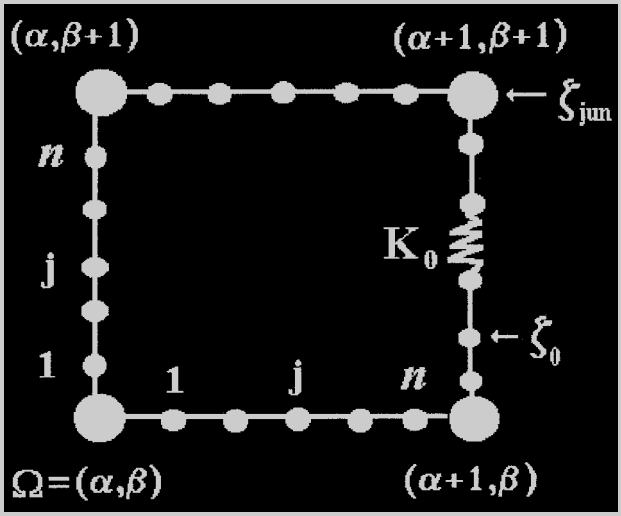
Full Paper: The local relaxation properties of polymer networks with a two-dimensional connectivity are considered. We use the mesh-like network model in which the average positions of junctions form the regular spatial structure consisting of square repeating units (network cells). The two-dimensional polymer network consisting of "bead and spring" Rouse chains and the simplified coarse-grained network model describing only the large-scale collective relaxation of a network are studied. For both dynamic network models the set of relaxation times and the transformation from Cartesian coordinates of network elements to normal modes are obtained. Using the normal mode transformation obtained, in Part 2 of this series the exact analytical expressions for various local dynamic characteristics of the polymer network having a two-dimensional connectivity will be calculated.



An elementary cell of a two-dimensional square network consisting of multisegmental "bead and spring" chains

Theory of relaxation properties of two-dimensional polymer networks, 1

Normal modes and relaxation times

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

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

(Received: December 7, 1999)

1. Introduction

Cross-linked polymers represent a broad and very important class of materials. Much interest in cross-linked polymers (polymer networks) is raised because they are widely used for numerous technical applications. Whereas the statistical properties of cross-linked polymer systems have been studied thoroughly, the processes determining their dynamic properties are not yet completely understood in polymer physics in comparison to those of polymer solutions or melts. This is mainly due to a complex character of physical phenomena manifested in polymer networks and to a great number of factors which influence dynamic properties of cross-linked polymer systems.

Polymer networks represent polymers in which the macromolecules are connected to each other by means of chemical cross-links and form an unified spatial structure. The fundamental feature of cross-linked polymers is that their relaxation properties are determined not only by the behavior of individual polymer chains but also by the collective long-scale relaxation of network chains. These collective interchain relaxation processes having characteristic scales greater than the average length of chains between cross-links arise from a strong connectivity between all chains in a network. As a result of the connectivity between chains, it is impossible to separate the dynamic behavior of a given chain from those of other chains in contrast to polymer melts and solutions.

  1022-1344/2000/0708–0407$17.50+.50/0

Real cross-linked polymers represent the three-dimensional network structures as a rule. However, it is very interesting to consider some special case of a polymer network with restricted geometry, namely, the polymer network with a two-dimensional connectivity. Such a polymer network may be realized, for example, in polymer films, on the surfaces of polymer samples, etc. Furthermore, the consideration of two-dimensional polymer networks is of special interest from the point of view of the general theory of polymer networks because the influence of chain connectivity on dynamic properties of two-dimensional polymer networks is expected to be weaker as compared to the three-dimensional case. In this series of papers we consider the relaxation properties of polymer networks having a two-dimensional connectivity. In general, different dynamic models of polymer networks with such a type of connectivity may be considered. For example, the dynamics of a two-dimensional network on the plane may be studied. In this paper we shall focus on the mesh-like polymer network having a two-dimensional connectivity in the three-dimensional Cartesian space. This dynamic network model may be visually imaged as a fishing net in water. Moreover, the regular polymer network is considered. This means that all network chains have identical contour lengths, and the average positions of junctions form the regular network structure consisting of square cells if the network were to be stretched on the plane.

The equilibrium properties of a square planar network have been studied previously by Ronka and Allegra[1]. They have considered the simplified coarse-grained model of a two-dimensional square network in which a long flexible chain between neighboring network junctions is modeled by a single Gaussian spring. It has been shown[1] that the mean-square radius of gyration of the network having a two-dimensional connectivity, increases logarithmically with the total number of chains in the network. This is in contrast to the three-dimensional Gaussian networks in which the analogous equilibrium quantity does not depend on the total number of network chains.[1]

The dynamic behavior of two-dimensional square networks consisting of "bead and spring" Rouse chains has been considered by Chompff and Duiser.[2] The mechanical spectrum of relaxation times τ of a two-dimensional polymer network has been obtained. It has been shown[2] that the relaxation spectrum of a square regular network has usual Rousean behavior $1/\sqrt{\tau}$ in the region of intrachain relaxation (i.e. at times smaller than the maximum relaxation time of a chain between cross-links) and behaves as $1/\tau$ in the region of interchain collective relaxation. Note that the behavior of the interchain part of the relaxation spectrum of a two-dimensional polymer network differs from that of three-dimensional networks in which the interchain long-time tail of relaxation spectrum behaves as $1/\tau^{3/2}$ (see, for example, refs.[3–7]).

