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**Full Paper:** Using normal mode transformation obtained in Part 1 of this series[1)], the exact analytical expressions for the mean-square displacements of junctions and non-junction beads, the autocorrelation functions of the end-to-end chain vectors between neighboring junctions, and those of subchain vectors of a two-dimensional regular network consisting of "bead and spring" Rouse chains are obtained. Contributions of intra- and interchain relaxation processes to the local dynamic characteristics considered are compared. The time behavior of dynamic quantities obtained is estimated for different scales of motions. The possibility of describing long-time relaxation of a two-dimensional network by a simplified coarse-grained network model is demonstrated. It is shown that the local relaxation properties of a two-dimensional polymer network (as well as a three-dimensional network) on scales smaller than the average distance between cross-links are very close to those of a single Rouse chain. The large-scale collective relaxation of the polymer networks having a two-dimensional connectivity differs considerably from that of the three-dimensional networks.

# Theory of relaxation properties of two-dimensional polymer networks, 2[a]

# Local dynamic characteristics

*Andrew A. Gurtovenko,* Yuli Ya. Gotlib*

Institute of Macromolecular Compounds, Russian Academy of Sciences,
Bolshoi Prospect 31, V. O., St. Petersburg, 199004, Russia
andrew@imc.macro.ru

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## 1. Introduction

In Part 1 of this series[1] we have obtained a set of relaxation times and the transformation from Cartesian coordinates of network elements to normal modes for a two-dimensional polymer network consisting of multisegmental Gaussian chains and for a simplified coarse-grained network model describing only the large-scale collective relaxation of a network. In this paper the exact analytical expressions for various local dynamic characteristics of a two-dimensional polymer network will be calculated using the normal mode transformation obtained.

The paper is organized as follows. For the polymer network consisting of multisegmental Gaussian chains, the mean-square displacements of junctions, and non-junction beads of network chains, the autocorrelation functions of the end-to-end chain vectors between neighboring junctions, and those of subchain vectors will be considered. These local dynamic characteristics of the polymer network having a two-dimensional connectivity were not studied previously. For all dynamic characteristics of a square network the comparison of the contributions of small-scale intrachain and collective interchain relaxation processes is made. The long-time relaxation properties of network junctions will be compared with analogous properties of junctions of a simplified coarse-grained model of a two-dimensional network, which may also be analyzed using normal mode transformation obtained in Part 1 of this series.[1] A comparison between local dynamic properties of two- and three-dimensional polymer networks will be made. Moreover, the relaxation properties of a square polymer network and a single Rouse chain will be also compared and discussed.

## 2. A two-dimensional polymer network consisting of multisegmental Gaussian chains

### *2.1. Relaxation properties of network junctions*

Now we shall consider the local dynamic characteristics of junctions of a two-dimensional polymer network consisting of multisegmental Gaussian chains. The mean-square

[a] For Part 1 see ref.[1]

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displacements of network junctions and the autocorrelation functions of the end-to-end chain vectors between neighboring junctions will be studied. These dynamic characteristics may be manifested, for example, in dielectric and mechanical relaxation of cross-linked polymers, incoherent dynamic scattering, NMR phenomena, etc.

The mean-square displacement $\Delta X^2(t)$ of the X projection of the position vector of a network element is determined as

$$\Delta X^2(t) = \langle (X(t) - X(0))^2 \rangle = 2(\langle X^2 \rangle - \langle X(0)X(t) \rangle) \quad (1)$$

where $\langle\ \rangle$ means the configurational average. The mean-square displacements describe the translational diffusion of network elements (junctions and non-junction beads of network chains). To calculate the quantity $\Delta X^2(t)$ for a junction of a two-dimensional network consisting of multisegmental Gaussian chains, the normal mode transformation obtained in Part 1 of this series should be used (see Eq. (22) in ref.[1]). Since the normal coordinates obtained in ref.[1] are independent and orthogonal, i.e., $\langle Q(\vec{\theta}; \psi; 0) Q(\vec{\theta}'; \psi'; t) \rangle = 0$ if $\vec{\theta} \neq \vec{\theta}'$ and (or) $\psi \neq \psi'$, the mean-square displacement $\Delta X^2(t)$ of a network junction includes only the autocorrelation functions of normal modes $\langle Q(0)Q(t) \rangle$. If $\psi \neq 0$ these autocorrelation functions have the following time behavior:

$$\langle Q(\vec{\theta}; \psi; 0) Q(\vec{\theta}; \psi; t) \rangle = \langle Q^2(\vec{\theta}; \psi; 0) \rangle \exp[-t/\tau(\psi)] \quad (2)$$

In order to obtain the equilibrium values of squares of normal modes $\langle Q^2 \rangle$, the law of equal distribution of energy according to classical degrees of freedom for a harmonic oscillator has to be used. As a result, we have for $\psi \neq 0$

$$\langle Q^2(\vec{\theta}; \psi; 0) \rangle = \frac{k_B T}{K_0 2(1 - \cos\psi)} \quad (3)$$

where $K_0 2(1 - \cos\psi)$ are the eigenvalues of potential energy of a two-dimensional network (see Eq. (18) in ref.[1]). The normal mode $Q$ with intrachain wave vector $\psi = 0$ provides an additional contribution to $\Delta X^2(t)$, which corresponds to the displacement of the center of mass of a network.

The consecutive use of the normal mode transformation for calculating mean-square displacement of a network junction yields

$$\Delta X_0^2(t) = \Delta X_C^2(t) + \frac{k_B T}{K_0} \frac{1}{N^2(n+1)} \times \sum_{\vec{\theta}} \sum_{\psi_1 \neq 0} \frac{1 - \exp[-t/\tau(\psi_1)]}{2(1 - \cos\psi)} \quad (4)$$

where $N^2$ is the total number of square cells in a network, and $n$ is the number of beads in the network chain between neighboring junctions. The relaxation times $\tau(\psi)$, intra- and interchain wave vectors $\psi_1$ and $\vec{\theta}$ are given by Eq. (6), (12), and (7) of Part 1 of this series,[1] respectively. The term $\Delta X_C^2(t)$ in Eq. (4) represents the square of displacement of the X projection of the center of mass of a two-dimensional polymer network, namely,

$$\Delta X_C^2(t) = \frac{2k_B T}{\varsigma_{NET}} t \quad (5)$$

where $\varsigma_{NET} = 2\ (n + 1) N^2 \varsigma_0$ is the total friction constant of the two-dimensional network as a whole. We are mostly interested in the time dependence of mean-square displacement of a network junction to the exclusion of the trivial displacement of center of mass of the network system, i.e. the time behavior of $\Delta X_0^2(t) - \Delta X_C^2(t)$ is of most interest. Therefore, the term $\Delta X_C^2(t)$ will be omitted below, and the time dependence of mean-square displacement with respect to the center of mass of a network will be considered. The mean-square displacement of a network junction $\Delta X^2(t)$ (see Eq. (4)) is determined by the wave vector $\psi_1$ only (purely intrachain branch $\psi_2$ is not included in $\Delta X^2(t)$ for the network junctions). It should be emphasized that the quantity $\psi_1$ depends on the phase shift $\vec{\theta}$ between network cells in a rather complicated manner (see Eq. (12) in ref.[1]). Therefore, the mean-square displacement of a network junction is determined by both the intra- and interchain relaxation processes.

