\Omega}}$, $\vec{r}^{(1)}_{\vec{\Omega},n}$, and $\vec{r}^{(2)}_{\vec{\Omega},n}$ are the radius vectors of the network junction and of rod ends; $\vec{F}^{(Br)}_{\vec{\Omega}}$, $\vec{F}^{(Br)}_{\vec{\Omega},n,1}$, and $\vec{F}^{(Br)}_{\vec{\Omega},n,2}$ are the stochastic Brownian forces exerted on a network junction, and on rod ends, respectively.

The system of equations (3) is solved by the method of normal modes. The 7 normal coordinates $\vec{q}_p$ (p = 1..7) are the linear combinations of the 7 vectors $\vec{r}_{\vec{\Omega}}$, $\vec{r}^{(1)}_{\vec{\Omega},n}$, and $\vec{r}^{(2)}_{\vec{\Omega},n}$:

$$\vec{q}_1(\vec{\Theta}) = \sum_{\vec{\Omega}} \vec{r}_{\vec{\Omega}} \cdot \exp[i\vec{\Omega}\vec{\Theta}], \text{ and } \vec{q}_{2,3,4,5,6,7}(\vec{\Theta}) = \sum_{\vec{\Omega}} \cdot \vec{r}^{(1,2)}_{\vec{\Omega},n=x,y,z} \exp[i\vec{\Omega}\vec{\Theta}] \tag{4}$$

where $\vec{\Theta}$ is the wave vector. The solution of dynamical equations for $\vec{q}_p$ has the form:

$$\vec{q}_j(\vec{\Theta},t) = \sum_{p=1}^{7} \vec{C}_{j,p} \exp[-\lambda_p t] \tag{5}$$

where $\vec{C}_{j,p}$ are determined by the initial conditions at $t=0$ and $\lambda_p$ are the eigenvalues for the matrix of coefficients of dynamical equations for $\vec{q}_p$; $\lambda_p$ are determined by equation:

$$(\tau_t^{-1}-\lambda)^2(\tau_r^{-1}-\lambda)^2\Bigg((a-\lambda)(\tau_t^{-1}-\lambda) \times (\tau_r^{-1}-\lambda) - \frac{(\tau_t^{-1}-\lambda)3K_1^2(1-X)}{(\zeta+2\zeta_1)\zeta_N} - (\tau_r^{-1}-\lambda)\frac{3K_1(1+X)}{\tau_t\zeta_N}\Bigg) = 0 \tag{6}$$

Here

$$\tau_r = \frac{\zeta+2\zeta_1}{K_1+2K},\ \tau_t = \frac{\zeta}{K_1},\ a = \frac{6K_1+4K_N\eta}{\zeta_N},$$
$$X(\Theta) = \frac{1}{3}[\cos(\Theta_x)+\cos(\Theta_y)+\cos(\Theta_z)] \tag{7}$$

As it can be seen from Equation (6), the set of the relaxation times, $\tau(\vec{\Theta}) = 1/\lambda(\vec{\Theta})$, contains 3 branches of the relaxation times which correspond to 3 solutions of the cubic equation corresponding to the third multiplier in the right-hand side of Equation (6) and depend on the wave vector $\vec{\Theta}$. Moreover, the relaxation spectrum includes the two twice-degenerated relaxation times $\tau_r$ and $\tau_t$ which correspond to rotational and translational motions of rods at fixed network junctions.

As it was mentioned the effective elasticity constant $K = K(K_1, K_N, h/l)$ is determined by the equality of the mean-square length of the elastic fragment to the length of the rod, $l$.

$$1 = \left(\frac{h}{l}\right)^2\left(\frac{K_1}{K_1+2K}\right)^2 + \frac{6kT/l^2}{K_1+2K}\left[1+\frac{1}{6}\frac{K_1^2}{KK_1+K_N(K_1+2K)}\right] \tag{8}$$

The case $h=0$ was discussed in [6,7]. Equations (6)–(8) determine dependence of the relaxation spectrum on the parameters of the model. As examples, the dielectric and mechanical relaxation properties of a polymer network with included rods are below considered in dependence of $K_1$, $l/h_0$, $\zeta_N/\zeta$, and $h/l$.

