JOURNAL OF CHEMICAL PHYSICS VOLUME 115, NUMBER 14 8 OCTOBER 2001

Dynamics of inhomogeneous cross-linked polymers consisting of domains of different sizes

A. A. Gurtovenko
Theoretische Polymerphysik, Universität Freiburg, Hermann-Herder Str. 3, D-79104 Freiburg, Germany and Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi Prospect 31, V.O., St. Petersburg, 199004, Russia

Yu. Ya. Gotlib
Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi Prospect 31, V.O., St. Petersburg, 199004, Russia

(Received 22 May 2001; accepted 18 July 2001)

The theoretical approach is developed to describe the dynamics of inhomogeneous cross-linked polymers consisting of cross-link agglomerations. An inhomogeneous polymer is treated as an ensemble of noninteracting cross-linked regions (domains) of different sizes. We model an internal architecture of the domains in a rather regular way and assume a power law decay of the relaxation modulus inside the domains, a decay usual for a broad class of cross-linked materials on microscopic scales. Assuming a broad size distribution of the domains in cross-linked polymers due to a random character of cross linking, we demonstrate a stretched exponential time behavior of the relaxation modulus on scales larger than the average size of inhomogeneities in the polymer. We apply this general approach to some special cases of cross-linked polymers, namely to polydisperse polymer networks, to inhomogeneous meshlike networks, and to inhomogeneously cross-linked polymeric gels. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1401819]

I. INTRODUCTION

Much interest in cross-linked polymers and gels occurs due to their numerous technical applications. As a consequence, the cross-linked polymers (polymer networks) have been a subject of intensive theoretical and experimental researches during many past decades. Due to a complex nature of network relaxation processes and a random character of cross linking, the theoretical approaches have concentrated on model systems. Starting with the earliest molecular theories,[1–4] a great number of the models of polymer networks has been developed.[5–33] The most of the network theories seems to be between the phantom[1,2] and the affine[3,4] models of polymer networks. The main difference between these two approaches resides in the treatment of motions of junctions (cross links). The junctions in the affine model are assumed to be topologically restricted and can move only in an affine manner with a deformation of the network. In contrast, in the phantom network model the junctions are not restricted and are treated in the same way as the segments of network chains. They can fluctuate freely near their average positions which are deformed affinely with strain. Besides the theoretical approaches, computer simulations became in the last decade a very useful tool to study statistical and dynamical properties of polymer networks.[34–43] They allow the theoretical predictions to be tested, providing a great control over cross-linking processes and topological structures in the polymer networks.

One of the most complicated and still not completely understood problems of polymer network dynamics seems to be related to inhomogeneities of real cross-linked polymers. There is a variety of factors which affect the network formation and the relaxation processes in polymer networks and gels. These factors include a broad distribution of network chain lengths, entanglements effects, dangling chains, fluctuations of cross-link density, cross-link agglomerations, a topological disorder, etc. The inhomogeneity of cross-linked polymers and the disagreement between the experiments and the usual network models are obvious now (see, e.g., Refs. 44–52). Therefore, the problem of the heterogeneity of polymer networks is of great interest and importance from both theoretical and experimental points of view. In this paper we focus on the consideration of one possible example of the above network inhomogeneities, namely, on the existence of regions with different properties in real cross-linked polymers.[53] Such a type of heterogeneities has been found in statistical gels by means of small-angle neutron scattering.[51,52] The random arrangement of cross links in polymer can create regions with the cross-linking density higher than average, leading to formation of percolation clusters. After contact with an excess of solvent, the solvent is mainly absorbed by the regions between the clusters, and gel swells heterogeneously.[51,52] Moreover, the dynamic and static light scattering experiments on hydrogels[54,55] have supported the existence of such inhomogeneities. As demonstrated in recent work of Oppermann and co-workers[56] for polyacrylamide hydrogels, the inhomogeneities can be visualized as densely cross-linked regions in a surrounding environment with smaller cross-link density. Therefore, an inhomogeneously cross-linked hydrogel consists of cross-link agglomerations, i.e., regions with relatively high polymer concentration, and more diluted or swollen regions.[56]

Having in mind the existence of the above cross-link agglomerations in polymeric gels, in this paper we model an

0021-9606/2001/115(14)/6785/9/$18.00

inhomogeneous cross-linked polymer as an ensemble of regions (called here domains) with relatively high cross-link density, which relax on the background of a more diluted environment. The simplest way to treat the dynamics of such a system is to consider the relaxation of different cross-linked domains independently of each other. Then the situation considered seems to be close to dilute polymer solutions in which cross-linking processes are going on: Sufficiently large formations (clusters) which already possess an internal network structure still move in the solvent independently of each other. Following the concept of an effective viscous medium,[57] it seems to be possible to extend this approach to more dense polymer systems such as cross-linked polymers in the bulk. Treating cross-linked network domains as objects with a rather regular internal structure and assuming a broad size distribution of the domains in the system, we intend to show a nonexponentinal decay of the time-dependent relaxation modulus (the response on the external perturbations) of the inhomogeneous polymer network as a whole.