Using the exact expression for the mean-square displacement of a junction of a two-dimensional regular network, one can study the asymptotic time behavior of dynamic quantity $\Delta X^2(t)$ and compare the contributions of intra- and interchain motions to mean-square displacement of a junction. To obtain the asymptotic behavior of $\Delta X^2(t)$ as well as other dynamic characteristics of a network, the following approximation will be used. The wave vector $\psi_1$ (see Eq. (12) in ref.[1]) at $l = 0$ is equal to the quantity $\psi_{net}$ (Eq. (14) in ref.[1]) and determines the interchain large-scale motions only. The normal modes at $l \neq 0$ correspond to the contribution of intrachain motions to mean-square displacement of a network junction. In the case of sufficiently long Gaussian chains between junctions, the phase shift $\vec{\theta}$ between network cells has a slight influence on the relaxation times $\tau(\psi_1)$ at $l \neq 0$. Therefore, one can assume in the first approximation that the wave vector $\psi_1(l, \vec{\theta})$ at $l \neq 0$ does not depend on the phase shift $\vec{\theta}$ between the motions of network cells. Thus, we have the following approximation for wave vector $\psi_1$ in the case of sufficiently long polymer chains between cross-links

$$\psi_1(l = 0) = \psi_{net} = \frac{1}{n+1} \arccos \frac{1}{2} (\cos\theta_1 + \cos\theta_2) \quad (6a)$$

$$\psi_1(l \neq 0) = 2l\pi/(n+1), \qquad l = 1, ..., n/2 \quad (6b)$$

Note that the set of wave vectors $\psi_1(l \neq 0)$ is doubly degenerated because two signs ± correspond to each value of $l$ in Eq. (12) in ref.[1]

Then the mean-square displacement of a junction with respect to the center of mass (Eq. (4)) may be presented in the following approximate form:

$$\Delta X_0^2(t) \cong \frac{k_B T}{K_0}\frac{1}{(n+1)}\frac{1}{N^2}\left[\sum_{\vec{\theta}}\frac{1-\exp[-t/\tau(\psi_{net})]}{2(1-\cos\psi_{net})} + 2N^2\cdot\sum_{\psi_1(l\neq 0)}\frac{1-\exp[-t/\tau(\psi_1(l\neq 0))]}{2(1-\cos\psi_1(l\neq 0))}\right] \quad (7)$$

The first term in brackets of Eq. (7) corresponds to the contribution of interchain long-scale motions to the mean-square displacement of a network junction. The second term corresponds to the intrachain contribution to $\Delta X_0^2(t)$. The first term in Eq. (7) represents the double sum taken over components $\theta_1$ and $\theta_2$ of the interchain wave vector. In order to simplify this term, the components of the wave vector $\vec{\theta}$ can be regarded as continuous variables in the case of a network with a great number of junctions ($N \gg 1$), and the long wave approximation[2–5] should be used ($\theta_{1;2} \ll \pi$). In this case the relaxation times of interchain collective motions $\tau_{net} = \tau(\psi_{net})$ may be presented as (see Eq. (6) and (14) in ref.[1]):

$$\tau_{net} \cong 8(n+1)^2\tau_0(1/\theta^2) \quad (8)$$

Here $\theta^2 = (\theta_2)^2 + (\theta_1)^2$ is the square of the interchain vector $\vec{\theta}$ and $\tau_0 = \varsigma_0/4K_0$ is the relaxation time of a single Gaussian subchain. The relaxation times $\tau_{net}$ in long wave approximation depend only on the square of the interchain wave vector $\vec{\theta}$. Therefore, it is convenient to introduce a polar coordinate system into double integrals and to integrate over an angular variable.

Using the above approximations, a comparison of the contributions of intra- and interchain relaxation processes to the mean-square displacement of a junction can be made for different scales of time. The initial slope of the time dependence of $\Delta X_0^2(t)$ may be easily obtained directly from rigorous expression given by Eq. (4). Treating Eq. (4) at $t < \tau_0$ we have

$$\Delta X_0^2(t) \cong \frac{k_B T}{K_0}\frac{1}{4}\frac{t}{\tau_0} \quad (9)$$

Intrachain motions dominate in the initial slope of the mean-square displacement of a junction (Fig. 1). The contribution of intrachain motions is $(n + 1)$ times greater than that of interchain collective motions. At times greater than $\tau_0$ but much smaller than the maximum relaxation time $\tau_{chain}$ of a chain between neighboring junctions (see Eq. (16) in ref.[1]), the mean-square displacement of a network junction behaves as:

$$\Delta X_0^2(t) \cong \frac{k_B T}{K_0}\frac{1}{\pi}\sqrt{\frac{t}{\tau_0}} \quad (10)$$

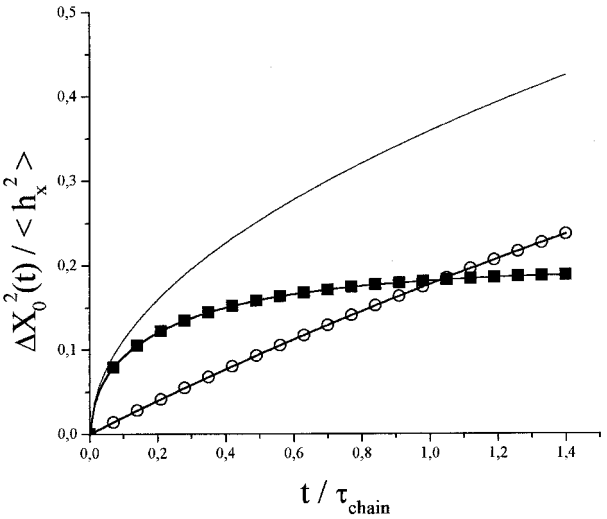


Fig. 1. Reduced mean-square displacement of a network junction $\Delta X_0^2(t)/\langle h_x^2\rangle$ (solid line). Lines with open circles (○) and solid squares (■) correspond to the contributions of inter- and intrachain relaxation processes, respectively. The quantity $\langle h_x^2\rangle$ is the mean square of the end-to-end chain vector between neighboring junctions, in this case $n = 20$

This time dependence is typical for that of a bead of long Gaussian chain.[6, 7] The intrachain motions also dominate in this time range. At times close to $\tau_{chain}$ the interchain collective motions begin to provide the noticeable contribution and the time behavior of $\Delta X_0^2(t)$ changes

$$\Delta X_0^2(t) \cong \frac{k_B T}{K_0}\frac{1}{\pi}\sqrt{\frac{t}{\tau_0}} + \frac{k_B T}{K_0}\frac{\pi}{8(n+1)}\frac{t}{\tau_0} \quad (11)$$

The first term in Eq. (11) corresponds to the contribution of intrachain motions (compare with Eq. (10)). The second term represents the initial slope of contribution of interchain collective motions (the times $\tau_0 < t < \tau_{chain}$ correspond to the short time range for these large-scale motions). The contributions of intra- and interchain motions to the mean-square displacement of a network junction become approximately equal at $t \cong \tau_{chain}$ (Fig. 1). At times greater than the relaxation time $\tau_{chain}$ of a chain between neighboring junctions ($t > \tau_{chain}$) the mean-square displacement $\Delta X_0^2(t)$ has asymptotic behavior

$$\Delta X_0^2(t) \cong \frac{k_B T}{K_0}\frac{(n+1)}{2\pi}\cdot\ln\left(\frac{t}{\tau_{chain}}\right) \quad (12)$$

At $t > \tau_{chain}$ the intrachain relaxation processes do not influence the time dependence of the mean-square displacement of a junction and give only a constant contribution. The interchain network motions provide the main contribution at $t > \tau_{chain}$ and completely determine the time dependence of $\Delta X_0^2(t)$. The mean-square displacement of a junction of two-dimensional polymer networks

increases according to logarithmic law at long times and has no finite limiting value in the case of infinitely large networks.

It should be noted that for the square network of finite size, which contains $N^2$ network cells, the asymptotic behavior given by Eq. (12) holds up to the maximum relaxation time of the network as a whole $\tau_{MAX} \sim N^2 \tau_{chain}$. At times greater than $\tau_{MAX}$ the mean-square displacement of a square network reaches the finite limiting value determined by the network size

$$\Delta X_0^2(t)\big|_{t\to\infty} \cong \frac{k_B T}{K_0} \cdot \frac{(n+1)}{\pi} \cdot \ln N \tag{13}$$

where $N$ is the number of network junctions along each network direction. Note that Eq. (13) may be directly obtained from Eq. (12) at $t = \tau_{MAX}$. One can see that the limiting value of mean-square displacement of a junction depends on the network size according to logarithmic law that is in agreement with results of Ronka and Allegra.[8] They have shown that the mean-square radius of gyration of the network increases logarithmically with total number of chains for networks having a two-dimensional connectivity.[8] The limiting value of quantity $\Delta X_0^2(t)$ is mostly determined by contribution of interchain motions, which is proportional to $\ln N$. In contrast, the intrachain contribution does not depend on the size of the network as a whole (Fig. 2). The interchain contribution $C_{inter}$ to a limiting value of mean-square displacement of a junction of the square network having finite size, is much greater than the intrachain contribution $C_{intra}$, namely, $C_{inter}/C_{intra} \approx (12/\pi)\ln(N/2)$. It should be especially emphasized that all curves in figures are plotted using exact analytical expressions obtained for dynamic characteristics of a network (see Eq. (4) in the case of mean-square displacement of a junction $\Delta X_0^2(t)$). The above mentioned approximations are used only to estimate the asymptotic behavior of dynamic characteristics considered.