## Dielectric Relaxation of Included Rods having Permanent Dipole Moments

We consider the dielectric relaxation of rods, the permanent dipole moments of which are directed along the long axes of rods. We assume that after the incorporation of rods into a polymer network, their dipole moments are oriented chaotically. In this case, the frequency dependence of complex dielectric permittivity, $\varepsilon(\omega)$, is determined in the linear-response approximation by the autocorrelation function of the end-to-end vector $\vec{b}$ of rod:

$$\frac{\varepsilon(\omega)-\varepsilon(\infty)}{\varepsilon(0)-\varepsilon(\infty)} = 1 - i\omega \cdot \int_0^\infty dt\cdot\exp[-i\omega t]\frac{\left\langle\vec{b}(t)\cdot\vec{b}(0)\right\rangle - \left\langle\vec{b}\right\rangle^2}{\left\langle\vec{b}^2\right\rangle - \left\langle\vec{b}\right\rangle^2} \tag{9}$$

The autocorrelation function of vector $\vec{b}$ has been calculated using the series into normal coordinates $\vec{q}_p$ (Equation (4)):

$$\left\langle\vec{b}(t)\vec{b}(0)\right\rangle - \left\langle\vec{b}\right\rangle^2 = \frac{4kT}{K_1+2K}\left[\exp[-t/\tau_r] + \sum_{p=1}^{3}\int\frac{d\vec{\Theta}}{(2\pi)^3} \cdot \frac{3K_1^2(1-X(\vec{\Theta})\cdot\exp[-\lambda_p(\vec{\Theta})t]}{2\lambda_p(\vec{\Theta})A_p(\vec{\Theta})\tau_r(\zeta+2\zeta_1)\zeta_N}\right] \tag{10}$$

where

$$A_p(\vec{\Theta}) = (\tau_r^{-1}-\lambda_p)^2 + \frac{3K_1^2(1-X(\vec{\Theta}))}{(\zeta+2\zeta_1)\zeta_N} + \frac{(\tau_r^{-1}-\lambda_p)^2}{(\tau_t^{-1}-\lambda_p)^2}\frac{3K_1^2(1+X(\vec{\Theta}))}{\zeta\cdot\zeta_N} \tag{11}$$

The autocorrelation function of $\langle \vec{b}(t) \vec{b}(0) \rangle$ is determined by two contributions – see Equation (10). One contribution corresponds to rotational relaxation time $\tau_r$ at fixed network junctions and another contribution is determined by the tree collective branches of relaxation spectrum which dependent on the wave vector. The translational relaxation time $\tau_t$ does not give a contribution into the orientational correlation function $\langle \vec{b}(t) \vec{b}(0) \rangle$. Thus, the relaxation spectrum of rods included into a polymer network is broader than that for separate rods which is characterized by a single rotational time $\tau_0 = \zeta l^2/4kT$. This fact results in the difference in the dielectric permittivities for separate rods and rods included into a network.

The dielectric loss factor $\varepsilon''(\omega)$ (imaginary part of the complex dielectric permittivity, $\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$) have been calculated using Equations (6)–(11) and (1), (2). Parameter $K_1$ characterizing the intensity of the quasi-elastic interactions between rods and network determines, in particular, the mean-square fluctuations of centres of rods $\langle \Delta r^2 \rangle$:

$$\frac{\langle \Delta \vec{r}^2 \rangle}{l^2} = \frac{3kT/l^2}{2K_1} + \frac{kT/l^2}{K_N + K_1 K/(K_1 + 2K)} \tag{12}$$

The increase of the quasi-elastic interaction between network and rods $K_1$ leads to the decrease of all times of the relaxation spectrum. We have obtained two maximums in dielectric loss factor. The high-frequency maximum corresponds to localized motions of the rods at fixed positions of network junctions. The low-frequency maximum is determined by collective dynamics of rods with network elements. With increasing $K_1$, the high frequency maximum $\varepsilon''(\omega)$ shifts to the high-frequency region, but the position of the low-frequency maximum varies comparatively weak (Fig. 3). The increase of $K_1$ leads also to the higher intensive involving of rods in the dynamics of the network. Therefore, the height of the low – frequency maximum of $\varepsilon''(\omega)$ increases, but that of high-frequency maximum, corresponding to localized motions of the rods, decreases. The friction coefficient $\zeta_N$ of the domain may be different from the friction coefficient of rods. The increase $\zeta_N/\zeta$ shifts the low-frequency maximum $\varepsilon''(\omega)$ to lower frequencies. The average intra-network tension acting on the chain may be characterized by parameter $h/l$ and depends on the density of cross-linking and on the degree of swelling of the network. The increase of $h/l$ shifts both maxima of $\varepsilon''(\omega)$ to higher frequencies (see Fig. 4). The intensity of the low-frequency maximum decreases and that of high-frequency maximum increases at increasing value of $h/l$. These results are determined by the