Many complex systems characterized by a disorder or (and) strong interactions show a relaxation decay obeying a stretched exponential (Kohlrausch–Williams–Watts) form:[58,59]

$$\phi(t) \sim \phi_0 \exp[-(t/\tau)^{\beta}], \tag{1}$$

where $\phi(t)$ is some relaxation function and $0<\beta<1$. Numerous examples include relaxation in glasses,[60–62] trapping processes,[63,64] relaxation processes in polymers and gels,[65–81] etc. As a consequence, there are a number of theoretical approaches which derived a nonexponentionality of relaxation from a microscopic point of view. We recall here defect diffusion model for dielectric relaxation in glassy materials,[82,83] kinetic model of coupled rotators for dielectric relaxation and light scattering in amorphous polymers,[84–88] long-time behavior in trapping processes,[63,64] direct energy transfer,[89] hierarchically constrained dynamics for glassy relaxation,[90] and coupling model for relaxation in complex correlated systems.[62] In general, a nonexponentiality may be caused by a superposition of different exponential processes or by a superposition of intrinsically nonexponential processes (so-called homogeneous and heterogeneous scenario, respectively).[71,81,91–94] Moreover, even in the case of a superposition of a number of exponential processes, an origin of the stretched exponential behavior may be different. For instance, the coupling model explains a nonexponentiality in complex correlated systems by an existence of strong correlations (or interactions) between relaxing units, which slow down the relaxation.[62] In this paper we demonstrate another possibility: A stretched exponential behavior (in particular, in inhomogeneous cross-linked polymers) may be caused by a broad size distribution of noninteracting relaxing units (network domains). Thus, the main goal of the paper consists in the demonstration of a possible origin of the nonexponentional relaxation in cross-linked polymers, which is related to structural heterogeneities of polymers. The paper is organized as follows. In the next section we describe the dynamic model of inhomogeneous cross-linked polymers consisting of regions (domains) of different sizes. The relaxation inside the domains is discussed in Sec. III. Section IV is devoted to the relaxation behavior of the inhomogeneous polymer network as a whole. Some particular examples of using the theoretical approach developed are presented in Sec. V. Finally, we end with short summary and conclusions of the paper.

II. DYNAMIC MODEL OF INHOMOGENEOUS CROSS-LINKED POLYMERS

We begin with the formulation of the theoretical approach for describing dynamics of inhomogeneous cross-linked polymers consisting of cross-link agglomerations. We treat a cross-linked polymer as an ensemble of noninteracting regions (domains) which have finite sizes and an internal network structure. An internal structure of the domains is modeled in a rather regular way: Each domain consists of n identical elements connected with each other in an arbitrary (but the same for all domains) way. A structure inside the domains can represent, for instance, a meshlike (cubic, tetrahedral or square) network, a fractal network, etc. The only difference between the domains resides in the different number n of relaxing elements in the domains. If the condition of dense packing is fulfilled inside the domains, the above difference in the number of elements leads to the corresponding difference in the domain sizes. In so doing, we reduce the randomness of cross linking to a broad size distribution of domains in the system.

We focus on viscoelastic dynamic properties of such inhomogeneous cross-linked polymers. We assume that the cross-linked domains are embedded in a viscous medium, which is ‘‘common’’ for all the domains. In the case of dilute polymer solutions and gels this viscous medium is a real solvent. The above consideration may be extended also on dry polymer networks. According to the well-known approach developed for polymer melts,[57] an effective viscous medium can be introduced into concentrated polymer systems. The effective medium describes viscous interactions of a given segment of a chain with all other segments; these interactions cannot be reduced to the intersegmental friction between a given pair of segments. Making an extension of this approach to cross-linked bulk polymers (elastomers), one can assume that a similar effective medium exists in dry polymer networks (see, e.g., Refs. 95 and 96). This medium takes into account a stochastic character of contacts of network chain segments and degrees of freedom, which are not included in the network model (side groups, dangling chains, etc.).

We consider the mechanical relaxation of an ensemble of network domains under an external perturbation which produces a velocity gradient in the viscous medium. In typical mechanical experiments the complex (shear) modulus $G^*(\omega)$ is measured as a response on a harmonic strain excitation. In this paper we are interested in the time-dependent relaxation modulus $G(t)$ (the response of the stress to a shear jump), which is determined from the complex modulus as $G^*(\omega)=i\omega\int G(\tau)\exp(-i\omega\tau)d\tau$ (see, e.g., Refs. 97 and 98). We assume that different domains relax independently of each other and have soft boundaries (boundary domain elements are not fixed). Due to the independent relaxation of domains embedded in the perturbed viscous medium, the viscoelastic response of an inhomogeneous cross-linked polymer can be imitated by the behavior of a number of generalized Maxwell elements[98] which are connected in parallel and correspond to the relaxation of different viscoelastic domains. As a result, the total relaxation modulus $G(t)$ (as well as the complex dynamic modulus) of the whole polymer represents a sum of relaxation moduli of different cross-linked domains.