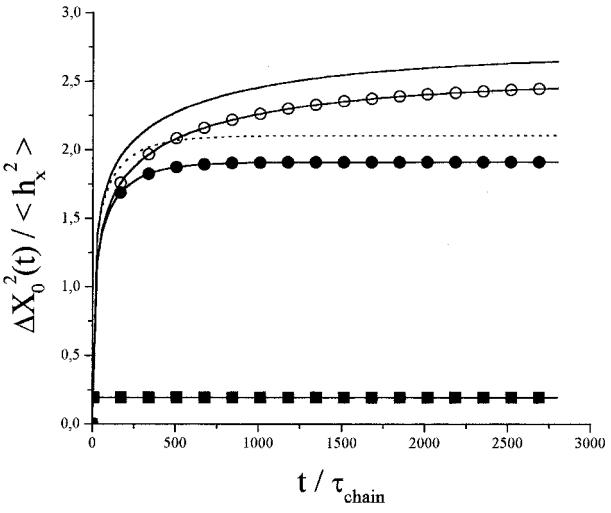


Fig. 2. Reduced mean-square displacement of a junction $\Delta X_0^2(t)/\langle h_x^2\rangle$ of the square networks of finite sizes with $N = 50$ (solid line) and $N = 25$ (dotted line). Lines with open circles (○) and solid circles (●) correspond to the contributions of interchain motions for networks with $N = 50$ and $N = 25$, respectively. Lines with solid squares (■) correspond to the contributions of intrachain motions for both networks of different sizes, in this case $n = 20$

Besides the mean-square displacement, the time autocorrelation function of the end-to-end chain vector between neighboring junctions also represents an important dynamic quantity characterizing Brownian motion of a network. The projections of the end-to-end chain vectors between neighboring junctions take the following form (there are two end-to-end chain vectors per cell of a square network)

$$h_{x1}(\alpha,\beta;t) = X_0(\alpha,\beta;t) - X_0(\alpha-1,\beta;t) \tag{14a}$$

$$h_{x2}(\alpha,\beta;t) = X_0(\alpha,\beta;t) - X_0(\alpha,\beta-1;t) \tag{14b}$$

As in the case of mean-square displacement, with the use of normal mode transformation (Eq. (22) in ref.[1]) for calculating time autocorrelation function $C(h_x;t) = \langle h_x(0)h_x(t)\rangle$ we have

$$C(h_x;t) = \frac{k_B T}{K_0}\frac{1}{4N^2(n+1)}\sum_{\vec{\theta}}\sum_{\psi_1}\exp[-t/\tau(\psi_1)] \times\left[\frac{2-\cos\theta_1-\cos\theta_2}{1-\cos\psi_1}\right] \tag{15}$$

With the use of numerical calculations, the equilibrium value of the mean square of distance between neighboring junctions $\langle h_x^2\rangle = C(h_x;0)$ averaged over all network chains may be approximately presented in the form

$$\langle h_x^2\rangle = \frac{1}{2N^2}\sum_{\Omega}[\langle h_{x1}^2(\Omega;0)\rangle + \langle h_{x2}^2(\Omega;0)\rangle] \cong \frac{1}{2}\frac{k_B T}{K_0}(n+1) \tag{16}$$

At short times ($t < \tau_0$) the autocorrelation function of the end-to-end chain vector between neighboring network junctions behaves as

$$C(h_x;t) \cong \langle h_x^2\rangle - \frac{k_B T}{K_0}\frac{1}{4}\frac{t}{\tau_0} \tag{17}$$

The time dependence of autocorrelation function $C(h_x;t) = \langle h_x(t)h_x(0)\rangle$ at short times corresponding to the initial slope is mostly determined by intrachain motions. However, the contribution of interchain collective spectrum to the total autocorrelation function $C(h_x;t)$ (time-dependent part and equilibrium value of mean-square distance $\langle h_x^2\rangle$) at short times is approximately four times greater than that of intrachain spectrum (Fig. 3). In the

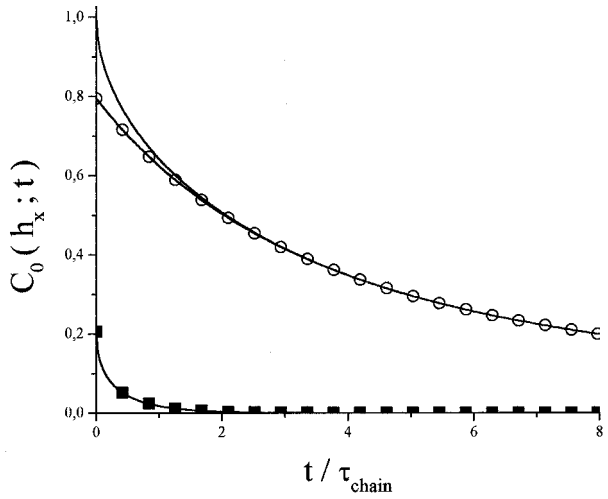


Fig. 3. Normalized autocorrelation function $C_0(h_x;t)$ of the end-to-end chain vector between neighboring junctions (solid line). Lines with open circles (○) and solid squares (■) correspond to the contributions of inter- and intrachain relaxation processes, respectively. The quantity $n$ is equal to 20

time range from relaxation time $\tau_0$ of a Gaussian subchain to relaxation time of a network chain between cross-links $\tau_{chain}$ (see Eq. (16) in ref.[1]) the quantity $C(h_x;t)$ behaves as

$$C(h_x;t) \cong \langle h_x^2 \rangle - \frac{k_B T}{K_0}\frac{1}{2\pi}\sqrt{\frac{t}{\tau_0}} \qquad (18)$$

The time dependence of $C(h_x;t)$ is still determined by intrachain relaxation processes, whereas the total contribution of these motions to autocorrelation function $C(h_x;t)$ is much smaller than that of interchain relaxation processes (Fig. 3). At times greater than the relaxation time of a network chain between cross-links $\tau_{chain}$, the quantity $C(h_x;t)$ behaves as:

$$C(h_x;t) \cong \frac{k_B T}{K_0}\frac{\pi}{4}(n+1)\left(\frac{\tau_{chain}}{t}\right) \qquad (19)$$

i.e., decreases to zero with time. The interchain motions completely dominate at $t > \tau_{chain}$, and their contribution to time dependence of $C(h_x;t)$ is much greater than that of intrachain relaxation processes (Fig. 3).

### 2.2. *Relaxation properties of non-junction beads of network chains*

In order to obtain rigorous analytical expressions for local dynamic characteristics of non-junction beads of a two-dimensional regular network, the normal mode transformation (see Eq. (19) of Part 1 of this series[1]) should be used. For the mean-square displacement of a non-junction bead we obtain the following expression:

$$\Delta X^2(j;t) = \Delta X_C^2(t) + \frac{k_B T}{K_0}\frac{1}{N^2(n+1)} \sum_{\vec{\theta}}\sum_{\psi_1 \neq 0}\frac{1-\exp[-t/\tau(\psi_1)]}{2(1-\cos\psi_1)} + \frac{k_B T}{K_0}\frac{2}{(n+1)}\sum_{\psi_2}\sin^2 j\psi_2 \frac{1-\exp[-t/\tau(\psi_2)]}{2(1-\cos\psi_2)} \qquad (20)$$

Here the relaxation times $\tau(\psi)$, intrachain vectors $\psi_1$ and $\psi_2$, and interchain wave vector $\vec{\theta}$ are given by Eq. (6), (12), (13), and (7) of Part 1 of this series,[1] respectively. The quantity $\Delta X_C^2(t)$ is the square of displacement of the X projection of the center of mass of a network, which is given by Eq. (5). Note that the mean-square displacement of a non-junction bead (as well as the dynamic characteristics of network junctions (see previous sub-section)) does not depend on the two-component index of a network cell $\Omega = (\alpha,\beta)$ because all the cells of a square network with periodic boundary conditions are equivalent. Moreover, the quantity $\Delta X^2(j;t)$ does not depend on the position of Gaussian chains in a network cell (index $p = 1;2$) either, because of the symmetry of a regular square network.