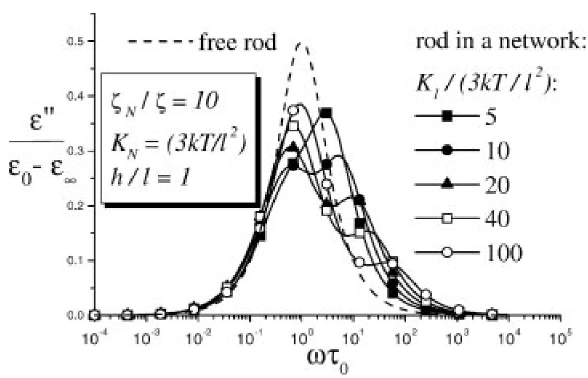


*Figure 3.*
Frequency dependence of the dielectric loss factor at different $K_1$.

 

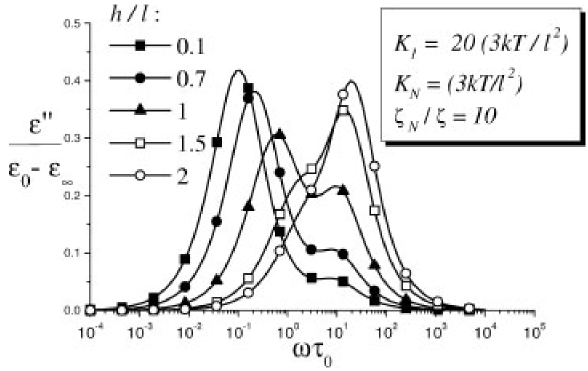


***Figure 4.***
Frequency dependence of the dielectric loss factor at different *h/l*.

decrease of the amplitudes of the motions of the network junctions with increase of tension (*h/l*).

#### Mechanical Relaxation of a Polymer Network with Included Rods

In this section we consider the frequency dependence of dynamical modulus manifested in mechanical relaxation. Dynamical modulus is known to be determined by a superposition of all the relaxation times in the system. [10–12] The renormalized dynamical model (Figure 2) used for the theory of dielectric properties of rods with dipolar groups in the first part of this paper takes into account contributions of only relaxation times greater than $\tau_n$ corresponding to the modes of initial network having the scale $n = h/h_0$. Therefore, it is necessary to add the increment of the relaxation times $\tau < \tau_n$ which correspond to shorter relaxation times of a domain of initial network of the size *h*. In first approximation the increment of the short-range network motions in $G''(\omega)$ which are not sensitive to the inclusion of rods may be estimated if we subtract the long-range increment in $G''(\omega)$ primary from whole $G''(\omega)$ for network. It means that dynamic modulus of the system is the sum of the increments of the short length and high frequency normal modes of the primary network the length of which is smaller than *h* and long normal modes (greater than *h*) i.e. the renormalized network motion. The dynamic loss modulus of the network with rods may be presented in the form:

$$G''_r(\omega) = G''(\omega) - G''_{l.fr.1}(\omega) + G''_{l.fr..2}(\omega) \quad (13)$$

where $G''(\omega)$ is loss modulus of the primary network including all normal modes, $G''_{l.fr.1}(\omega)$ is the low frequency part of loss modulus of the primary network. The difference $G''(\omega) - G''_{l.fr.1}(\omega)$ is the high frequency increment of the primary network which is proposed to be equal to additional high frequency increment of the renormalized network, and the$G''_{l.f..2}(\omega)$ is increment in loss-factor of the renormalized network with rods.

$$G''(\omega) = 3kT\nu(1/N)^3 \sum_{k=1}^{N}\sum_{l=1}^{N}\sum_{m=1}^{N} \frac{\omega\tau_{k,l,m}}{1+(\omega\tau_{k,l,m})^2} \quad (14)$$

$$G''_{l.fr.1}(\omega) = 3kT\nu(1/N)^3 \sum_{k=1}^{N/n}\sum_{l=1}^{N/n}\sum_{m=1}^{N/n} \frac{\omega\tau_{k,l,m}}{1+(\omega\tau_{k,l,m})^2} \quad (15)$$