Each domain in a network system is characterized by a certain number of elements inside the domain (or by a finite size of the domain) and provides its own contribution to the total modulus; its contribution depends on the domain size. To proceed further, we need to assume a certain form of distribution function of number of elements in domains. At first, we let the number distribution $f(n)$ have a rather general form, namely,

$$f(n)=Cn^{\sigma}\exp[-an^{\delta}], \tag{2}$$

where δ and σ are the parameters of the distribution ($\delta>0$), n is the number of elements in a given domain, and C is the normalized constant equal approximately to $\delta a^{(\sigma+1)/\delta}\Gamma^{-1}[(\sigma+1)/\delta]$. The number distribution $f(n)$ given by Eq. (2) leads immediately to an appearance of the average number $\overline{n}$ of elements in the domains

$$\overline{n}=\tilde{C}a^{-1/\delta}, \tag{3}$$

where

$$\tilde{C}\simeq\Gamma\left(\frac{\sigma+2}{\delta}\right)\bigg/\Gamma\left(\frac{\sigma+1}{\delta}\right),$$

a constant which is about unity. Hence, the parameter a of distribution, $a\sim\overline{n}^{-\delta}$, is directly related to the number of relaxing elements $\overline{n}$ in a domain of average size. We assume that we are in the case of sufficiently large domains. This means that cross-linked domains contain (on the average) a large number of elements, i.e., $\overline{n}\gg1$ and $a\ll1$.

The concrete forms of a number distribution [Eq. (2)], i.e., parameters δ and σ, may be found from some physical reasons at the consideration of concrete cross-linked polymer systems. For instance, a distribution of chain lengths in polymer networks may have an exponential form [i.e., $\delta=1$ in Eq. (2)] due to a random character of cross-linking processes, which leads to a Poisson-type distribution of cross links (see Sec. V). Note that the above domain approach can be applied not only to polymer networks and gels, but also to some special classes of composite polymers which consist of slightly cross-linked elastomeric blocks embedded in rigid matrix (environment). In this case an effective viscous medium should be introduced inside all the domains, and the relaxation of different domains is independent from each other. For such composite polymers one expects the fluctuations of the number of cross links in different domains (blocks) around some average value. These fluctuations may be described by Gaussian distribution which can be reduced to the form given by Eq. (2) with $\delta=2$ for the case of sufficiently large number of cross links in domains.

III. RELAXATION INSIDE CROSS-LINKED DOMAINS

The complex shear modulus (and, correspondingly, the relaxation modulus) of cross-linked polymers and gels (especially at the sol–gel transition) often show microscopically a power law behavior.[99–105] Therefore, we focus here on a class of domains which obey such a power law type of internal relaxation, i.e., one has for the relaxation modulus $G(t)$ inside the domains:

$$G(t)\simeq\nu k_BT\left(\frac{t}{\tau_0}\right)^{-\gamma}, \tag{4}$$

where ν is the number of relaxing elements (from which the domains are built) per unit volume, γ is the constant ($\gamma>0$), and τ_0 is a certain characteristic (minimal) relaxation time of a domain. Since all the cross-linked domains consist of the identical relaxing elements and have the identical internal architecture, the minimal relaxation time τ_0 should be the same for all the domains.

Viscoelastic properties of materials can be described also by means of the relaxation spectrum $H(\tau)$ (or the distribution function of relaxation times τ on a logarithmic scale), which is connected with the relaxation modulus $G(t)$ as follows:[98]

$$G(t)=\int H(\tau)\exp[-t/\tau]d\ln\tau. \tag{5}$$

For sufficiently large systems (i.e., for large domains with $n\gg1$ in our case), the distribution of eigenvalues $\lambda(\xi)$ and relaxation times $\tau(\xi)$ is described by the continuous variable ξ which numbers modes, and the relaxation spectrum $H(\tau)$ is defined as (see, e.g., Ref. 29)

$$H(\tau)=-\nu k_BT\frac{1}{n}\frac{d\xi}{d\ln\tau}. \tag{6}$$

A rather slow, power-law behavior of $G(t)$ inside the domains [Eq. (4)] allows us to use for Eq. (5) the Alfrey's approximation[98,106] and to find the approximate behavior of the relaxation spectrum:

$$H(\tau)\simeq\nu k_BT\gamma\left(\frac{\tau}{\tau_0}\right)^{-\gamma}, \tag{7}$$

i.e., the relaxation spectrum $H(\tau)$ inside the domains obeys also a power law decay. Note that the positive parameter γ may be smaller as well as larger than 1 depending on different internal architectures of domains (see Sec. V).

Since cross-linked domains have finite sizes, they can be characterized by their maximal relaxation times $\tau_{\max}(n)$ which depend on the number of elements n in the domains (or, on the domain sizes). A power law behavior of $G(t)$ inside the domains [Eq. (4)] holds up to times around the maximal relaxation time $\tau_{\max}(n)$ of a given domain. It is easy to show from the combined consideration of Eqs. (6) and (7) that a power law relaxation [Eqs. (4) and (7)] leads to the following relation for relaxation times:

$$\tau(\xi)\simeq\tau_0\left(\frac{n}{\xi}\right)^{1/\gamma}. \tag{8}$$

Therefore, one has immediately for $\tau_{\max}(n)$ [see Eq. (8) at $\xi=1$]:

$$\tau_{\max}(n)\simeq\tau_0 n^{\alpha} \tag{9}$$

with

$$\alpha=\frac{1}{\gamma}. \tag{10}$$

Note that from physical reasons the maximal relaxation time $\tau_{\max}(n)$ should increase with n, i.e., exponent α should be positive.