One can see from Eq. (20) that the mean-square displacement of a non-junction bead depend on the bead position $j$ along the network chain ($j = 1,...,n$). At first, we consider the mean-square displacement $\Delta X^2(t)$ of a non-junction bead, which is averaged over bead positions along the multisegmental chain

$$\Delta X^2(t) \equiv \langle \Delta X^2(j;t) \rangle_j = \frac{1}{n}\sum_{j=1}^{n}\Delta X^2(j;t) \qquad (21)$$

Averaging Eq. (20) over bead positions, we obtain

$$\Delta X^2(j;t) = \Delta X_C^2(t) + \frac{k_B T}{K_0}\frac{1}{N^2(n+1)} \times \sum_{\vec{\theta}}\sum_{\psi_1 \neq 0}\frac{1-\exp[-t/\tau(\psi_1)]}{2(1-\cos\psi_1)} + \frac{k_B T}{K_0}\frac{1}{(n+1)}\sum_{\psi_2}\frac{1-\exp[-t/\tau(\psi_2)]}{2(1-\cos\psi_2)} \qquad (22)$$

In contrast to network junctions (Eq. (4)), the mean-square displacement of a non-junction bead of a network chain is determined by wave vectors $\psi_1$ and $\psi_2$. In addition to the main branch described by wave vector $\psi_1$ (Eq. (12) in ref.[1]), the purely intrachain branch $\psi_2$ (Eq. (13) in ref.[1]) corresponding to relaxation of a network chain with fixed ends appears. Therefore, the relative contribution of intrachain motions to the quantity $\Delta X^2(t)$ increases as compared to that of a network junction.

The approximate estimation of time dependence which was applied in the consideration of dynamic characteris-

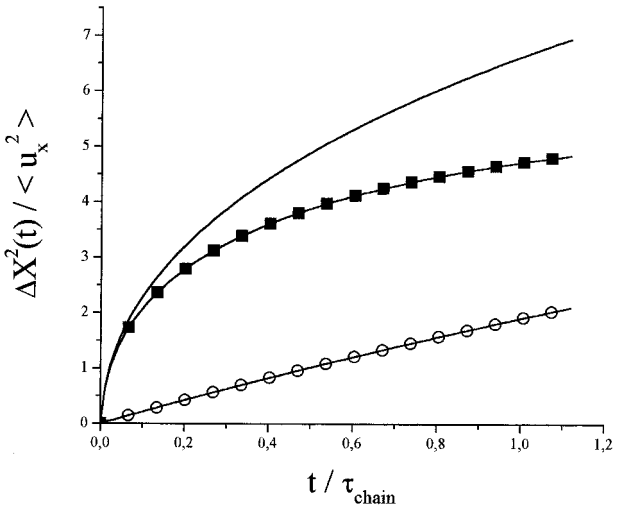


Fig. 4. The time dependence of reduced mean-square displacement of a non-junction bead $\Delta X^2(t)/\langle u_x^2\rangle$ up to time $t \cong \tau_{chain}$ (solid line). Lines with open circles (○) and solid squares (■) correspond to the contributions of inter- and intrachain relaxation processes, respectively. The quantity $\langle u_x^2\rangle$ is the mean square of a subchain vector. In this case $n = 20$

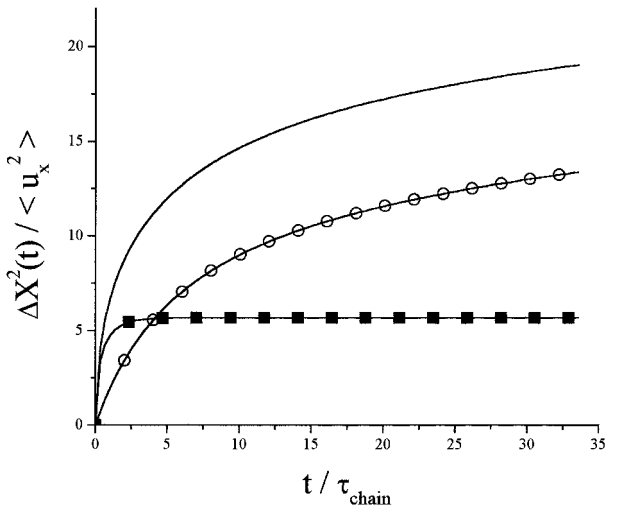


Fig. 5. The time dependence of reduced mean-square displacement of a non-junction bead $\Delta X^2(t)/\langle u_x^2\rangle$ up to time $t \cong 30\,\tau_{chain}$. The denotation of curves is the same as in Fig. 4

tics of network junctions (see previous sub-section) may also be used to analyze the mean-square displacements of non-junction beads. As in the case of a network junction, we shall study the time dependence of mean-square displacement of a non-junction bead $\Delta X^2(t)$ with respect to center of mass of a two-dimensional network. The initial slope ($t < \tau_0$) of $\Delta X^2(t)$ averaged over the bead position along the network chain is given by:

$$\Delta X^2(t) \cong \frac{k_B T}{K_0}\frac{1}{2}\frac{t}{\tau_0} \tag{23}$$

It is two times greater than that for a network junction (Eq. (9)). The contribution of intrachain relaxation processes dominates in the initial slope (Fig. 4) and is $2(n + 1)$ times greater than that of interchain collective motions. In the time range from $\tau_0$ to relaxation time $\tau_{chain}$ of a network chain between junctions, the intrachain relaxation processes provide the main contribution (Fig. 4), and the quantity $\Delta X^2(t)$ behaves as

$$\Delta X^2(t) \cong \frac{k_B T}{K_0}\frac{2}{\pi}\sqrt{\frac{t}{\tau_0}} \tag{24}$$

The mean-square displacement of a non-junction bead in this time range is also two times greater than that of a network junction (Eq. (10)). Note that such a type of time dependence is typical of the mean-square displacement of a bead of a single Gaussian chain.[6,7] At long times ($t > \tau_{chain}$) the mean-square displacement $\Delta X^2(t)$ averaged over bead positions along the network chain has the following asymptotic behavior

$$\Delta X^2(t) \cong \frac{k_B T}{K_0}\frac{(n+1)}{2\pi}\cdot\ln\left(\frac{t}{\tau_{chain}}\right) \tag{25}$$

The time dependence of $\Delta X^2(t)$ in this time range is completely determined by interchain motions, the intrachain motions provide only the constant contribution to mean-square displacement at $t > \tau_{chain}$. The contributions of intra- and interchain relaxation processes become equal at $t \cong 5\tau_{chain}$ (Fig. 5). Thus, in the same way as displacement of a junction, the mean-square displacement of a non-junction bead of a two-dimensional polymer network increases infinitely according to logarithmic law in the case of infinitely large network systems. For the two-dimensional network of finite size such a type of time behavior holds up to maximum relaxation time of the network as a whole $\tau_{MAX} \sim N^2\tau_{chain}$. At greater times the quantity $\Delta X^2(t)$ reaches the finite limiting value determined by Eq. (13). The interchain contribution $C_{inter}$ to limiting value of $\Delta X^2(t)$ in the case of the square network of finite size is much greater than intrachain contribution $C_{intra}$, which does not depend on the size of network as a whole: $C_{inter}/C_{intra} \approx (4/\pi)\ln(N/2)$ (compare with analogous expression for network junction).