The main aim of this series of papers is to study in detail the local dynamic characteristics of junctions and non-junction chain segments of the polymer network with a two-dimensional connectivity. These important local characteristics were not considered so far and may be manifested in dielectric relaxation, dynamic modulus of cross-linked polymers, incoherent dynamic scattering, NMR, etc. Furthermore, the theoretical results of this work may be directly compared with data of recent computer simulation of regular two-dimensional networks.[8,9] The paper is organized as follows. The two-dimensional regular network consisting of multisegmental Gaussian chains and the simplified coarse-grained network model describing only the large-scale collective relaxation of a network are considered. For both dynamic network models the set of relaxation times will be obtained. Furthermore, we shall construct the transformation from Cartesian coordinates of network elements to normal coordinates (normal modes) for both network models. The exact analytical expressions for various local dynamic characteristics of regular polymer networks having a two-dimensional connectivity will be obtained in a following paper of this series using the normal mode transformation constructed.

2. Two-dimensional polymer network consisting of multisegmental Gaussian chains

2.1. Dynamic model of a network

The two-dimensional polymer network consisting of multisegmental Gaussian chains is considered. Such a type of network system represents the two-dimensional analog of a cubic Gaussian network considered previously.[7] It should be especially emphasized that the network considered represents a two-dimensional structure only in the sense of connectivity of network chains, i.e. we consider the dynamics of a two-dimensional Gaussian network in the three-dimensional Cartesian space ("fishing net in water"). We study the dynamics of mesh-like network model, and the average positions of network junctions form the regular spatial structure consisting of square cells. An elementary cell (or, a repeating unit) of the square regular network consists of a junction and two "bead and spring" Rouse chains[10] (Fig. 1). A phantom Gaussian network is considered, the excluded volume interactions and entanglement effects are neglected.

Each Rouse chain between cross-links contains n beads and, correspondingly, $(n + 1)$ subchains connecting them. All subchains have identical contour lengths and act as springs with the elasticity constant K_0. The dynamic behavior of the Gaussian network, moving relative to effective viscous medium under stochastic Brownian forces, is studied. The friction constants of a network

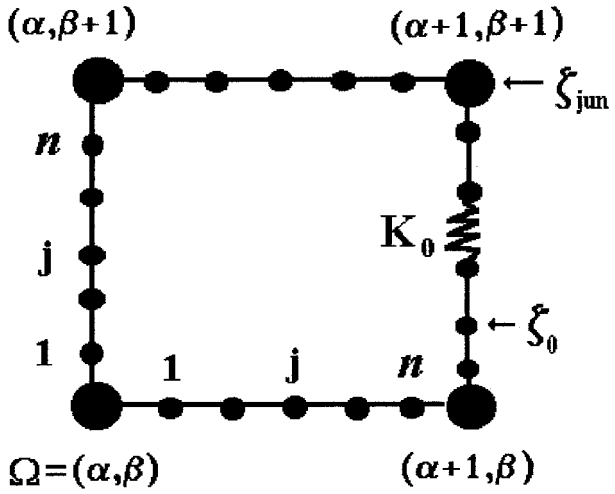


Fig. 1. An elementary cell of a two-dimensional square network consisting of multisegmental "bead and spring" chains

junction and a non-junction bead of the network chain are denoted as ς_{jun} and ς_0, respectively. Only the X projections of position vectors of the network elements are considered because X, Y, and Z projections for a Gaussian network are independent of each other. Each cell of the two-dimensional square network is marked by a two-component index $\Omega = (\alpha,\beta)$ (Fig. 1). A network consists of N junctions (cross-links) along each network direction, i.e. the indices α and β change from 1 to N. Therefore, the total number of square network cells is equal to N^2. The X coordinates of a network junction and a non-junction bead are denoted as $X_0(\Omega;t)$ and $X_p(\Omega;j;t)$, respectively. Here index p means the number of multisegmental Gaussian chains in the network cell $\Omega = (\alpha,\beta)$ (i.e. $p = 1;2$ for square network) and index $j = 1...n$ means the position of a non-junction bead along the network chain between neighboring junctions ($j = 0$ and $j = n + 1$ in the case of a network junction).

The equation of motion of a non-junction bead of the network chain has the following form:

$$\varsigma_0 \frac{d}{dt} X_p(\Omega;j;t) + K_0[2X_p(\Omega;j;t) - X_p(\Omega;j+1;t) - X_p(\Omega;j-1;t)] = F_{Br} \qquad (1)$$

where F_{Br} is the stochastic Brownian force (see, for example, ref.[11]). The equations of motions for non-junction beads of a two-dimensional network have the same form as those of a three-dimensional cubic network.[7] The difference between two- and three-dimensional polymer networks consisting of "bead and spring" Rouse chains is manifested only in the equations of motion of network junctions. The network junction of a two-dimensional square network is connected by subchains to four neighboring non-junction beads in contrast to the cubic network in which the junction is connected to six non-junction beads. The corresponding equation of motion of a junction of the network with a two-dimensional connectivity is given by:

$$\varsigma_{jun} \frac{d}{dt} X_0(\alpha,\beta;t) + K_0[4X_0(\alpha,\beta;t) - X_1(\alpha,\beta;1;t) - X_1(\alpha-1,\beta;n;t) - X_2(\alpha,\beta;1;t) - X_2(\alpha,\beta-1;n;t)] = F_{Br} \qquad (2)$$

The main aim of this series of papers is to study the local dynamic characteristics of a two-dimensional polymer network, which depend slightly on the boundary conditions of the macroscopic network as a whole. In the consideration of analogous local characteristics of a three-dimensional polymer network, the periodic boundary conditions have been used.[7] Moreover, the same boundary conditions have been also used in recent computer simulations of two-dimensional polymer networks.[8,9] Therefore, the square network system with periodic boundary conditions will be considered in this paper. These boundary conditions mean that

$$X_1(0,\beta;n;t) = X_1(N,\beta;n;t) \qquad (3a)$$

$$X_2(\alpha,0;n;t) = X_2(\alpha,N;n;t) \qquad (3b)$$

As it will be shown below, the use of the periodic boundary conditions allows us to obtain the exact analytical solution for a given mechanical system at the arbitrary numbers of network junctions N and non-junction beads n in a network chains between cross-links.