At times larger than the maximal relaxation time $\tau_{\max}(n)$ of a given domain we obtain an exponential decay of the relaxation modulus $G(t;n)$ of the domain:

$$G(t;n)\simeq\nu k_B T\frac{1}{\alpha}\frac{1}{n}\left(\frac{\tau_{\max}(n)}{t}\right)\exp\left(-\frac{t}{\tau_{\max}(n)}\right). \tag{11}$$

Such a type of time behavior of $G(t;n)$ is caused by the cutoff of the relaxation spectrum of a given domain due to its finite size. At long times, $t>\tau_{\max}(n)$, the main contribution to the relaxation modulus is provided by exponential term which is governed by the maximal relaxation time $\tau_{\max}$ [Eq. (11)]. A more weak, power-law term in Eq. (11) represents a "memory" of the system (the domain of finite size) about contributions of the relaxation times shorter than $\tau_{\max}$. It should be emphasized here that the long-time behavior of the relaxation modulus of the domains [$t>\tau_{\max}(n)$] is determined by the maximal relaxation time $\tau_{\max}(n)$ and, therefore, depends on the number of elements in a given domain. This is in contrast to the internal "intradomain" relaxation which has a power law character for all the domains and does not depend on n [Eq. (4)].

Thus, after a rather slow, power-law relaxation inside domains [Eq. (4)], the relaxation modulus shows an exponential decay with a single relaxation time $\tau_{\max}(n)$; this relaxation time depends on the number of relaxing elements in the domains [Eq. (9)].

IV. RELAXATION OF INHOMOGENEOUS CROSS-LINKED POLYMERS

Now we calculate the time-dependent relaxation modulus $G(t)$ of inhomogeneous cross-linked polymers consisting of domains of different sizes. As mentioned above, the relaxation modulus $G(t)$ of the heterogeneous system considered represents a sum over relaxation moduli of different domains. We consider here the mechanical relaxation in a network at sufficiently long times, $t\gg\tau_0$. More precisely, we are interested in the long-time region where almost all cross-linked domains show already a simple exponential decay of their relaxation moduli $G(t;n)$ given by Eq. (11). Using the number distribution function $f(n)$, Eq. (2), for averaging over all the cross-linked domains, one can note that the main contribution to the long-time relaxation of an inhomogeneous polymer network is provided by the following term:

$$\begin{aligned}G(t)\big|_{t\gg\tau_0}&\sim\left(\int f(n)G(t;n)\big|_{t\gg\tau_{\max}(n)}\,dn\right)\\&\sim\int n^{\sigma}\exp[-an^{\delta}]\frac{1}{n}\left(\frac{\tau_{\max}(n)}{t}\right)\\&\quad\times\exp\left(-\frac{t}{\tau_{\max}(n)}\right)dn.\end{aligned} \tag{12}$$

Taking into account the dependence of the maximal relaxation time $\tau_{\max}(n)$ on the domain size [Eq. (9)] and using the saddle-point procedure[107] with large parameter $(t/\tau_0)\gg1$ to evaluate the integral in Eq. (12) for sufficiently long times, $t\gg\tau_0$, we obtain finally

$$\begin{aligned}G(t)\simeq\overline{\nu}_{\mathrm{dom}}k_B T C_1\left(\frac{t}{\tau^*}\right)^{(\sigma-3\delta/2)/(\alpha+\delta)}\\\times\exp\left[-\left(\frac{t}{\tau^*}\right)^{\delta/(\alpha+\delta)}\right],\end{aligned} \tag{13}$$

where $\overline{\nu}_{\mathrm{dom}}=\nu/\overline{n}$ is the number of domains of average size per unit volume ($\overline{n}$ is the average number of relaxing elements in domains) and

$$\begin{aligned}C_1=\sqrt{2\pi}\,\Gamma\left(\frac{\sigma+2}{\delta}\right)\Gamma^{-2}\left(\frac{\sigma+1}{\delta}\right)\delta^{-1/2}\alpha^{(2\sigma-3\delta)/2\delta}\\\times(\alpha+\delta)^{(3\delta-2\sigma-\alpha)/2\alpha}.\end{aligned}$$

The characteristic relaxation time τ^* which determines a stretched exponential term in Eq. (13) has clear physical meaning. If a certain distribution of number of elements in domains is introduced in a heterogeneous system [Eq. (2)], a new characteristic time parameter appears. This parameter corresponds to the longest relaxation time τ_D of a domain realized with the maximal probability, i.e., of a domain of the average size [see Eq. (9) at $n=\overline{n}$]:

$$\tau_D=\tau_{\max}(\overline{n})=\tau_0\overline{n}^{\alpha}=\tau_0 a^{-\alpha/\delta}\hat{C}, \tag{14}$$

where

$$\hat{C}\simeq\Gamma^{\alpha}\left(\frac{\sigma+2}{\delta}\right)\Bigg/\Gamma^{2\alpha}\left(\frac{\sigma+1}{\delta}\right).$$

It is very natural (and seems to be correct from a physical point of view) that the characteristic relaxation time τ^* in Eq. (13) is found to be close to τ_D, namely,

$$\tau^*=C_2\tau_D, \tag{15}$$

where

$$C_2\simeq\Gamma^{2\alpha}\left(\frac{\sigma+1}{\delta}\right)\Gamma^{-\alpha}\left(\frac{\sigma+2}{\delta}\right)\delta\alpha^{\alpha/\delta}(\alpha+\delta)^{-(\alpha+\delta)/\delta}.$$