As mentioned above, the mean-square displacement of a non-junction bead depends on the bead position along the network chain. This dependence is completely determined by the purely intrachain branch $\psi_2$ (third term in Eq. (20)). It can be shown that the above dependence on the bead position $j$ is manifested only at sufficiently long times $t > \tau_{chain}$. For the asymptotic behavior of mean-square displacement of a non-junction bead $\Delta X^2(j;t)$ we obtain (cf. Eq. (25)):

$$\Delta X^2(t) \cong \frac{k_B T}{K_0}\left[j\left(1-\frac{j}{n+1}\right)+\frac{(n+1)}{2\pi}\ln\left(\frac{t}{\tau_{chain}}\right)\right] \tag{26}$$

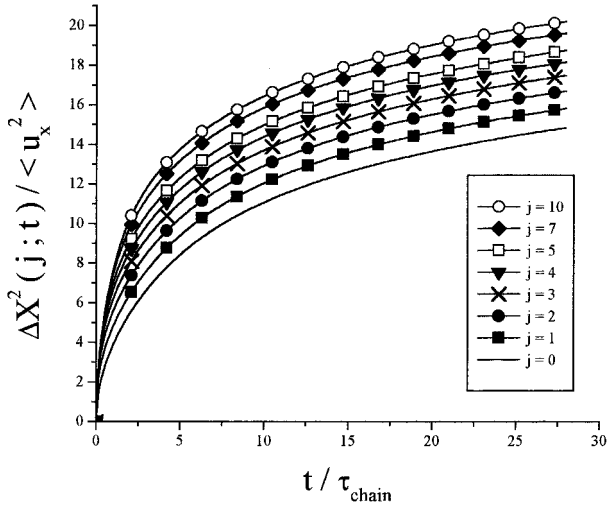


Fig. 6. Reduced mean-square displacements $\Delta X^2(j;t)/\langle u_x^2\rangle$ of different non-junction beads of a network chain ($n = 20$). Curves $j = 10$ and $j = 0$ correspond to the middle bead of a network chain and the junction, respectively

One can see that the bead position $j$ has influence on the limiting value of the intrachain contribution only, the time dependencies of averaged and non-averaged mean-square displacements of non-junction beads at $t > \tau_{chain}$ are identical (see Eq. (25) and (26)). In Fig. 6 the mean-square displacements of non-junction beads are plotted for different beads of a network chain ($j = 1,...,n$) for the case $n = 20$. The bead in the middle of a network chain ($j = 10$) "feels" the restrictions related to the inclusion into the network structure least of all. In contrast, the network junction ($j = 0$) has the lowest diffusive mobility. The diffusive mobility of intermediate non-junction beads increase with distance from the network junction (Fig. 6).

Now we consider another dynamic quantity describing local relaxation of non-junction beads – the time autocorrelation function of the end-to-end chain vector between neighboring non-junction beads (subchain vector). The X projection of a subchain vector $u_x$ is determined as:

$$u_x(\Omega;j;t) = X(\Omega;j;t) - X(\Omega;j-1;t) \tag{27}$$

With the use of normal mode transformation for non-junction beads (Eq. (19) in ref.[1]), for the autocorrelation function $C(u_x;t) = \langle u_x(0)u_x(t)\rangle$ we obtain:

$$C(u_x(j);t) = \frac{k_B T}{K_0}\frac{1}{2N^2(n+1)}\sum_{\vec{\vartheta}}\sum_{\psi_1}\exp[-t/\tau(\psi_1)] + \frac{k_B T}{K_0}\frac{1}{(n+1)}\sum_{\psi_2}\cos^2\left(j-\frac{1}{2}\right)\psi_2 \times \exp[-t/\tau(\psi_2)] \tag{28}$$

Using Eq. (28), the equilibrium value of the mean square of a subchain vector $\langle u_x^2\rangle$ averaged over all subchains of a two-dimensional network may be calculated

$$\langle u_x^2\rangle = \frac{1}{N^2}\frac{1}{2(n+1)}\sum_{\alpha,\beta}\sum_{j=1}^{n+1}(\langle u_{1x}^2(j;0)\rangle + \langle u_{2x}^2(j;0)\rangle) = \frac{k_B T}{K_0}\left[1-\frac{1}{2(n+1)}\right] \tag{29}$$

It should be noted that in the limiting case $n = 0$ the quantity $\langle u_x^2\rangle$ corresponds to the equilibrium value $\langle h_x^2\rangle_{CG}$ for a simplified coarse-grained network model and is equal to $k_B T/2K$ (see below Section 3). In contrast, in the limiting case $n \to \infty$ corresponding to a single Gaussian chain, the mean square of the subchain vector $\langle u_x^2\rangle$ is equal to $k_B T/K_0$, i.e. to the analogous equilibrium quantity of a linear Gaussian chain.[6, 7, 9]

Eq. (28) indicates that the autocorrelation function of a subchain vector $C(u_x(j);t)$ depends on the position of a subchain along the multisegmental Gaussian chain between network junctions ($j = 1,...,n+1$). In the same way as for mean-square displacement of a non-junction bead, it is convenient at first to consider the autocorrelation function $C(u_x;t)$ averaged over subchain positions along the network chain:

$$C(u_x;t) = \frac{1}{n+1}\sum_{j=1}^{n+1} C(u_x(j;t);t) \tag{30}$$

After averaging we obtain

$$C(u_x;t) = \frac{k_B T}{K_0}\frac{1}{2(n+1)}\left[\frac{1}{N^2}\sum_{\vec{\vartheta}}\sum_{\psi_1}\exp[-t/\tau(\psi_1)] + \sum_{\psi_2}\exp[-t/\tau(\psi_2)]\right] \tag{31}$$

The autocorrelation function $C(u_x;t)$ averaged over the subchain position along the network chain behaves at short times ($t < \tau_0$) as:

$$C(u_x;t) \cong \langle u_x^2\rangle - \frac{k_B T}{K_0}\frac{1}{2}\frac{t}{\tau_0} \tag{32}$$

Eq. (32) corresponds to the expansion in a series of $\exp(-t/\tau)$ at short times $t < \tau_0$ (see Eq. (31)). At times from $\tau_0$ to $\tau_{chain}$ this initial slope is replaced with a power-law behavior typical of a single Rouse chain[6, 7, 9]

$$C(u_x;t) \cong \frac{k_B T}{K_0}\frac{2}{\pi}\sqrt{\frac{\tau_0}{t}} \tag{33}$$

The intrachain relaxation processes provide the main contribution to the time dependence of autocorrelation function $C(u_x;t)$ up to $t \approx \tau_{chain}$ (Fig. 7). In the time range $\tau_0 \ll t \ll \tau_{chain}$ the contribution of interchain collective motions is about $(n + 1)$ times smaller than that of intrachain motions. The interchain collective motions begin to be manifested at times greater than the relaxation time

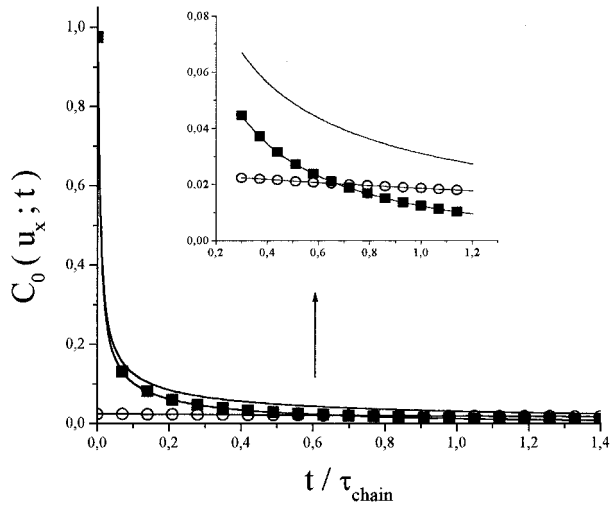


Fig. 7. Normalized autocorrelation function $C_0(u_x;t)$ of a subchain vector (solid line). Lines with open circles (○) and solid squares (■) correspond to the inter- and intrachain contributions, respectively. In this case $n = 20$