2.2. Normal modes and relaxation times

In order to obtain the analytical expressions for various dynamic characteristics of a two-dimensional Gaussian network, it is necessary to solve the equations of motion of network elements (Eq. (1) and (2)). We shall use the normal mode treatment (see, for example, ref.[6,7,11]). The general form of transformation from Cartesian coordinates X of network elements to normal coordinates Q (normal modes) has the following form:

$$X_p(\alpha,\beta;j;t) = \sum_{\theta_1\theta_2}\sum_{\psi} \exp(i\alpha\theta_1)\exp(\beta\theta_2) \times (A_p \sin j\psi + B_p \cos j\psi) Q(\theta_1,\theta_2;\psi;t) \qquad (4a)$$

$$X_0(\alpha,\beta;t) = \sum_{\theta_1\theta_2}\sum_{\psi} \exp(i\alpha\theta_1)\exp(i\beta\theta_2) \cdot B_0 \cdot Q(\theta_1,\theta_2;\psi;t) \qquad (4b)$$

Here $\vec{\theta} = (\theta_1,\theta_2)$ is the interchain wave vector determining the phase shift between displacements of neighboring network cells for a given normal mode. The interchain wave vector of square polymer network is the two-

component quantity in contrast to the cubic Gaussian network where wave vector $\vec{\theta}$ has three components[4, 7]. The intrachain wave vector ψ determines the phase shift between neighboring non-junction beads along the network chain. Note that the coefficients A_1, A_2, B_0, B_1, and B_2 may depend on wave vectors ψ and $\vec{\theta}$.

Substituting the normal mode transformation (Eq. (4a)) into the equations of motion of non-junction beads (Eq. (1)) one can obtain the equations of motion of normal modes Q

$$\varsigma_0 \frac{d}{dt} Q(t) + K_0\, 2(1 - \cos\psi) Q(t) = F_{Br}(Q) \tag{5}$$

where F_{Br} is the stochastic Brownian force[11]. The time dependence of each normal mode has the simple form $Q(t) = Q(0)\exp[-t/\tau]$ where τ is the relaxation time of a given normal mode. The equations of motion of normal modes without stochastic Brownian forces F_{Br} give the set of relaxation times of a two-dimensional Gaussian network

$$\tau(\psi) = \frac{\varsigma_0}{K_0\, 2(1 - \cos\psi)} \tag{6}$$

Note that the expression for relaxation times of a two-dimensional network in the formal sense has a similar form to that for a single chain.[10, 11] However, in the case of a network the intrachain wave vector ψ has a rather complicated structure and depends on the interchain wave vector $\vec{\theta}$. Using the periodic boundary conditions (Eq. (3)) and the normal mode transformation (Eq. (4a)) one can obtain the components of interchain wave vector $\vec{\theta} = (\theta_1, \theta_2)$

$$\theta_{1;2} = \frac{2\pi}{N} S_{1;2}; \qquad S_{1;2} = 0, ..., N - 1; \tag{7}$$

where N is the number of network junctions along the given network direction.

In order to obtain the intrachain wave vector ψ and, therefore, the relaxation times of a two-dimensional Gaussian network, it is necessary to combine the equation of motion of a network junction (Eq. (2)) and the additional boundary conditions in the network junctions, namely,

$$X_0(\alpha, \beta; t) = X_1(\alpha - 1, \beta; n + 1; t) \tag{8a}$$

$$X_0(\alpha, \beta; t) = X_2(\alpha, \beta - 1; n + 1; t) \tag{8b}$$

$$X_0(\alpha, \beta; t) = X_1(\alpha, \beta; 0; t) \tag{8c}$$

$$X_0(\alpha, \beta; t) = X_2(\alpha, \beta; 0; t) \tag{8d}$$

The exact analytical solution for a given two-dimensional mechanical system becomes possible if the friction constant of a network junction is two times greater than that of a non-junction bead

$$\varsigma_{jun} = 2\varsigma_0 \tag{9}$$

This condition corresponds to the superposition of non-junction beads (with friction constant ς_0) of two intersecting multisegmental chains in the network junction. It this case the equation of motion of a network junction (Eq. (2)) may be presented in the formal sense as the sum of two equations of motion of non-junction beads (Eq. (1)). In other cases, i. e. if Eq. (9) is not fulfilled, the solution may be obtained using numerical calculations. Note that the rigorous analytical solution for a three-dimensional network exists if $\varsigma_{jun} = 3\varsigma_0$ (see ref.[4, 7]). The combination of Eq. (2), (8), and (9) gives two different sets of wave vectors ψ (compare with Eq. (9) and (10) in ref.[7] for a three-dimensional polymer network)

$$\cos(n + 1)\psi_1 = \frac{1}{2}(\cos\theta_1 + \cos\theta_2) \tag{10}$$

$$\sin(n + 1)\psi_2 = 0 \tag{11}$$

Therefore, the intrachain wave vector ψ of a two-dimensional polymer network has the following structure

$$\psi_1 = \frac{2\pi}{n+1} l \pm \frac{1}{n+1} \arccos\frac{1}{2}(\cos\theta_1 + \cos\theta_2); \quad l = 0...n/2 \tag{12}$$

$$\psi_2 = \frac{\pi}{n+1} k; \qquad k = 1...n \tag{13}$$

In Eq. (12) sign + should be chosen at $l = 0$ and signs ± at $l \neq 0$. Note that Eq. (12) is written for the case when the quantity n is an even number. It does not restrict the theory because one can consider the case of odd n as well.

