Theory of Relaxation Spectra of Polymer Networks with Interchain Friction and Long-range Hydrodynamic Interactions

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SUMMARY: The dynamic network model taken into account the friction relative to incompressible effective viscous medium (EVM), the hydrodynamic interactions of a network with the EVM, and the interchain friction is considered. Two collective network relaxation spectra (RS) arise. The first RS corresponds to the network motion relative to immobile EVM, the EVM does not take part in this motion. The second RS includes the combined viscous motion of the network and EVM because of long-range hydrodynamic interactions. This RS is finite and narrow for infinitely large network. The symmetry of this motion is in concordance with that of incompressible EVM. The existence of interchain friction leads to the narrowing of both types of relaxation spectra.

In previous theories of relaxation properties of polymer networks it has been shown that the increments of intrachain relaxation processes and those of interchain cooperative network relaxation can be considered separately in a good approximation. Therefore, the long-range (low-frequency) network relaxation may be treated using the discrete or continuous "coarse-grained" network models [1]. This approach is used in this paper to consider in a more rigorous way the interactions between the network component of motion (network normal modes) and the effective viscous medium (EVM) in which the network is embedded. This viscous medium consists of small-scale degrees of freedom of a polymer network, which relax more rapidly than the network component. It should be emphasized that in previous theories the EVM has been considered as immobile or as that moving with given constant velocity gradient.

This paper is devoted to a more detailed consideration of the network dynamics, which takes into account the friction relative to EVM, the hydrodynamic interactions, the interchain friction and the incompressibility of EVM in bulk polymer network simultaneously. We consider the network dynamics in the non-reptational regime. It is known that in concentrated polymeric system (like melt) the non-correlated stochastic motions of the segments of

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neighbouring macromolecules lead to the screening of the hydrodynamic interactions between the segments of a given macromolecule.

However, the residual hydrodynamic interactions exist also in concentrated systems [2] (including melts or elastomers) but in this case they are controlled by the macroscopic viscosity. Therefore, if we consider the low-frequency cooperative network relaxation described by "coarse-grained" dynamic network model the hydrodynamic interaction can not be neglected. The incompressibility of the EVM will be also taken into consideration. The another effect that should be taken into account is the interchain friction between network elements which is not included in the friction "network-EVM". The dissipation function and interchain friction forces depend on the relative velocities of the neighbouring elements of a network.

At the study of long-range network motion the continuous dynamic model for the network and mobile EVM carried along with the network can be used. The equation of motion of EVM has the usual form

$$\eta\left[\frac{\partial^2 V_X(x,y,z;t)}{\partial x^2}+\frac{\partial^2 V_X(x,y,z;t)}{\partial y^2}+\frac{\partial^2 V_X(x,y,z;t)}{\partial z^2}\right]= \frac{\partial P(x,y,z)}{\partial x}-\varsigma\left[V_X(x,y,z;t)-\frac{d}{dt}R_X(x,y,z;t)\right] \qquad (1)$$

and the similar equations can be written for V_y, V_z. Here V_x, V_y, and V_z are the X, Y, and Z components of velocity of EVM in the volume dxdydz, P is the internal pressure in EVM, and η is the viscosity of EVM.

The equations of a continuous Gaussian network can be written as

$$K\left[\frac{\partial^2 R_X}{\partial x^2}+\frac{\partial^2 R_X}{\partial y^2}+\frac{\partial^2 R_X}{\partial z^2}\right]+\eta_{\text{int}}\left[\frac{\partial^2 \dot{R}_X}{\partial x^2}+\frac{\partial^2 \dot{R}_X}{\partial y^2}+\frac{\partial^2 \dot{R}_X}{\partial z^2}\right]+ \varsigma\left[\frac{d}{dt}R_X-V_X(x,y,z,t)\right]=0 \qquad (2)$$

Here R_X, R_Y, and R_Z are the deviations of network elements in the volume dxdydz; K is the equilibrium elasticity modulus of a network, ς is the constant of friction relative to EVM for a network element in the unit volume, and η_{int} is the effective interchain viscosity arising from the interchain friction. The Equation 1 is valid for incompressible liquid with the condition of incompressibility

$$\frac{\partial V_X}{\partial x} + \frac{\partial V_Y}{\partial y} + \frac{\partial V_Z}{\partial z} = 0 \qquad (3)$$

It is convenient to use the Fourier transformation and to introduce the normal modes $R_{X\vec{k}}(t) = R_{X\vec{k}}(0)\exp\left[-t\lambda\left(\vec{k}\right)\right]$ and $V_{X\vec{k}}(t) = V_{X\vec{k}}(0)\exp\left[-t\lambda\left(\vec{k}\right)\right]$ where

$$\tau\left(\vec{k}\right) = \lambda^{-1}\left(\vec{k}\right) \qquad (4)$$

are the relaxation times of a system "network and EVM". The Equations 1 and 3 lead to the well-known expression for P_k in $\vec{k}$ -space

$$ik^2 P_k = \varsigma\lambda\left(k_X R_{Xk} + k_Y R_{Yk} + k_Z R_{Zk}\right) \qquad (5)$$