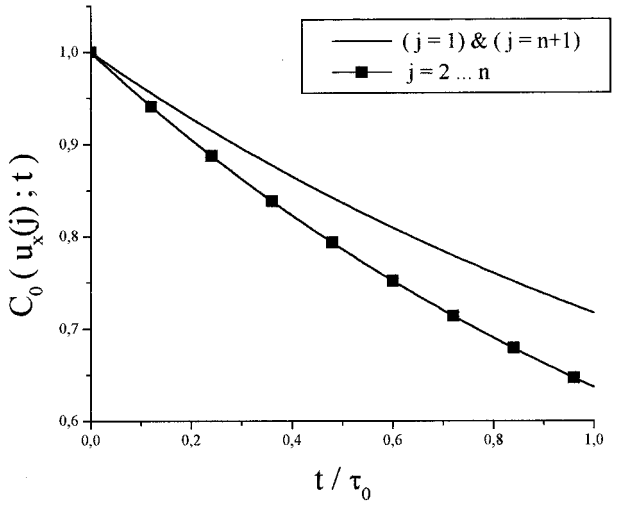


Fig. 8. Normalized autocorrelation functions $C_0(u_x(j);t)$ of different subchain vectors of a network chain ($n = 20$) at times $t < \tau_0$. Solid line corresponds to the peripheral subchains ($j = 1$ and $j = n + 1$), and line with solid squares (■) corresponds to the inner subchains ($j = 2,...,n$)

$\tau_{chain}$ of network chains as a whole, and $C(u_x;t)$ decreases more rapidly

$$C(u_x;t) \cong \frac{k_B T}{K_0}\frac{\pi}{4}\frac{1}{(n+1)}\left(\frac{\tau_{chain}}{t}\right) \qquad (34)$$

Note that the autocorrelation function $C(u_x;t)$ at $t > \tau_{chain}$ decreases considerably with respect to the equilibrium value $C(u_x;t) = \langle u_x^2\rangle$ (at $t \cong \tau_{chain}$ it becomes about $(n + 1)$ times smaller than $\langle u_x^2\rangle$). Therefore, the influence of interchain relaxation processes on the quantity $C(u_x;t)$ is negligible in the time range from $\tau_0$ to $\tau_{chain}$ (Fig. 7).

It is interesting to study the dependence of the autocorrelation function of subchain vectors $C(u_x(j);t)$ on the position of a subchain $j$ along the multisegmental chain between network junctions. Eq. (28) shows that this dependence is governed by the term determined by intrachain wave vector $\psi_2$. This means that the autocorrelation function of a subchain vector will be sensitive to the subchain position along the chain in the region of preferably intrachain relaxation, i.e. at times smaller than the relaxation time $\tau_{chain}$ of network chain as a whole. At short times corresponding to the initial slope ($t < \tau_0$), the autocorrelation function of subchains which are directly attached to the network junctions ($j = 1$ and $j = n + 1$) behaves as:

$$C(u_x;t) \cong \langle u_x^2\rangle - \frac{k_B T}{K_0}\frac{3}{8}\frac{t}{\tau_0} \qquad (35)$$

For other non-junction beads ($j = 2,...,n$) Eq. (32) obtained for the autocorrelation function averaged over bead positions holds. Thus, even for the shortest times $t < \tau_0$ the autocorrelation function of a non-junction bead is very sensitive to the fact that the given subchain connects either the junction and non-junction bead (peripheral subchains of the network chain between junctions) or two non-junction beads (inner subchains). It is seen that the peripheral subchains relax more slowly as compared to the inner subchains of a chain between network junctions (see Eq. (32) and (35), and Fig. 8).

In the time range from $\tau_0$ to $\tau_{chain}$ the autocorrelation function of a subchain vector behaves as

$$C(u_x(j);t) \cong \frac{k_B T}{K_0}\frac{3}{\pi}\sqrt{\frac{\tau_0}{t}} - \frac{k_B T}{K_0}\frac{2}{3\pi}(2j-1)^2\left(\frac{\tau_0}{t}\right)^{3/2} \qquad (36a)$$

for subchains with $j = 1,...,n/2$ and

$$C(u_x(j);t) \cong \frac{k_B T}{K_0}\frac{3}{\pi}\sqrt{\frac{\tau_0}{t}} - \frac{k_B T}{K_0}\frac{2}{3\pi}(2n-2j+3)^2\left(\frac{\tau_0}{t}\right)^{3/2} \qquad (36b)$$

for subchains with $j = (n/2) + 1,...,(n + 1)$. Note that Eq. (36) are written for the case when $n$ is an even number. Eq. (36) indicate that the dependence of the autocorrelation function $C(u_x(j);t)$ on the subchain position $j$ in the time range $\tau_0 < t < \tau_{chain}$ is manifested in the next time-dependent term of the expansion as compare to the averaged quantity $C(u_x;t)$ (see Eq. (33)). In Fig. 9 the autocorrelation functions of subchain vectors is plotted for subchains having different positions $j$ along the network chain ($j = 1,...,n + 1$) for the case $n = 20$. The peripheral subchains connecting the junction and non-junction bead ($j = 1$ and, due to symmetry, $j = 21$) show the slowest relaxation. In contrast, the middle subchain

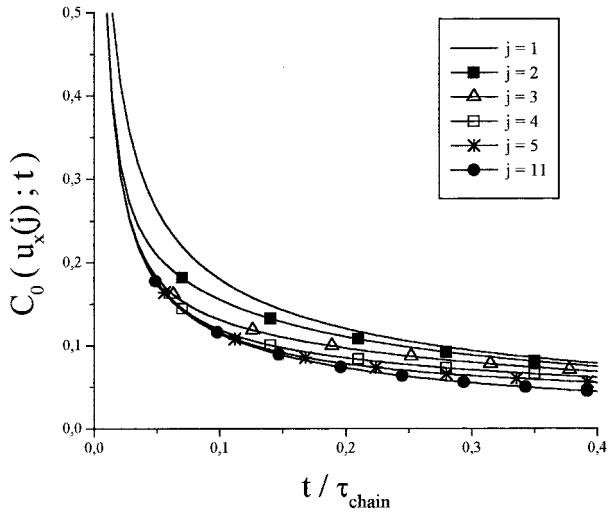


Fig. 9. Normalized autocorrelation functions $C_0(u_x(j);t)$ of different subchain vectors of a network chain ($n = 20$) at times $t \gg \tau_0$. Curves $j = 11$ and $j = 1$ correspond to the middle and peripheral subchains, respectively

($j = 11$) relax the most rapidly. The relaxation times of the inner subchain mediates between the middle and peripheral subchains (Fig. 9).

Although we do not consider in this paper the macroscopic viscoelastic characteristics (for example, dynamic modulus and viscosity), some remarks concerning relaxation spectrum manifested in mechanical viscoelastic relaxation of a two-dimensional polymer network can be made. The autocorrelation function $C(u_x;t)$ represents the sum of exponential terms $\exp[-t/\tau]$ with the identical weights equal to 1 for all relaxation times of a network (see Eq. (31)). A similar form is also typical of the time dependent relaxation modulus $G(t)$ (see, for example, ref.[10]). It should be especially noted that the relaxation modulus $G(t)$ is determined by relaxation times $\tau' = \tau/2$ because the relaxation spectrum of average squares of normal modes $\langle Q^2 \rangle$ is excited in mechanical relaxation.[6, 4] In turn, the relaxation modulus $G(t)$ determines the relaxation spectrum $H(\tau)$ (or the distribution function of relaxation times $\tau$ in logarithmic scale)[10]: $G(t) = G(0)\int H(\tau)\exp[-t/\tau]d\ln\tau$. Therefore, using the expression obtained for $C(u_x;t)$ (Eq. (31)) one can estimate approximately the asymptotic behavior of the relaxation spectrum. The relaxation spectrum $H(\tau)$ of a two-dimensional polymer network is found to behave as $1/\sqrt{\tau}$ in the region of intrachain relaxation (at $t \ll \tau_{chain}$). This behavior is close to that of a single Rouse chain.[6, 11] At greater times corresponding to the purely interchain network relaxation ($t \gg \tau_{chain}$), the relaxation spectrum $H(\tau)$ decreases more rapidly according to the $1/\tau$ law. The asymptotic behavior of relaxation spectrum estimated for the two-dimensional regular network is in agreement with results obtained previously in ref.[12]

## 3. Comparison with a coarse-grained network model

As was mentioned in Part 1 of this series,[1] the interchain collective relaxation of a two-dimensional network may be described by a simplified coarse-grained network model in which the small-scale intrachain motions are not taken into consideration. A comparison between long-time relaxation properties of the coarse-grained network model and the network consisting of multisegmental Gaussian chains is of special importance because of the simplicity of the coarse-grained model of a two-dimensional network.