It is seen that the total number of wave vectors ψ at a given value of interchain wave vector $\vec{\theta} = (\theta_1, \theta_2)$ is equal to the total number of degrees of freedom in a square network cell $\Omega = (\alpha, \beta)$, namely, is equal to $(2n + 1)$. Eq. (12) and (13) indicate the existence of two different branches of relaxation spectrum: $\tau(\psi_1)$ and $\tau(\psi_2)$. The branch $\tau(\psi_2)$ determined by wave vector ψ_2 (see Eq. (13)) does not depend on the phase shift $\vec{\theta}$ between displacements of neighboring network cells and is very similar to the set of relaxation times of a single Rouse chain.[10, 11] The main and more complicated branch of relaxation spectrum $\tau(\psi_1)$ depends on the phase shift along the network chain $2l\pi/(n + 1)$ and on the phase shift between network cells $\vec{\theta}$ as well (see Eq. (12)). If l in Eq. (12) is equal to zero, the wave vector

$$\psi_{net}(\theta_1, \theta_2) \cong \psi_1(l = 0) = \frac{1}{n+1} \arccos\frac{1}{2}(\cos\theta_1 + \cos\theta_2) \tag{14}$$

and corresponding relaxation times $\tau(\psi_{net})$ do not depend on the motions of network chains inside of the cells of a

network and describe only the long-scale collective relaxation corresponding to the displacements of network cells. If $l \neq 0$ (see Eq. (12)) each relaxation time of a network chain $\tau(\psi_1)$ splits into the band consisting of a great number of sublines due to the change of interchain wave vector $\vec{\theta} = (\theta_1, \theta_2)$. Note that the broadening $\Delta\psi_1(l) = \psi_{\text{net}}$ of intrachain modes (and corresponding relaxation time) is smaller than the difference $(\psi_1(l+1) - \psi_1(l))$ between neighboring $\psi_1(l)$ values at $l \neq 0$. This means that the bands corresponding to the broadened relaxation times of a network chain are not superposed.

A certain characteristic relaxation time τ_{chain} exists in a network system, which separates the purely interchain motions with relaxation times $\tau(\psi_{\text{net}})$ and the small-scale intrachain motions with relaxation times $\tau(\psi_1)$ at $l \neq 0$ and $\tau(\psi_2)$, which are determined by the phase shift between neighboring beads along the network chain. This relaxation time τ_{chain} represents the maximum relaxation time of a network chain as a whole. On the other hand, the quantity τ_{chain} is equal to the minimum relaxation time of long-scale interchain motions corresponding to the displacements of network cells. To sum up, one can write

$$\tau_{\text{chain}} = \tau(\psi_1)|_{\substack{l=1 \\ \vec{\theta}=(\pi,\pi)}} = \tau(\psi_2)|_{k=1} = \tau(\psi_{\text{net}})|_{\vec{\theta}=(\pi,\pi)} \quad (15)$$

Using Eq. (6), (12), and (13) one can obtain the characteristic relaxation time

$$\tau_{\text{chain}} \cong \frac{4}{\pi^2}(n+1)^2\tau_0 \quad (16)$$

where n is the number of beads in a chain between cross-links and $\tau_0 = \varsigma_0/4K_0$ is the relaxation time of a Gaussian subchain or the minimum relaxation time of a two-dimensional network (see Eq. (6) at $\psi = \pi$).

In paper 2 of this series we shall use the transformation from Cartesian coordinates to normal modes to calculate local dynamic characteristics of a two-dimensional polymer network. For example, the autocorrelation functions $\langle X(0)X(t)\rangle$ of the X projections of junctions and non-junction beads, which are manifested in mean-square displacements, may be presented using normal mode transformation as the sum of autocorrelation functions of normal modes $\langle Q(0)Q(t)\rangle$ which relax according to the simple exponential law. In order to construct the normal mode transformation, five coefficients A_1, A_2, B_0, B_1, and B_2 in Eq. (4) must be obtained using the equations of motion of network junctions (Eq. (2)) and the boundary conditions in network junctions (Eq. (8)). The determination of the normal mode transformation is a rather complex and nontrivial problem. It is mostly caused by the fact that the two-dimensional network considered contains two types of "particles": junctions and non-junction beads, which differ by their friction constants (see Eq. (9)). The detailed calculations are presented in Appendix. It should be noted that Eq. (2) and (8) give the expressions for normal mode transformation, which are accurate within the arbitrary numerical constants or the certain functions of wave vectors (see Appendix). To obtain the final expressions for the transformation from Cartesian coordinates of network elements to normal modes, it is necessary to use the additional conditions concerning the transformation of dissipation function and potential energy of a two-dimensional network. The normal mode transformation (Eq. (4)) should transform the dissipation function $R(X)$ of a square Gaussian network

$$R(X) = \frac{1}{2}\sum_{\Omega}\left[2\varsigma_0\dot{X}_0^2(\Omega;t) + \varsigma_0\sum_{j=1}^{n}(\dot{X}_1^2(\Omega;j;t) + \dot{X}_2^2(\Omega;j;t))\right] \quad (17a)$$

to the diagonal form with equal weights of all normal modes, i.e.

$$R(Q) = \frac{1}{2}\varsigma_0\sum_{\vec{\theta}}\sum_{\psi}\dot{Q}^2(\vec{\theta};\psi;t) \quad (17b)$$

Moreover, in this transformation the potential energy of a network system

$$U(X) = \frac{1}{2}K_0\sum_{\Omega}\sum_{j=1}^{n+1}\sum_{p=1}^{2}[X_p(\Omega;j;t) - X_p(\Omega;j-1;t)]^2 \quad (18a)$$

also should become a diagonal form

$$U(Q) = \frac{1}{2}K_0\sum_{\vec{\theta}}\sum_{\psi}2(1-\cos\psi_p)Q^2(\vec{\theta};\psi;t) \quad (18b)$$