Here $\nu$ is number cross-links of the primary network in unit of volume, $N^3$– is fool number of cross-links of the network, $\tau_{k,l,m}$ are the relaxation times of the primary network, consisting of $N$ cells in every direction [10]:

$$\tau_{k,l,m} = (\zeta_{N0}/2K_{N0})/(3 - \cos(\pi k/N) - \cos(\pi l/N) - \cos(\pi m/N)) \quad (16)$$

The value $k$, $l$, $m$ satisfy the condition $1<(k,\ l,\ m)<N$. The long range normal modes in the primary network correspond to the scale of motion greater than $nh_0$ are characterized by $1<k<N/n$. The value $G''_{l.fr.2}$ contains the increment of the relaxation spectrum of the renormalized network including 7 branches (see [6,7]).

$$G''_{l.f..2}(\omega) = (3kT\nu/N^3) \times \sum_{\alpha=1}^{7}\sum_{k'=1}^{N'}\sum_{l'=1}^{N'}\sum_{m'=1}^{N'} \frac{\omega\tau^{\alpha}_{k',l',m'}}{1+(\omega\tau^{\alpha}_{k',l',m'})^2} \quad (17)$$

The relaxation times $\tau^{\alpha}_{k',l',m'}$ present 7 branches (3 collective branches and 2 twice-degenerated relaxation times). The other approximated method is also based on the possible separation of two type of motion. The first type of motion reflects the relatively slow motions of the domains as a whole with corresponding constants ($K_N, \zeta_N, \zeta, K_1$). The second type of motions included in $G''(\omega)$ is based on the considering of the short motions in the region of the primary network included inside of the given domain of the renormalized network which is smaller than the whole system. It may be shown that for large enough $n$ the two approaches of evaluation of $\zeta/\zeta_N$ are very close one to another.

The increments of different branches of the complex low-frequency relaxation spectra of the network with rods considered below were strongly overlapped in mechanical relaxation similar to the case of dielectric relaxation of rods. But in distinction from dielectric relaxation the pure translational branches of the rods motions and the "translational" part of the network motion also take part in the dynamic modulus.

If the rods are longer than the average distance between neighboring junction ($l >> h_0$), and the average distance between neighboring rods $h$ is comparable with $l$ the possibility to divide the increments of the dynamics of rods and those of the dynamics of the network strongly depends on the ratio $\zeta/\zeta_N$ (Fig. 5). For comparatively long and not very thick rods ($n \approx 10$) we have the case of intermediate density of rods. In our case when the average distance between rods is $\approx l$ the part of the volume (the volume fraction of rods) is smaller than 1 and when the ratio $\zeta/\zeta_N \leq 1$ the relative increment of the rods to $G''(\omega)$ (or $G'(\omega)$ may be small). It will be not seen on the background of short-range network

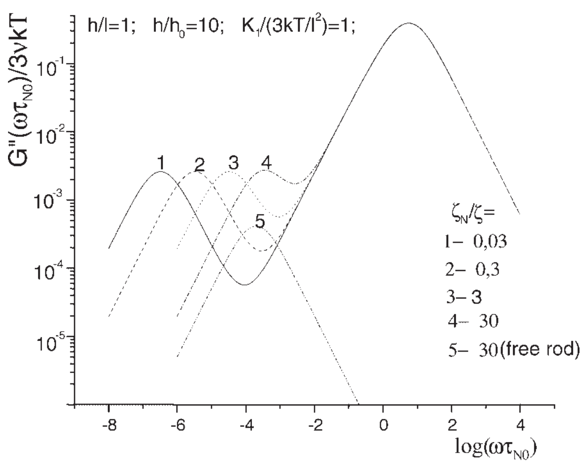


**Figure 5.**
Dependence of the loss modulus on $\log(\omega\tau_{N0})$ at the different ratios of domain friction and friction of the rod.