If the motions on sufficiently large scales are considered, the sets of relaxation times of both network models should correspond to the long-time collective relaxation only. For large-scale motions ($\theta_{1;2} \ll \pi$) the set of relaxation times obtained for the coarse-grained network model (see Eq. (26) in ref.[1]) may be rewritten as

$$\tau(\vec{\theta}) \cong 8\tau_{\min}(1/\theta^2) \tag{37}$$

where $\tau_{\min} = \varsigma/8K$ is the minimum relaxation time of a simplified network model, and $\theta^2 = (\theta_1)^2 + (\theta_2)^2$ is the square of interchain wave vector $\vec{\theta}$. The corresponding set of relaxation times $\tau_{net}$ of a network of multisegmental chains are determined for large-scale network motions by Eq. (8). The relaxation times of a two-dimensional network consisting of multisegmental Gaussian chains (Eq. (8)) have to be equal to those of simplified coarse-grained network (Eq. (37)) in the region of large-scale collective motions. Therefore, the characteristic times of both network models should be related in the following way:

$$\tau_{\min} = (n+1)^2\tau_0 \tag{38}$$

Then the relations between parameters (elasticity and friction constants) of both dynamic models of a network may be obtained. The elasticity constant $K$ of a spring between neighboring junctions of a coarse-grained network model corresponds to the elasticity constant of the multisegmental chain as a whole. The multisegmental Gaussian chain between network junctions contains $(n + 1)$ subchains acting as springs with elasticity constants $K_0$, i.e. we have

$$K = K_0/(n+1) \tag{39}$$

With the use of Eq. (38) and (39), the relation between friction constants $\varsigma$ and $\varsigma_0$ may be obtained

$$\varsigma = 2(n+1)\varsigma_0 \tag{40}$$

Thus, the friction constant of a junction of coarse-grained network model should be the sum of the friction constant of a junction of network of multisegmental

Gaussian chains $2\varsigma_0$ (see Eq. (9) of Part 1 of this series[1]) and the friction constant $4(n/2)\varsigma_0$ of halves of four multisegmental chains directly attached to a given junction of two-dimensional polymer network.

It is also interesting to compare the relaxation properties of junctions of a two-dimensional polymer network consisting of multisegmental Gaussian chains with those of a simplified coarse-grained model of a network. Using the normal mode transformation (see Eq. (28) of Part 1 of this series[1]) we obtain for the mean-square displacement of a junction of coarse-grained network model

$$\Delta X^2(t) = \Delta X_C^2(t) + \frac{k_B T}{K}\frac{1}{N^2} \times \sum_{\vec{\theta}\neq(0,0)} \frac{1-\exp[-t/\tau(\vec{\theta})]}{2(2-\cos\theta_1-\cos\theta_2)} \qquad (41)$$

where the relaxation times $\tau(\vec{\theta})$ and the interchain wave vector $\vec{\theta} = (\theta_1,\theta_2)$ are given by Eq. (26) and (7) of Part 1 of this series[1], respectively. The displacement of the X projection of the center of mass of a coarse-grained network model $\Delta X_C^2(t)$ is given by Eq. (5) with the total friction constant $\varsigma_{NET}$ of a network equal to $N^2\varsigma$. At times smaller than the minimum relaxation time $\tau_{min}$ of a coarse-grained network model, the mean-square displacement of a junction $\Delta X^2(t)$ with respect to center of mass of a network behaves as:

$$\Delta X^2(t) \cong \frac{k_B T}{K}\frac{1}{4}\frac{t}{\tau_{min}} \qquad (42)$$

At times $t > \tau_{min}$ the quantity $\Delta X^2(t)$ increases according to logarithmic law for infinitely large networks

$$\Delta X^2(t) \cong \frac{k_B T}{K}\frac{1}{2\pi}\cdot\ln\left(\frac{\pi^2}{4}\frac{t}{\tau_{min}}\right) \qquad (43)$$

A comparison of the mean-square displacements of network junctions of a coarse-grained network model (Eq. (43)) and a network of multisegmental chains (Eq. (12)) with the use of the relation between their characteristic times (Eq. (38)) shows that the dynamic behavior of both network models at sufficiently long times $t \gg \tau_{min}$ are equivalent (Fig. 10).

With the use of normal mode transformation (Eq. (28) in ref.[1]), one can also obtain the exact analytical expression for the autocorrelation function of the end-to-end chain vector between neighboring junctions of a coarse-grained network model

$$C(h_x;t) = \frac{1}{2}\frac{1}{N^2}\frac{k_B T}{K}\sum_{\vec{\theta}}\exp[-t/\tau(\vec{\theta})] \qquad (44)$$

The equilibrium value of the mean square of the end-to-end distance between neighboring junctions $C(h_x;0) = \langle h_x^2\rangle_{CG}$ of a simplified network model is given by

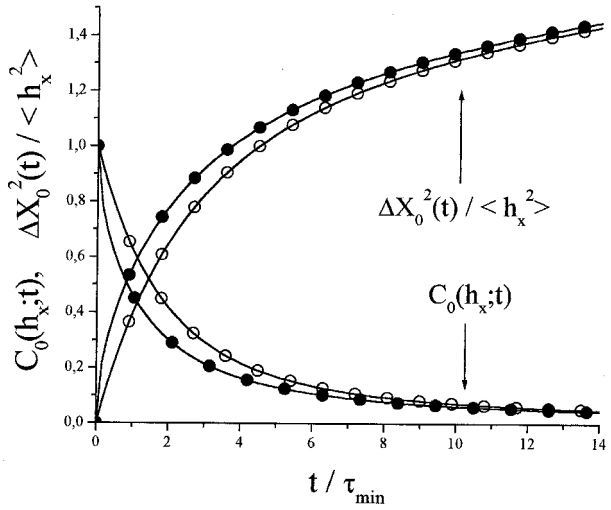


Fig. 10. Reduced mean-square displacement of a junction $\Delta X_0^2(t)/\langle h_x^2\rangle$ and normalized autocorrelation function $C_0(h_x;t)$ of the end-to-end chain vector between neighboring junctions for a square network consisting of multisegmental Gaussian chains (lines with solid circles (●)) and for a simplified coarse-grained network model (lines with open circles (○)). In this case $n = 20$

$$\langle h_x^2\rangle_{CG} = \frac{1}{2}\frac{k_B T}{K} \qquad (45)$$

At short times ($t < \tau_{min}$) the autocorrelation function $C(h_x;t)$ has the behavior

$$C(h_x;t) \cong \langle h_x^2\rangle_{CG} - \frac{k_B T}{K}\frac{1}{4}\frac{t}{\tau_{min}} \qquad (46)$$

At greater times ($t > \tau_{min}$) the quantity $C(h_x;t)$ decreases as

$$C(h_x;t) \cong \frac{k_B T}{K}\frac{1}{\pi}\left(\frac{\tau_{min}}{t}\right) \qquad (47)$$

The substitution of Eq. (38) into Eq. (47) shows that the long-time tails of autocorrelation functions $C(h_x;t)$ of a coarse-grained network model and a network consisting of multisegmental Gaussian chains (Eq. (19)) are completely equivalent (Fig. 10).

Thus, one can conclude that the simplified coarse-grained network model provides a good fit to the local relaxation properties of network junctions at times greater than the minimum relaxation time of this simplified model (Fig. 10). Note that in the limiting case ($n = 0$) of two-dimensional network consisting of multisegmental Gaussian chains, which corresponds to the coarse-grained network model, the set of relaxation times (Eq. (6) of Part 1 of this series[1]) and the considered dynamic characteristics of junctions (Eq. (4) and (15)) are exactly equivalent to those of the simplified network model (Eq. (26) of Part 1 of this series,[1] Eq. (41) and (44)). Moreover, the equilibrium value of the mean square of the end-to-end distance between neighboring junctions $\langle h_x^2\rangle_{CG}$ of a coarse-

grained network model (Eq. (45)) is equal to that of a network of multisegmental chains (Eq. (16)) if the relationship between elasticity constants of both network models (Eq. (39)) is taken into account. This fact has a simple physical meaning and confirms the theory presented. Thus, there is a complete agreement between the network consisting of multisegmental Gaussian chains and the simplified coarse-grained model of a network at a proper relationship between the parameters of these dynamic models. Hence, the possibility of using the simplified coarse-grained network model to describe the long-time dynamic behavior of a two-dimensional network is demonstrated.