Finally, for the transformation of Cartesian coordinates of non-junction beads of the network chains between cross-links we obtain

$$\begin{aligned}X_1(a,\beta;j;t) = {} & \frac{1}{\sqrt{n+1}}\frac{1}{N}\left[\frac{1}{\sqrt{2}}\sum_{\vec{\theta}\neq(0,0)}\sum_{\psi_1}\exp[i(a\theta_1+\beta\theta_2)]\right. \\ & \times\frac{\exp(i\theta_1)\sin j\psi_1 + \sin(n+1-j)\psi_1}{\sin(n+1)\psi_1}Q_1(\theta_1,\theta_2;\psi_1;t) \\ & + \frac{1}{\sqrt{2}}\sum_{\psi_1}(\cos j\psi_1 + \sin j\psi_1)Q_1(0,0;\psi_1;t) \\ & - \sum_{\vec{\theta},\psi_2'}\exp[i(a\theta_1+\beta\theta_2)]\frac{\sqrt{2}f(\vec{\theta};\psi_2')\sin j\psi_2'}{1-\cos(n+1)\psi_2'\exp(-i\theta_1)} \\ & \exp(-i\theta_1)Q_2(\theta_1,\theta_2;\psi_2';t) - \sum_{\substack{\theta_1\neq0\\ \theta_2\neq0}}\sum_{\psi_2''}\exp[i(a\theta_1+\beta\theta_2)] \\ & \exp(-i\theta_1)\frac{\sqrt{2}f(\vec{\theta};\psi_2'')\sin j\psi_2''}{1-\cos(n+1)\psi_2''\exp(-i\theta_2)}Q_2(\theta_1,\theta_2;\psi_2'';t) \\ & + \sqrt{2}\sum_{\theta_2\neq0}\sum_{\psi_2''}\exp(i\beta\theta_2)\sin j\psi_2''Q_2(0,\theta_2;\psi_2'';t) \\ & \left. - \sum_{\psi_2''}\sin j\psi_2''Q_2(0,0;\psi_2'';t)\right] \end{aligned} \quad (19a)$$

$$X_2(a,\beta;j;t) = \frac{1}{\sqrt{n+1}}\frac{1}{N}\left[\frac{1}{\sqrt{2}}\sum_{\vec{\theta}\neq(0,0)}\sum_{\psi_1}\exp[i(a\theta_1+\beta\theta_2)]\right.$$
$$\times\frac{\exp(i\theta_2)\sin j\psi_1+\sin(n+1-j)\psi_1}{\sin(n+1)\psi_1}Q_1(\theta_1,\theta_2;\psi_1;t)$$
$$+\frac{1}{\sqrt{2}}\sum_{\psi_1}(\cos j\psi_1+\sin j\psi_1)Q_1(0,0;\psi_1;t)$$
$$+\sum_{\vec{\theta},\psi_2'}\exp[i(a\theta_1+\beta\theta_2)]\frac{\sqrt{2}f(\vec{\theta};\psi_2')\sin j\psi_2'}{1-\cos(n+1)\psi_2'\exp(-i\theta_2)}$$
$$\exp(-i\theta_1)Q_2(\theta_1,\theta_2;\psi_2';t)+\sum_{\substack{\theta_1\neq0\\ \theta_2\neq0}}\sum_{\psi_2''}\exp[i(a\theta_1+\beta\theta_2)]$$
$$\exp(-i\theta_1)\frac{\sqrt{2}f(\vec{\theta};\psi_2'')\sin j\psi_2''}{1-\cos(n+1)\psi_2''\exp(-i\theta_2)}Q_2(\theta_1,\theta_2;\psi_2'';t)$$
$$+\sqrt{2}\sum_{\theta_1\neq0}\sum_{\psi_2''}\exp(ia\theta_1)\sin j\psi_2''Q_2(\theta_1,0;\psi_2'';t)$$
$$\left.+\sum_{\psi_2''}\sin j\psi_2''Q_2(0,0;\psi_2'';t)\right] \qquad (19b)$$

Here n is the number of beads in the network chain between cross-links, $\psi(\theta_1)$ is the wave vector corresponding to both the intra- and interchain relaxation processes (Eq. (10) and (12)). The wave vector ψ_2 (Eq. (11) and (13)), which is the purely intrachain quantity and does not depend on the phase shift $\vec{\theta}$ between network cells, is presented as two wave vectors:

$$\cos(n+1)\psi_2' = -1 \quad \text{or} \quad \psi_2' = \frac{\pi(2k-1)}{n+1} \qquad (20a)$$

and

$$\cos(n+1)\psi_2'' = 1 \quad \text{or} \quad \psi_2'' = \frac{2\pi k}{n+1} \qquad (20b)$$

where $k = 1...n/2$. The function $f(\vec{\theta};\psi_2)$ in Eq. (19) is determined as

$$f(\vec{\theta};\psi_2) = \sqrt{\frac{2[1-\cos(n+1)\psi_2\cos\theta_1][1-\cos(n+1)\psi_2\cos\theta_2]}{2-(\cos\theta_1+\cos\theta_2)\cos(n+1)\psi_2}} \qquad (21)$$

One can see from Eq. (19) that the normal coordinates of a two-dimensional polymer network consisting of multisegmental Gaussian chains are separated into two sets (Q_1 and Q_2) corresponding to different branches of the relaxation spectrum. Normal modes $Q_1(\vec{\theta};\psi_1;t)$ correspond to the spectrum branch containing both the intra- and interchain relaxation processes. Normal modes $Q_2(\vec{\theta};\psi_2;t)$ are determined by the purely intrachain branch of the relaxation spectrum, which corresponds to the relaxation of network chains with fixed ends. Note that the normal mode transformation for non-junction beads (Eq. (19)) has a rather complicated form because of the multiple degeneration of relaxation times $\tau(\psi_2)$ of the purely intrachain branch of relaxation spectrum. The degeneration of each relaxation time $\tau(\psi_2)$ is equal to the total number of network cells of a two-dimensional Gaussian network, i. e. is equal to N^2. In contrast to non-junction beads, the normal mode transformation for network junctions does not include the normal modes $Q_2(\vec{\theta};\psi_2;t)$ determined by relaxation times similar to those of polymer chains with fixed ends and, therefore, has the more simple form (see Eq. (19) at $j = 0$)

$$X_0(a,\beta;t) = \frac{1}{\sqrt{2(n+1)}}\frac{1}{N}\sum_{\vec{\theta}}\sum_{\psi_1}\exp[i(a\theta_1+\beta\theta_2)]$$
$$Q_1(\theta_1,\theta_2;\psi_1;t) \qquad (22)$$