 

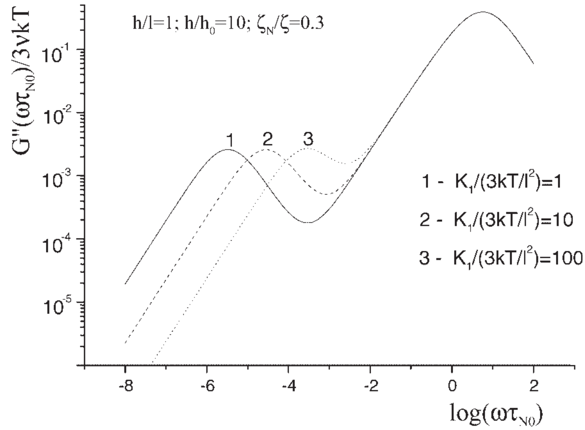


***Figure 6.***
Dependence of the loss modulus on $\log(\omega\tau_{N0})$ at the different values of parameter $K_1/(3kT/l^2)$.

motions. The separated increment of the rods in the $G''(\omega)$ and $G'(\omega)$ can be strongly distinguished in the cases when $\zeta/\zeta_N >> 1$ and for relatively small $K_1$. In the case of high $\zeta/\zeta_N$ and small $K_1$ the motion of the rod is shifted to low frequency and can be seen on the background of the network relaxation. If $K_1$ increases the relaxation peak of the rod moves to higher frequencies, but its magnitude decreases. This peak can be very faint seen on the background of the $G''(\omega)$ for primary network (Fig. 6).

Therefore the including of the long rods in the network at relatively low volume fraction of rods leads to the modification of the relaxation properties of the network mainly in the low frequency region ($\omega \approx 1/\tau_{N0} = 2K_{N0}/\zeta_{N0}$). The relaxation spectrum manifesting in the dynamic modulus of the network with included rods (i.e. in the mechanical properties) differs from that in the dielectric relaxation due to the increment of the pure translational and collective mainly translational modes which doesn't manifest in the dielectrics. In contrast to dielectric relaxation in the dynamic relaxation we obtain the overlapping of orientational and translational motions of the rods

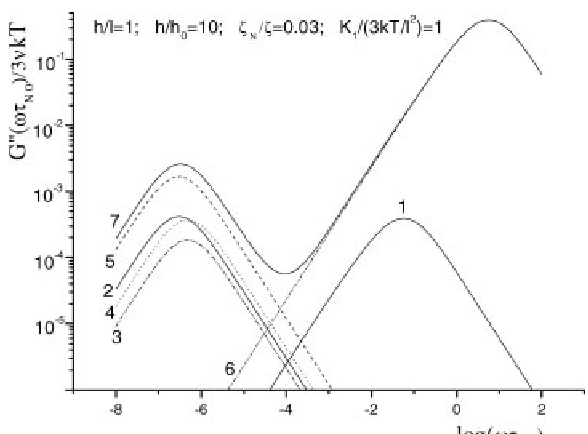


***Figure 7.***
Dependences of increments of different modes to loss modulus on $\log(\omega\tau_{N0})$: collective translation mode (1); collective network mode (2); collective rotation mode (3); individual rotation rod mode (4); individual translation rod mode (5); high frequency part of the spectrum of the primary network (6); the sum of all increments (7).

 

and the collective modes of the network chains. The increments of different branches of the collective motion of the rods in the network are demonstrated on the Fig. 7.

## Conclusion

The theory of relaxation spectra manifested in dielectric and mechanical relaxation properties of a polymer network with included rod-like particles has been developed for sufficiently long rods the length of which is greater than the average distance between neighboring cross-links of the network.

The theory proposed here should be further developed in two directions. At first, if the number concentration of long rods is so high, that they can overlap, we must take into account the direct volume interaction between rods. The same effects may be at high concentration of short but thick rods. The other direction of the development of the theory may be connected with relaxation of relatively short rods smaller than the distance between junctions of the network but strongly interacting with neighbouring chains. Some results in this direction were obtained by authors [8]. The special type of effects at high concentration of long rods may be connected with possible ordering effects and tendency to liquid crystalline order due to orientational interactions between rods and between rods and segments of the network chain [9].

The more rigorous approach may either use more detailed treatment of the interaction between rods and primary network in the framework of another dynamic model or change the parameters of the dynamic model used here. In real systems the entanglements between the network chains and rods can lead to very strong bonding between rods and any parts of the network neighboring with rod. Only one part of the network may be considered as bounded quasielastically with rod (with $K_1$ in our model) but another part of network will move (in first approximation) together with neighboring rods. It means that even if we preserve our dynamic model the friction parameter $\zeta$ must include the increment of the network chains which are strongly connected with rods (not quasi-elastically) and will (move) together with the rod.

At any case the including of the rods if we use the same dynamic model will preserve the type of relaxation spectrum in the network with rods considered here but the effects due to inclusion of rods may be more strong.

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