Equation (13) indicates that the relaxation modulus $G(t)$ of an inhomogeneous cross-linked polymer consisting of noninteracting domains of different sizes shows a stretched exponential decay in the long-time region, at $t\gg\tau_D$. This is the main result of the paper. We demonstrated that a power law behavior of the relaxation modulus $G(t)$, which is typical for a broad class of cross-linked materials on microscopic scales (i.e., inside the domains in our model), is replaced with a stretched exponential relaxation on scales larger than the average size of inhomogeneities in cross-linked polymers. The stretched exponential index $\delta/(\alpha+\delta)$ in Eq. (13) ranges between 0 and 1 for all positive values of δ and α. It should be noted that a formal mathematical origin of the above nonexponentiality with the stretched exponential index equal to $\delta/(\alpha+\delta)$ resides in the procedure of asymptotic evaluation of integral in Eq. (12). The same *mathematical* origin of a stretched exponential decay was reported in some previous investigations which deal with free-volume theory of glassy relaxation,[108] with electric birefringence in dilute solutions of polyelectrolyte,[77] with trapping processes,[109] and others. The main feature of the theoretical approach developed in this paper consists in a *physical* origin of such a type of relaxation [Eq. (13)]: We state here that a stretched exponential decay of the relaxation modulus $G(t)$ can be caused by a structure heterogeneity of cross-linked polymers.

It should be noted that a nonexponential decay of the relaxation modulus $G(t)$ [Eq. (13)] appears in the long-time region, $t \gg \tau_D$. At such times the relative decreasing of $G(t)$ becomes very considerable as compared with the initial value of the relaxation modulus $G(0)$, namely, $G(\tau_D)/G(0) \sim 1/\overline{n}$ where $\overline{n}$ is the number of relaxing elements in the domain of average size. In the case of domains of sufficiently large (on the average) sizes, a stretched exponential relaxation may appear therefore in the region corresponding to very small values of $G(t)$. In principle, this fact may prevent in some cases the observation of the nonexponential relaxation in inhomogeneous cross-linked polymers.

V. SOME EXAMPLES

A. Polydisperse polymer networks

After considering the rather general case, we turn now to some concrete examples. First of all, we consider the simplest example of internal topology of domains, namely, the domains containing only single polymer chains. From a physical point of view, this means that we are mostly interested in the intrachain (in the range of distance between cross links) relaxation of a polymer network. In other words, we assume that there is a separation between the time scales of network chain motions and those of the cross-link motions.[110] If we consider the case of sufficiently short chains between cross links, whose lengths are not larger than an entanglement distance (so-called moderately cross-linked networks[110]), one can treat the dynamics of polymer chains in domains in the framework of Rouse model.[57,111] In this case the relaxing elements inside the domains are Rouse segments, and the difference in the number of elements in different domains corresponds to the polydispersity of the given polymer network. The main reason to consider at first such a type of domains consists in the fact that the number distribution function of the domains (or distribution of chain lengths between cross links) appears here in a rather natural way. For an ideal stochastic, uncorrelated process of cross linking (in this case the distribution of cross links obeys a Poisson form), the distribution of the number of segments in the chains between cross links has an exponential form:[110]

$$f(n) \sim \exp[-an]. \tag{16}$$

Such an exponential distribution of network chain lengths has been also obtained in Ref. 112 and verified through computer simulations.[113] Thus, we can apply our domain approach developed above by setting $\delta=1$ and $\sigma=0$ in Eq. (2). Parameter a means the inverse average number of segments in network chains (or, the average length of network chains). The behavior of the relaxation spectrum of a Rouse chain is well known (see, e.g., Refs. 57 and 111) and obeys a power law decay with exponent γ in Eq. (7) equal to 1/2. The relaxation modulus $G(t)$ inside the domains has also a power law behavior [see Eq. (4) at $\gamma=1/2$] up to times around the maximal relaxation time $\tau_{\max}(n)$ of a Rouse chain consisting of n segments, which is given by the well-known relation[57,111] [see also Eqs. (9) and (10) at $\gamma=1/2$]:

$$\tau_{\max}(n) \simeq \tau_s n^2, \tag{17}$$

where τ_s is the relaxation time of a single Rouse segment. Thus, the third parameter, α, is equal to 2. Using Eq. (13) for obtaining the asymptotic behavior of the considered inhomogeneous network leads to

$$G(t) \simeq \overline{\nu}_{\text{chain}} k_B T \left(\frac{t}{\tau^*}\right)^{-1/2} \exp\left[-\left(\frac{t}{\tau^*}\right)^{1/3}\right], \tag{18}$$

where $\overline{\nu}_{\text{chain}}$ is the number of polymer chains of average length per unit volume. For simplicity we omit in Eq. (18) numerical constants (and below as well). The characteristic relaxation time τ^* is close to the maximal (Rouse) relaxation time of a network chain of average length [see Eqs. (14) and (15) at $\delta=1$, $\alpha=2$, and $\sigma=0$] and can be represented as $\tau^* \simeq \zeta \overline{n}^2/K$ where ζ is the friction constant of a bead (monomer), K is the elasticity constant of a Rouse "spring," and $\overline{n}$ is the average number of Rouse segments in network chains. Thus, we obtain for the polydisperse polymer network a stretched exponential long-time behavior of $G(t)$, with exponent of 1/3, and, in fact, reproduce previous result of Sommer.[110] Sommer has also demonstrated a rather good agreement between this theoretical prediction and the experimental data for natural rubber.[114,115] It should be noted here that this stretched exponential behavior is derived under assumption of a separation of time scales of motions of chains and cross links. Therefore the above nonexponential relaxation holds up to time scales corresponding to the relaxation of cross-linking points. At longer times it may be masked by the cross-link motions.