It should be noted that the transformation from Cartesian coordinates to normal modes (Eq. (19) and (22)) is orthogonal but is not normalized because it represents both the rotation of Cartesian axes (when the potential energy is transformed (Eq. (18)) and the scale stretching (when the dissipation function is transformed (Eq. (17)) simultaneously. This scale stretching is caused by the difference between friction constants of junctions ς_{jun} and non-junction beads ς_0 (see Eq. (9) and (17)). In paper 2 of this series we shall use the normal mode transformation constructed to obtain the exact analytical expressions for various local dynamic characteristics of a two-dimensional regular network consisting of multisegmental Gaussian chains.

3. Simplified coarse-grained model of a two-dimensional polymer network

As emphasized in the previous Section, the dynamic behavior of the two-dimensional polymer network may be separated into intra- and interchain relaxation. A certain "boundary" relaxation time τ_{chain} of these two types of relaxation processes is the relaxation time of the network chain as a whole (see Eq. (16)). The interchain collective relaxation of a network may be described by means of a simplified coarse-grained network model in which the intrachain relaxation processes are not taken into consideration.[1, 5–7, 12] The coarse-grained model of a two-dimensional square network consists of junctions (beads) and springs connecting junctions into an unified regular network structure (Fig. 2). The elasticity constant K of a single spring between neighboring junctions corresponds to that of a multisegmental Gaussian chain between these junctions. All dissipation effects related to the friction of network chains with respect to effective viscous medium are described by the friction of network junctions. The friction constant ς of a network junction is determined by the friction of chain halves directly attached to a given junction. Thus, this simplified coarse-

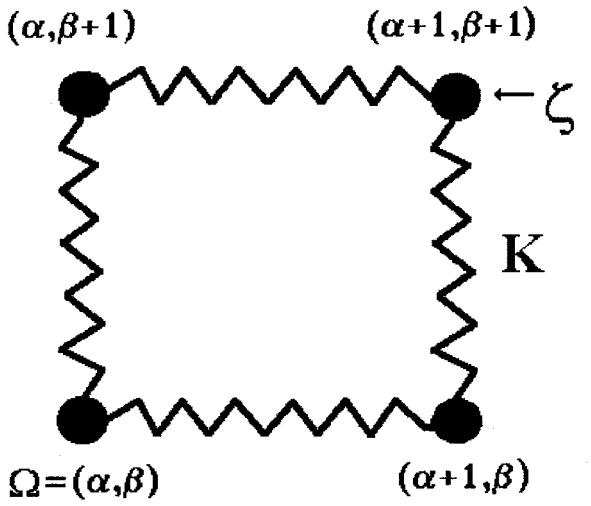


Fig. 2. An elementary cell of a simplified coarse-grained square network

grained model of a two-dimensional polymer network describes only the collective motions of network chains on scales greater than the average distance between neighboring cross-links. Note that the equilibrium properties of the coarse-grained model of a square polymer network have been considered in ref.[1]

Every cell of a coarse-grained network model is marked by a two-component index $\Omega = (\alpha,\beta)$ (Fig. 2). It is assumed that the two-dimensional network consists of N junctions along each network direction, the total number of square cells in the network is equal to N^2. The equation of motion of a junction of the coarse-grained network model is given by:

$$\varsigma\frac{d}{dt}X(\alpha,\beta;t) + K[4X(\alpha,\beta;t) - X(\alpha+1,\beta;t) - X(\alpha-1,\beta;t) - X(\alpha,\beta+1;t) - X(\alpha,\beta-1;t)] = F_{Br} \quad (23)$$

where $X(\alpha,\beta;t)$ is the X projection of the position vector of a network junction $\Omega = (\alpha,\beta)$, and F_{Br} is the stochastic Brownian force.[11] As in the previous Section, the normal mode treatment will be used to obtain the solutions of equations of motion of network junctions (Eq. (23)). We shall construct the transformation from Cartesian coordinates of network junctions to normal modes Q in the following form:

$$X(\alpha,\beta;t) = \sum_{\vec{\theta}}(A_1\sin\alpha\theta_1 + B_1\cos\alpha\theta_1) \times (A_2\sin\beta\theta_2 + B_2\cos\beta\theta_2)Q(\theta_1,\theta_2;t) \quad (24)$$

where A_1, A_2, B_1, and B_2 are numerical constants, $\vec{\theta} = (\theta_1,\theta_2)$ is a two-component interchain wave vector determining the phase shift between displacements of neighboring network cells. The substitution of Eq. (24) into Eq. (23) allows us to obtain the equations of motion of normal modes

$$\varsigma\frac{d}{dt}Q(t) + 2K(2-\cos\theta_1-\cos\theta_2)Q(t) = F_{Br} \quad (25)$$

and, therefore, the set of relaxation times of a two-dimensional coarse-grained network model

$$\tau(\theta_1,\theta_2) = \frac{\varsigma}{2K(2-\cos\theta_1-\cos\theta_2)} \quad (26)$$