## 4. Comparison with a three-dimensional polymer network

A comparison between local dynamic characteristics of two- and three-dimensional polymer networks is of special interest because the effects related to the connectivity of polymer chains into an unified network structure are expected to be manifested in relaxation of two-dimensional networks in a weaker way as compared to the three-dimensional case. The local dynamic characteristics of a three-dimensional cubic network have been considered previously by the authors in ref.[5] The intrachain wave vector $\psi$, determining the set of relaxation times, has the similar form for two- and three-dimensional networks. It contains the complicated branch $\psi_1$ corresponding to both the intra- and interchain relaxation processes and the purely intrachain branch $\psi_2$ corresponding to the relaxation of a polymer chain with fixed ends. The latter branch $\psi_2$ is doubly degenerated in the case of three-dimensional polymer networks.[5] As a result, the normal modes of a cubic network have the more complicated structure, namely, they contain three different sets of normal modes[5]. The phase shift $\vec{\theta}$ between displacements of neighboring cells of the network with a two-dimensional connectivity is determined by two independent components $\theta_1$ and $\theta_2$ in contrast to the three-dimensional network system in which there is the three-component interchain wave vector.[5]

The mean-square displacements of junctions of two- and three-dimensional polymer networks have the same behavior at sufficiently short times up to a relaxation time $\tau_{chain}$ of a chain between neighboring junctions because in this time range $\Delta X^2(t)$ is mostly governed by small-scale intrachain motions. The considerable difference between networks with different dimensionality of chain connectivity appears in the region where the interchain collective relaxation processes provide the main contribution to the mean-square displacements of network junctions, i.e. at times $t > \tau_{chain}$. It has been shown[5] that the mean-square displacement $\Delta X_0^2(t)$ of a junction of a cubic network at long times $t > \tau_{chain}$ behaves as const $- \sqrt{\tau_{chain}/t}$

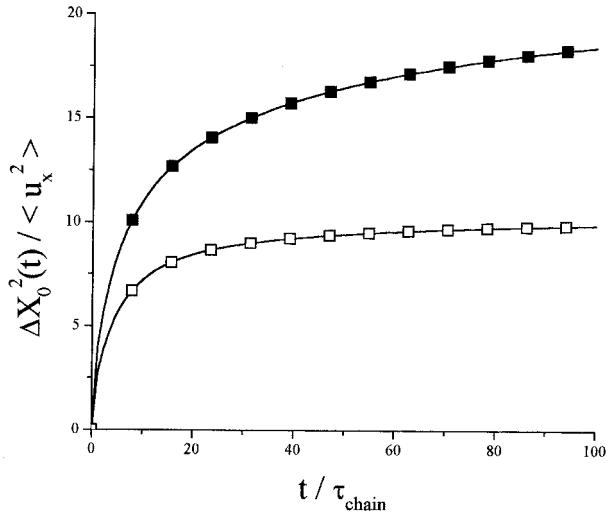


Fig. 11. Reduced mean-square displacement of a junction $\Delta X_0^2(t)/\langle u_x^2\rangle$ of two-dimensional (line with solid squares (■)) and three-dimensional (line with open squares (□)) polymer networks. In this case $n = 20$

and tends to the finite limiting value even in the case of an infinite large network (Fig. 11). In contrast to the cubic network, the mean-square displacement of a junction of a square network with respect to the center of mass at $t > \tau_{chain}$ increases as $\ln(t/\tau_{chain})$ and has no finite limit in the case of infinite large network (Fig. 11). This increase in mean-square displacement at long times is completely determined by interchain motions of a network. Therefore, the ratio of inter- and intrachain contributions also increase with time (Fig. 2). In contrast, in the case of the cubic network, the contribution of interchain motions to the limiting value $\Delta X_0^2(t)(t \to \infty)$ is about six times greater than that of intrachain motions and remains constant with time.[5] In the case of a two-dimensional network of finite size, the mean-square displacement of a junction reaches the finite limiting value that increases according to logarithmic law with the network size. It is also in contrast to the three-dimensional network in which the limiting value of $\Delta X^2(t)$ does not depend on the size of the network as a whole[5]. Similar conclusions can be also made with respect to the mean-square displacements of non-junction beads of two- and three-dimensional networks.

The autocorrelation functions $C(h_x;t)$ of the end-to-end chain vector between neighboring junctions of square and cubic networks have the same behavior at times $t < \tau_{chain}$, i.e. in the region where the time dependence of $C(h_x;t)$ is mostly determined by intrachain motions (Fig. 12). At greater times the interchain collective motions provide the main contribution to the time dependence of $C(h_x;t)$, and the autocorrelation functions of two- and three-dimensional polymer network begin to differ. It has been shown for cubic networks[5] that $C(h_x;t)$ decreases at $t > \tau_{chain}$ as $(\tau_{chain}/t)^{3/2}$. The autocorrelation function

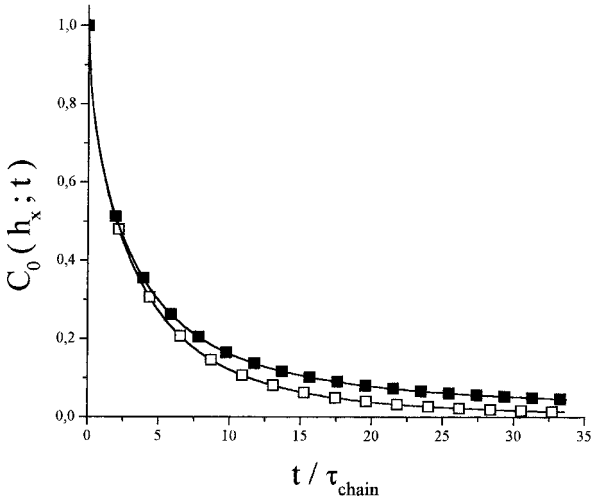


Fig. 12. Normalized autocorrelation function $C_0(h_x;t)$ of the end-to-end chain vector between neighboring junctions for square (line with solid squares (■)) and cubic (line with open squares (□)) polymer networks ($n = 20$)

$C(h_x;t)$ of a two-dimensional network behaves as ($\tau_{chain}/t$), i. e. decreases more slowly at long times as compared to a cubic network (Fig. 12). This corresponds to the different behavior of the relaxation spectrum $H(\tau)$ of two- and three-dimensional networks in the region of interchain collective relaxation ($\tau > \tau_{chain}$): $H(\tau) \sim \tau^{-1}$ for square polymer networks and $H(\tau) \sim \tau^{-3/2}$ for cubic ones. A similar difference is manifested in the consideration of autocorrelation functions $C(u_x;t)$ of subchain vectors. However, this difference between square and cubic networks is practically indistinguishable because it appears in the time behavior of $C(u_x;t)$ when this autocorrelation function decreases considerably and becomes about ($n + 1$) times smaller than the equilibrium value of the mean square of a subchain vector $\langle u_x^2 \rangle$.

## 5. Conclusion

To sum up, one can say that the local relaxation properties of the regular polymer network having a two-dimensional connectivity is very close to that of uncross-linked polymer systems at times smaller than the relaxation time $\tau_{chain}$ of a network chain between cross-links, i. e. in the region of preferably intrachain relaxation. Such a situation takes part also for three-dimensional networks.[5, 13, 14] At greater times ($t > \tau_{chain}$) corresponding to large-scale collective relaxation, the dynamic behavior of a two-dimensional polymer network differs considerably from that of a three-dimensional one. For example, the mean-square displacements of network elements in the case of infinitely large square networks do not tend to finite limiting value in contrast to cubic polymer networks, and the end-to-end chain vectors between neighboring junctions of a two-dimensional network relaxes more slowly as compared with the network having three-dimensional connectivity.[5] The long-time collective relaxation of a two-dimensional network may be described in a good approximation by a simplified network model at the appropriate relationship between elasticity and friction constants of simplified and a more realistic network models.

To conclude, the next step concerning investigation of dynamics of two-dimensional polymer networks is to compare the theoretical predictions obtained with results of recent computer simulation of regular two-dimensional polymer networks.[15, 16]

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