B. Meshlike inhomogeneous polymer networks

The next example is related to a more complex internal topology of cross-linked domains. In contrast to the systems, in which the domains consist of single polymer chains, we consider now an inhomogeneous polymer network as an ensemble of domains having a meshlike internal network structure. The cross-linked domains show now a more complicated internal dynamics as compared with single polymer chains, due to the connectivity of the polymer chains into an unified spatial network structure inside the domains. An internal architecture of domains is treated as a 3D regular cubic network. Working in the framework of Rouse model,[57,111] we focus here on the pure network relaxation only, which is related to the connectivity of chains in a cubic network structure. As shown previously[96,116] for regular cubic polymer networks built from Rouse chains, the relaxation spectrum of the network consists of two different regions, corresponding to small-scale (intrachain) and to large-scale (interchain) motions. The intrachain part of the spectrum is very close to that of single Rouse chains. On larger scales the interchain, pure network relaxation can be reproduced closely by a simple coarse-grained network model. In this coarse-grained model a Rouse chain between junctions is replaced with a single Rouse segment (spring) with corresponding redetermination of the elasticity and the friction constants in the network model.[96,116]

Thus, we treat the cross-linked domains as coarse-grained polymer networks of finite sizes. Each cubic domain is characterized by a number of cross-links (junctions) n inside the domain. Note that the number of cross links is directly related to the number of polymer chains since in the cubic network domains three polymer chains are (on the average) attached to a given junction. On scales larger than the distance between neighboring network junctions, the relaxation modulus (as well as the relaxation spectrum) of a cubic polymer network obeys a power law decay with exponent $\gamma = 3/2$ in Eqs. (7) and (4):[32,95,96,116]

$$G(t) \simeq \nu k_B T \left(\frac{t}{\tau_{\mathrm{chain}}} \right)^{-3/2}, \tag{19}$$

where ν is the number of cross links per unit volume and τ_{chain} is the relaxation time of a chain between network junctions, which is the same for all the domains. Since the meshlike network domains have finite sizes (or finite numbers of cross links n), the power law behavior is replaced with exponential decay [Eq. (11)] round the maximal relaxation time of a given domain [see Eqs. (9) and (10) at $\gamma = 3/2$]:

$$\tau_{\max}(n) \simeq \tau_{\mathrm{chain}} n^{2/3}, \tag{20}$$

so that the parameter α is equal to 2/3 for this type of cross-linked domains. Note that Eq. (20) is valid for a 3D network domain of a symmetrical cubic form (not for a domain of an elongated form) and can be found directly by means of the consideration of the internal relaxation of a 3D cubic network of finite size.[117] For describing long-time dynamic behavior of the whole inhomogeneous network consisting of cross-linked domains of different sizes, we use here a three-dimensional analog of a Poisson-type distribution $f(n)$ given by Eq. (16). If a process of cross linking has a random and an uncorrelated character, the distribution function of the numbers of cross links in the domains has the form (cf. Refs. 117 and 118):

$$f(n) \sim n^2 \exp[-an]. \tag{21}$$

Note that the same number distribution (but from different physical reasons) was previously used in aggregate model.[119–121] In our model we have therefore $\delta = 1$ and $\sigma = 2$ [see Eq. (2)], and Eq. (13) leads to the following long-time stretched exponential behavior of the relaxation modulus $G(t)$ of an inhomogeneous meshlike polymer network (cf. Refs. 117 and 118):

$$G(t) \simeq \overline{\nu}_{\mathrm{dom}} k_B T \left(\frac{t}{\tau^*} \right)^{3/10} \exp\left[-\left(\frac{t}{\tau^*} \right)^{3/5} \right], \tag{22}$$

where $\overline{\nu}_{\mathrm{dom}}$ is the number of cubic network domains of average size per unit volume and τ^* is close to the maximal relaxation time of the domain of average size [Eq. (14)]. In contrast to the preceding section, the characteristic relaxation time $\tau^* \simeq \tau_{\mathrm{chain}} \overline{n}^{2/3}$ here is far from the maximal (Rouse) relaxation time τ_{chain} of network chains due to the long-range type of heterogeneities (the domains considered consist of a large number of network chains, $\overline{n} \gg 1$). Thus, for 3D meshlike inhomogeneous networks the relaxation modulus $G(t)$ obeys a power law behavior [Eq. (19)] for sufficiently short times and has a stretched exponential decay [Eq. (22)] at longer times ($t \gg \tau_{\mathrm{chain}}$ and $t \gg \tau_D$).