As in the case of a network consisting of multisegmental Gaussian chains, one can also use the periodic boundary conditions for the coarse-grained network model considered. Then, the equations of motion of boundary junctions along the α direction of a square network take the form

$$\varsigma\frac{d}{dt}X(1,\beta;t) + K[4X(1,\beta;t) - X(2,\beta;t) - X(N,\beta;t) - X(1,\beta+1;t) - X(1,\beta-1;t)] = F_{Br} \quad (27a)$$

$$\varsigma\frac{d}{dt}X(N,\beta;t) + K[4X(N,\beta;t) - X(N-1,\beta;t) - X(1,\beta;t) - X(1,\beta+1;t) - X(1,\beta-1;t)] = F_{Br} \quad (27b)$$

The equations of motions of boundary junctions along the β network direction have a similar form. The combined consideration of these periodic boundary conditions and the normal mode transformation (Eq. (24)) allows us to obtain a set of interchain wave vectors $\vec{\theta} = (\theta_1;\theta_2)$, which is found to be the same as for the network of multisegmental Gaussian chains (see Eq. (7)). The corresponding relaxation times of a coarse-grained network model are determined by Eq. (26) and range from a minimum relaxation time $\tau_{min} = \varsigma/8K$ (see Eq. (26) at $\vec{\theta} = (\pi,\pi)$) to infinity for the infinitely large network. Note that the characteristic relaxation time τ_{min} of a coarse-grained network model has an order of magnitude equal to the relaxation time of a chain between cross-links.

In the same way as in the previous Section, with the use of Eq. (24), (27) and the condition of diagonalization of potential energy one can obtain the final expression for the transformation from Cartesian coordinates of network junctions to normal modes

$$X(\alpha,\beta;t) = \frac{2}{N}\sum_{\vec{\theta}}\cos(\alpha\theta_1-\pi/4)\cos(\beta\theta_2-\pi/4)Q(\theta;t) \quad (28)$$

where the interchain wave vector $\vec{\theta} = (\theta_1,\theta_2)$ is given by Eq. (7). The normal mode transformation obtained is orthogonal because it represents the rotation of Cartesian axes only. It should be noted that this transformation is not unique. For example, one can obtain the normal mode transformation in a form similar to that for the junctions of a network consisting of multisegmental Gaussian chains (see Eq. (22)), namely,

$$X(a,\beta;t) = \frac{1}{N}\sum_{\vec{\theta}} \exp[i(a\theta_1 + \beta\theta_2)]Q(\theta;t) \qquad (29)$$

In Part 2 of this series we shall use the normal mode transformation obtained to calculate local dynamic characteristics of the coarse-grained model of a two-dimensional regular network.

4. Conclusion

To sum up, we obtained a set of relaxation times and a normal mode transformation for a two-dimensional regular network consisting of multisegmental Gaussian chains and for a simplified coarse-grained network model as well. In a following paper the local dynamic characteristics of both dynamic network models will be calculated using these normal mode transformations. A comparison between the network of multisegmental chains and the coarse-grained model of a network will be carried out. The relaxation properties of the polymer networks with two- and three-dimensional connectivity will be also compared.

Acknowledgement: It is a pleasure to acknowledge the financial support of *Russian Foundation of Basic Research* (grant 99-03-33313), *Russian Federal Program "Integration"* (grant 326.38), INTAS (grant 99-01114), and *Volkswagenstiftung* (grant 1/72 638).

Appendix

Now we shall outline the method of calculating coefficients A_1, A_2, B_0, B_1, and B_2 which determine the transformation from Cartesian coordinates of elements of a two-dimensional square network to normal modes (Eq. (4)). To obtain the normal mode transformation we have to combine the equation of motion of a junction (Eq. (2)) and the boundary conditions in the junction (Eq. (8)). Substituting Eq. (4) into Eq. (8c) and (8d) we obtain the relation:

$$B_0 = B_1 = B_2 = B \qquad (30)$$

The substitution of normal mode transformation (Eq. (4)) into the equation of motion of a junction (Eq. (2)) and into the first two boundary conditions in the junction (Eq. (8a) and (8b)) gives the following system of algebraic equations:

$$\begin{aligned} 2B\cos\psi &- A_1[\sin\psi + \exp(-i\theta_1)\sin n\psi] \\ &- A_2[\sin\psi + \exp(-i\theta_2)\sin n\psi] \\ &- B\cos n\psi[\exp(-i\theta_1) + \exp(-i\theta_2)] = 0 \end{aligned} \qquad (31a)$$

$$B[\exp(i\theta_1) - \cos(n+1)\psi] = A_1\sin(n+1)\psi \qquad (31b)$$

$$B[\exp(i\theta_2) - \cos(n+1)\psi] = A_2\sin(n+1)\psi \qquad (31c)$$

The existence in the network system considered as two independent sets of wave vectors ψ_1 and ψ_2 (Eq. (12) and (13)) leads to the appearance of two sets of normal coordinates $Q_1(\psi_1;\vec{\theta};t)$ and $Q_2(\psi_2;\vec{\theta};t)$. If $\sin(n+1)\psi \neq 0$, Eq. (31b) and (31c) give the following relations:

$$A_1 = B\frac{\exp(i\theta_1) - \cos(n+1)\psi}{\sin(n+1)\psi} \qquad (32a)$$

$$A_2 = B\frac{\exp(i\theta_2) - \cos(n+1)\psi}{\sin(n+1)\psi} \qquad (32b)$$

The above relations should correspond to the normal modes $Q_1(\psi_1;\vec{\theta};t)$ determined by the wave vector ψ_1 because $\sin(n+1)\psi_2 = 0$ (see Eq. (11)). The substitution of Eq. (32) into Eq. (4a) gives the following terms in the normal mode transformation for $X_p(a,\beta;j;t)$:

$$\begin{aligned} B\sum_{\theta_1\theta_2}\sum_{\psi_1} &\exp[i(a\theta_1 + \beta\theta_2)] \\ &\times \frac{\exp(i\theta_p)\sin j\psi_1 + \sin(n+1-j)\psi_1}{\sin(n+1)\psi_1} Q_1(\theta_1,\theta_2;\psi_1;t) \end{aligned} \qquad (33)$$