After exclusion of P_k the Equations 1, 2, and 5 give the equations describing the relation between $\vec{V}(k) = \left(V_{Xk}, V_{Yk}, V_{Zk}\right)$ and $\vec{R}(k) = \left(R_{Xk}, R_{Yk}, R_{Zk}\right)$

$$\left(\varsigma + \eta k^2\right)V_{Xk} = \frac{k_X\varsigma\lambda}{k^2}\left(k_X R_{Xk} + k_Y R_{Yk} + k_Z R_{Zk}\right) - \varsigma_0\lambda R_{Xk} \qquad (6a)$$

$$V_{Xk} = \left(Kk^2 - \lambda\left(\eta_{int}k^2 + \varsigma\right)\right)R_{Xk} \qquad (6b)$$

It can be shown that two types of solution of Eq. 6 exist, which present two branches (or types) of relaxation spectra of a network embedded in EVM. The first branch corresponds to the situation when the EVM remains immobile, i.e.

$$V_{Xk} = V_{Yk} = V_{Zk} = 0 \qquad (7)$$

In this case we have

$$div\vec{R} \neq 0 \qquad \text{and} \qquad rot\vec{R} = 0 \qquad (8).$$

At this type of motion the EVM does not participate. This type of symmetry of network motion is not consistent with the motion of incompressible EVM with $div\vec{V} = 0$. This branch was previously discussed for discrete network models moving relative to immobile EVM [1), 3)]

The relaxation times $\tau\left(\vec{k}\right)$ have the form

$$\tau(k) = \frac{\varsigma + \eta_{int}k^2}{Kk^2} \qquad (9)$$

or

$$\tau = \frac{\varsigma}{Kk^2} + \frac{\eta_{int}}{K} = \tau_0(k) + \tau_{int} \qquad (10)$$

The first term $\tau_0(k)$ in Eq. 10 is the relaxation time of a network without interchain friction, which is emerged in immobile viscous medium. The second term τ_{int} does not depend on the

scale of motion for given normal mode (or $\vec{k}$) and characterizes the relaxation time of simple Voigt-Kelvin element. The interchain friction strongly affects the comparatively short-scale motions at the scales $r \cong 2\pi/k$

$$r < r^* = 2\pi\sqrt{\eta_{int}/\varsigma} \tag{11}$$

For long-scale motions ($r > r^*$) the quantity τ is given by

$$\tau \sim \tau_0 = \frac{\varsigma}{Kk^2} \tag{12}$$

and does not depend on η_{int}.

There are many physical reasons that the low-frequency network motion corresponding to the motion of comparatively great elements of a network has to reflect also the incompressibility of a network as a whole. In this case the condition $div(d\vec{R}/dt)$ should be fulfilled, and the first type of motion may be inactive (or has very slow intensity). On the other hand, there could be local short-range motions of junctions, which do not obey the condition of incompressibility. Therefore, only the more detailed molecular theory (or computer simulation) can give the information concerning the properties of this type of relaxation.

The second "non-trivial" type of motion exists when the EVM is swept along by the network. For this motion the network behaves as an incompressible system (similar to EVM) and

$$div\vec{R} = 0 \tag{13}$$

The EVM can take part in this motion and we obtain the second branch with relaxation times $\tau(k)$ which can be represented in the simple visual form

$$\tau(k) = \tau_{int} + \frac{1}{\left(1/\tau_0(k)\right) + \left(1/\tau_\eta\right)} \tag{14}$$

Here τ_{int} and $\tau_0(k)$ are the same as in Eq. 10, and τ_η is the relaxation time of a network which is uniformly stretched in parallel to viscous medium. The Eq. 14 can be described by simple mechanical model (Fig. 1).

The specific feature of the second type of relaxation spectrum (Eq. 14) with moving EVM (i.e. with long-range hydrodynamic interactions) is the finiteness of this relaxation spectrum. For the long-range normal modes ($k \to 0$, $r(k) \to \infty$, and $\tau_0(k) \to \infty$) the relaxation time τ tends to the limit

$$\tau_{max} = \tau_{int} + \tau_\eta = \frac{\eta_{int}}{K} + \frac{\eta}{K} \tag{15}$$

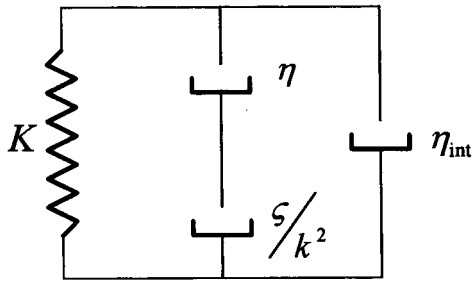

Fig. 1: The effective viscoelastic model for the given normal mode k for the collective type of motion (Eq. 14) of the network in the EVM.

The relaxation time $\tau(k)$ very weakly depends on the scale of motions at scales $r > r^{**}$ where

$$r^{**} \sim \frac{2\pi}{k^{**}} > 2\pi\sqrt{\frac{\eta}{\varsigma}} \qquad (16)$$

The quantity r^{**} can be considered as a measure of the viscous correlations in a network immersed in mobile viscous medium. At the motions with scales $r >> r^{**}$ (or $k << k^{**}$) the system behaves as that with only interchain friction which is proportional to $\eta + \eta_{int}$. The EVM is swept along by a network so that the friction arising from the difference of velocities of EVM and network tends to zero.