Besides three-dimensional meshlike polymer networks, it is interesting to consider meshlike networks with restricted geometry, e.g., two-dimensional square networks.[9,122–124] Such a type of polymer networks may be realized, for instance, in polymer films and layers, on the surfaces of polymer samples, etc. Moreover, the 2D polymer networks are of special interest because the influence of the chain connectivity on the dynamics of such polymer networks is expected to be weaker as compared to the 3D networks. We treat a 2D inhomogeneous network in the same way as the above discussed 3D case. The 2D network is modeled as a number of planar domains which represent regular square networks.[9,122–124] We describe an internal dynamics of the domains in the framework of Rouse model and are mostly interested in the pure network relaxation (i.e., we use a 2D coarse-grained network model). At times larger than the relaxation time of a chain between junctions, the relaxation modulus $G(t)$ of a regular square network has the following behavior:[9,123,124]

$$G(t) \simeq \nu k_B T \left(\frac{t}{\tau_{\mathrm{chain}}} \right)^{-1}, \tag{23}$$

i.e., intermediates between the single Rouse chains and the 3D cubic networks [see Eq. (19)]. The quantity ν in Eq. (23) is the number of cross links per unit surface. Since the 2D domains are finite, there is a certain maximum relaxation time $\tau_{\max}(n)$ depending on the number of cross links n in a given domain [see Eqs. (9) and (10)]:

$$\tau_{\max}(n) \simeq \tau_{\mathrm{chain}} n. \tag{24}$$

Assuming a random character of cross linking, we use for averaging over all the square network domains the following number distribution function [cf. Eqs. (16) and (21), and note the two dimensionality of the system considered]:

$$f(n) \sim n \exp[-an]. \tag{25}$$

Therefore we have here $\alpha = 1$, $\delta = 1$, and $\sigma = 1$, and Eq. (13) for long times leads to

$$G(t)\simeq \overline{\nu}_{\mathrm{dom}} k_B T \left(\frac{t}{\tau^*}\right)^{-1/4} \exp\left[-\left(\frac{t}{\tau^*}\right)^{1/2}\right], \tag{26}$$

where $\overline{\nu}_{\mathrm{dom}}=\nu/\overline{n}$ is the number of planar domains of average size per unit surface. Thus, we obtained another example of a long-time stretched exponential behavior. In principle, one can apply the above domain approach to inhomogeneous meshlike polymer networks with a rather arbitrary regular internal architecture of domains, for which the relaxation spectrum inside the domains obeys a power law decay given by Eq. (7). It may be, for instance, a network consisting of domains with a tetrahedral (diamondlike) internal structure.

C. Domain model of inhomogeneously cross-linked gels

As mentioned in the Introduction, polymeric gels often represent an inhomogeneous structure consisting of cross-link agglomerations moving in a surrounding environment with smaller cross-link density.[51–56] Now we intend to apply the theoretical approach developed in this paper for describing dynamics of inhomogeneous gels. As previously, we assume that the gel consists of noninteracting domains of different sizes, which can correspond to the cross-link agglomerations in real gels. Microscopically the gels show often a power law decay of the complex modulus (and, correspondingly, of the relaxation modulus). The simplest phenomenological model to reproduce the microscopic behavior of gels is a ladder model.[125] Recently this model was used to describe the viscoelastic behavior of gels at the sol–gel transition as well as the different stages of gelation[126] (see also Ref. 127). Thus, we focus here on domains which have an internal ladder architecture.

A ladder network consists of ladderlike structure with identical springs along one of the struts and dashpots with identical viscosities on the rungs of the ladder.[126,127] We are interested here in a ladder model of finite size. A finite ladder structure can be obtained by finishing ladder either with a spring or with a dashpot.[126] The first case corresponds to a solidlike behavior of the domain after the internal relaxation ends (post-gel regime), the latter case corresponds to a liquidlike behavior (pre-gel regime).[126] In principle, the domain approach developed may be valid for both cases but from a physical point of view in the pre-gel regime the condition of an independent relaxation of the different domains is easier to justify: In this case we find readily cross-link agglomerations (domains) inserted into a more dilute environment. Common to all the ladder arrangements is that they show a power law behavior for complex modulus $G^*(\omega)\sim\omega^{\gamma}$ with $\gamma=1/2$.[126–128] Therefore, one has for the corresponding relaxation modulus $G(t)$ inside a domain of ladder internal structure, which consists of n relaxing elements (springs):

$$G(t)\simeq \nu k_B T \left(\frac{t}{\tau_l}\right)^{-1/2}, \tag{27}$$

where ν is the number of relaxing elements per unit volume, and τ_l is the characteristic relaxation time of the ladder network domain, which is equal to the ratio of the viscosity of a dashpot and the elasticity constant of a spring in the ladder. Following Eqs. (9) and (10), a ladder model of finite size (or of finite number n of elements) can be characterized by the maximal relaxation time

$$\tau_{\max}(n)\simeq \tau_l n^2. \tag{28}$$

Note that the same dependence of $\tau_{\max}$ on the length of the ladder model was numerically found in Ref. 126. Assuming that the cross-link agglomerations (the domains with a ladder internal structure) are three dimensional and using the corresponding number distribution, Eq. (21), for averaging over all the cross-link agglomerations, one finds from Eq. (13) the asymptotic behavior for $G(t)$ for sufficiently long times, $t\gg\tau_l$:

$$G(t)\simeq \overline{\nu}_{\mathrm{dom}} k_B T \left(\frac{t}{\tau^*}\right)^{1/6} \exp\left[-\left(\frac{t}{\tau^*}\right)^{1/3}\right], \tag{29}$$

where $\overline{\nu}_{\mathrm{dom}}$ is (as usual) the number of cross-link agglomerations (domains) of average size per unit volume, and τ^* is the characteristic relaxation time close to the maximal relaxation time of the domain of average size. Thus, we demonstrated that the domain approach can be easily applied also for describing the dynamic behavior of inhomogeneous cross-linked gels. The approach leads, in particular, to a stretched exponential decay of the relaxation modulus for inhomogeneous gels on sufficiently large scales, namely, on scales larger than the average size of structural inhomogeneities in the gel.