Such a form for these terms is valid for all values of θ_1 and θ_2 (see Eq. (10)) with the exception of vectors $\vec{\theta} = (0,0)$ and $\vec{\theta} = (\pi,\pi)$ which lead to $\sin(n+1)\psi = 0$. For simplicity we shall assume that $\vec{\theta} \neq (\pi,\pi)$. This means that the number of junctions N along every network direction is an odd number (see Eq. (7)). Naturally, one can also consider the case when N is an even number in a quite analogous way as odd N. For wave vector ψ_1 at $\vec{\theta} = (0,0)$ Eq. (31) is satisfied identically at arbitrary coefficients A_1, A_2, and $B \neq 0$. Therefore, for the normal mode transformation of $X_p(a,\beta;j;t)$ at $\psi_1(\vec{\theta} = (0,0))$ we have the following terms:

$$\sum_{\psi_1}(B\cos j\psi_1 + A_p\sin j\psi_1)\,Q_1(0,0;\psi_1;t) \qquad (34)$$

If $\sin(n+1)\psi = 0$ and $B = 0$, Eq. (31) leads to the relation:

$$\begin{aligned} &A_1[1 - \exp(-i\theta_1)\cos(n+1)\psi] \\ &\quad + A_2[1 - \exp(-i\theta_2)\cos(n+1)\psi] = 0 \end{aligned} \qquad (35)$$

This relation corresponds to normal modes $Q_2(\psi_2;\vec{\theta};t)$ and may be rewritten in the form:

$$A_1 = \frac{-C}{[1 - \exp(-i\theta_1)\cos(n+1)\psi]} \qquad (36a)$$

$$A_2 = \frac{C}{[1 - \exp(-i\theta_2)\cos(n+1)\psi]} \qquad (36b)$$

Substituting Eq. (36) into normal mode transformation of a non-junction bead (Eq. (4a)), we obtain the following terms for $X_p(a,\beta;j;t)$

$$\sum_{\vec{\theta}} \sum_{\psi_2} \frac{C(-1)^p \exp[i(a\theta_1 + \beta\theta_2)] \sin j\psi_2}{1 - \cos(n+1)\psi_2 \exp(-i\theta_p)} \exp(-iQ_1)\, Q_1(\theta_1, \theta_2; \psi_2; t) \quad (37)$$

Such a form of these terms holds only if the denominator in Eq. (37) does not equal zero. It is obvious that Eq. (37) is valid for wave vectors $\psi_2 = \psi_2'$ (see Eq. (20a)). For $\psi_2 = \psi_2''$ (see Eq. (20b)) the terms given by Eq. (37) have the singularity at $\theta_1 = 0$ and $\theta_2 = 0$. To obtain the contribution of such terms into normal mode transformation, it is necessary to use Eq. (35) directly. Then the following terms for $X_1(a,\beta;j;t)$ are obtained:

$$\sum_{\theta_2 \neq 0} \sum_{\psi_2''} A \exp(i\beta\theta_2) \sin j\psi_2'' Q_2(0, \theta_2; \psi_2''; t) \quad (38a)$$

$$\sum_{\psi_2''} A_1 \sin j\psi_2'' Q_2(0, 0; \psi_2''; t) \quad (38b)$$

and for $X_2(a,\beta;j;t)$

$$\sum_{\theta_1 \neq 0} \sum_{\psi_2''} \tilde{A} \exp(ia\theta_1) \sin j\psi_2'' Q_2(\theta_1, 0; \psi_2''; t) \quad (39a)$$

$$\sum_{\psi_2''} A_2 \sin j\psi_2'' Q_2(0, 0; \psi_2''; t) \quad (39b)$$

It should be especially emphasized that all coefficients A_1, A_2, A, $\tilde{A}$, B, and C in Eq. (33), (34), (37), (38), and (39) may be the numerical constants as well as the functions of wave vectors $\vec{\theta}$ and ψ. Finally, to obtain these coefficients it is necessary to use the conditions of diagonalization the potential energy and dissipation function of a two-dimensional polymer network (Eq. (17) and (18)). Just after the use of these conditions concerning transformation to diagonal form the function $f(\vec{\theta};\psi_2)$ (see Eq. (21)) appears in the final expressions for normal mode transformation (Eq. (19)).

[1] G. Ronca, G. Allegra, *J. Chem. Phys.* **1975**, *63*, 4104.
[2] A. J. Chompff, J. A. Duiser, *J. Chem. Phys.* **1966**, *45*, 1505.
[3] J. S. Ham, *J. Chem. Phys.* **1957**, *26*, 625.
[4] Yu. Ya. Gotlib, K. M. Salikhov, *Akust. Z.* **1963**, *9*, 301.
[5] Yu. Ya. Gotlib, G. Golovachev, *J. Non-Cryst. Solids* **1994**, *172*, 850.
[6] Yu. Ya. Gotlib, A. A. Gurtovenko, *Macromol. Theory Simul.* **1997**, *6*, 523.
[7] A. A. Gurtovenko, Yu. Ya. Gotlib, *Macromolecules* **1998**, *31*, 5756.
[8] A. A. Darinskii, I. M. Neelov, N. K. Balabaev, F. Sundholm, *Vysokomol. Soedin., Ser. A* **1998**, *40*, 1110.
[9] I. M. Neelov, A. A. Darinskii, N. K. Balabaev, F. Sundholm, *Vysokomol. Soedin., Ser. A* **1998**, 40, 1963.
[10] P. E. Rouse, *J. Chem. Phys.* **1953**, *21*, 1272.
[11] M. Doi, S. F. Edwards, "*The Theory of Polymer Dynamics*", Clarendon, Oxford 1986.
[12] Yu. Ya. Gotlib, A. A. Gurtovenko, *Macromol. Theory Simul.* **1996**, *5*, 969.