For very strong interchain friction in a network, which can arise due to the chain entanglements that prevent the rearrangement of a given chain relative to the neighbours (i.e. for $\eta_{int}/\eta >> 1$), we have $(\tau_{max}/\tau_{min}) \sim 1$. The relaxation spectrum of the second type for homogeneous network is very narrow. In real heterogeneous networks the essential broadening may exist due to the broad distribution of the values of η_{int} in a network. In the opposite case (if $\eta_{int}/\eta << 1$) the width of the relaxation spectrum depends on the network structure and heterogeneity. The minimum relaxation time in a coarse-grained network model is near to τ_{chain} [3)]

$$\tau_{min} \approx \tau_{chain} \qquad (17)$$

One can easily estimate the order of magnitude of τ_{max} (and, therefore (τ_{max}/τ_{min})) for the simplest case of a network without interchain friction. In this case the relaxation spectrum (Eq. 14) is the broadest one. Let us consider the network consisting of ν chains between

junctions with N segments in every chain. According to ref. [2], the quantity η_{melt} for the same set of chains is

$$\eta_{melt} \sim \left(C\varsigma_{segm}Nb^2/16\right) \tag{18}$$

where C is the concentration of segments in the unit volume, ς_{segm} is the local friction constant of a segment, and b is the length of a segment. According to well-known theory of elasticity of Gaussian networks [4], the elasticity modulus K is given by

$$K = \Phi \nu k_B T \tag{19}$$

Here ν is the number of elastically active chains per unit volume. In our case we have

$$\nu = C/N \tag{20}$$

The quantity Φ is the so-called form-factor that is near to 1 for a network formed from the melt of long chains by means of random cross-linking.

If the quantity η_{EVM} is believed as a first approximation to be approximately equal to η_{melt}, one can estimate the maximum relaxation time $\tau_{\max}$ as follows

$$\tau_{\max} = \frac{\eta}{K} = \frac{N^2 b^2 \varsigma_{segm}}{36 k_B T} \tag{21}$$

On the other hand, the maximum relaxation time of an unique Rouse chain τ_{chain} between junctions in non-reptational regime is given by [1]

$$\tau_{chain} \cong \frac{N^2 b^2}{3\pi^2 k_B T}\varsigma_{segm} \tag{22}$$

The comparison of Eqs. 21 and 22 indicates that in this case the relaxation spectrum is very narrow, namely, the spectrum contains one line $\tau = \tau_{\max}$. One can see also that the value of r^{**} (Eq. 16) may be presented in the form

$$\left(r^{**}\right)^2 \cong Nb^2 \tag{23}$$

if the quantity ς for the chains without reptation is estimated as the total friction in unit volume $\varsigma = \varsigma_{segm}C$. This results is consistent with the assumption that the average characteristic distance is proportional to the average chain length.

A broader relaxation spectrum may arise in some special cases. For example, one can consider a regular (cubic or tetrahedral) polymer network formed in solution by the chains with reactive end groups. Then the swollen network collapses forming a dry network [5]. In this case the average dimension of the network cell can be smaller than the average dimension of the Gaussian chain between the junctions if it would be in melt. If we propose the same estimations

for η and ς, the quantity r_{min} occurs to be smaller than $\langle h^2_{melt} \rangle$, and then the ratio τ_{max}/τ_{min} may be much greater than unity ($\tau_{max}/\tau_{min} \cong N^{1/3}$ if $Cb^3 \cong 1$), and the relaxation spectrum becomes broader, i.e.

$$\frac{\tau_{max}}{\tau_{min}} = 1 + \frac{\langle h^2_{melt} \rangle}{h^2_0} = 1 + const \cdot N^{1/3} \qquad (24).$$

In heterogeneous network models the distribution of the contour chain lengths exists, and each network chain can be attached to distant junctions in space as well as to neighbouring junctions. In these networks broad distribution of values of τ_{min} appears, and the relaxation spectrum is also broader. These effects and their manifestation in viscoelastic and other relaxation phenomena need a special investigation and will be discussed in future.

Conclusion

The existence of the long-range hydrodynamic interactions in the polymer networks leads to the appearance of the "non-trivial" type of relaxation spectra (RS) with finite width. The direct interchain friction will also narrow the RS.

References

1. Yu. Ya. Gotlib, A. A. Gurtovenko, *Macromol. Theory Simul.*, **6**, 523 (1997)
2. M. Doi, S. V. Edwards, The Theory of Polymer Dynamics, Oxford University Press, Oxford (1986)
3. A. A. Gurtovenko, Yu. Ya. Gotlib, *Macromolecules*, **31**, 5756 (1998)
4. J. D. Ferry, Viscoelastic properties of polymers, J. Wiley & Sons, New York, 1980, 3rd edition
5. A. J. Grosberg, A. R. Khokhlov, Statistical Physics of Macromolecules, Nauka, Moscow, 1989, p. 205