VI. CONCLUSION

In this paper we developed a theoretical approach to describe the dynamics of inhomogeneous cross-linked polymers, the inhomogeneities being related to presence in real cross-linked polymers of regions with different properties, due to the random character of the cross-linking process. We modeled an inhomogeneous cross-linked polymer as an ensemble of domains (cross-link agglomerations) of different sizes, which relax independently from each other on the background of a more dilute (as compared with cross-link agglomerations), surrounding environment. The cross-linked domains were treated as objects with a rather regular internal structure, which was assumed to be the same for all the cross-linked domains. In so doing, we reduce the randomness of cross-linking processes to a broad size distribution of the domains in the inhomogeneous cross-linked polymers.

On scales smaller than the average size of inhomogeneities in the system, the relaxation modulus $G(t)$ shows a power law time behavior usual for a broad class of cross-linked materials on microscopic scales. Assuming then a Poisson-type size distribution of the domains in the heterogeneous system, we showed, however, that this power law behavior of $G(t)$ is replaced with a stretched exponential decay on scales larger than the characteristic (average) size of inhomogeneities in the cross-linked polymers. The main result of the paper is the demonstration of the fact that a broad size distribution of noninteracting relaxing units in cross-linked polymers can lead to nonexponentialities in mechanical relaxation of polymers, i.e., in a ‘‘polymeric’’ origin of the stretched exponential decay found for the relaxation modulus. This is in contrast to, for example, the glassy relaxation where a nonexponentiality is mostly caused by the strong interactions between the relaxing units. We applied our general approach to some special cases of cross-linked polymers, namely to polydisperse polymer networks, to inhomogeneous meshlike networks, and to inhomogeneously cross-linked polymeric gels.

To conclude, it should be noted that the domain approach developed was derived from two main assumptions: First, real cross-linked polymers and gels may consist of regions with different properties and, second, the dynamical behavior of these regions (domains) may be treated independently of each other. The first assumption is very natural from a physical point of view due to a random character of the cross-linking process and is confirmed experimentally for polymeric gels (see, e.g., Refs. 51–56). The second assumption may be restricted for some specific polymer systems by a certain characteristic scale. The independent relaxation seems to be valid for inhomogeneous polymeric gels consisting of cross-link agglomerations (especially in the pre-gel regime) and for rather dilute polymer solutions in which the cross-linking process is still in progress (see Sec. V C and also the Introduction). Such an independent relaxation of the domains in the case of polydisperse polymer networks (see Sec. V A) is restricted by characteristic scales on which the chain motions and the cross-link motions are separated.

In the case of dense polymer systems (such as dry polymer networks) we have to introduce an effective viscous medium (but not a real solvent) in which relaxing units (domains) move (see Sec. V B). This effective medium in undiluted polymers consists of the chains of the same network and describes the viscous interactions of a given network chain with all other chains. Therefore, even under assumption that a more diluted (as compared with domains), surrounding environment of the domains consists of non-cross-linked linear chains, this effective medium should contain the chains which begin in a given cross-linked domain and end in another domain, providing the connectivity between different domains in a dry inhomogeneous network. In other words, the relaxing units (domains) capture only a part of the story, since real polymer networks have a long-range structure. This fact is reflected in the appearance of a nonzero value for their equilibrium modulus.[98] Therefore, the above assumption about an independent relaxation of the cross-linked domains in dry polymer networks may be valid only within a certain scale range, where the connectivity of the domains into a unified structure does not yet provide a considerable contribution to relaxation. On larger scales, the independent dynamics of the domains [and, therefore, the predicted stretched exponential decay of $G(t)$] can be masked by the cooperative motion of relaxing units (domains). A simple way to take into account the above connectivity of the relaxing units is to ''decorate'' the bonds of a regular lattice (say square or cubic), by replacing the bonds with subunits of an arbitrary internal architecture.[129] It may be a subject of our further investigations.

ACKNOWLEDGMENTS

One of the authors (A.A.G.) acknowledges the support of the Alexander von Humboldt Foundation. This work was supported by the Russian Foundation of Basic Research (Grant No. 99-03-33313), by the INTAS (Grant No. 99-1114), and by the ESF Scientific Programme SUPERNET. Helpful discussions with Professor H.-G. Kilian and Professor A. Blumen are gratefully acknowledged.

[1] H. M. James and E. Guth, J. Chem. Phys. **11**, 455 (1943).

[2] H. M. James and E. Guth, J. Chem. Phys. **15**, 669 (1947).

[3] P. J. Flory and J. Rehner, J. Chem. Phys. **11**, 512 (1943).

[4] F. T. Wall, J. Chem. Phys. **11**, 527 (1943).

[5] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, New York, 1953).

[6] J. S. Ham, J. Chem. Phys. **26**, 625 (1957).

[7] L. R. G. Treloar, *The Physics of Rubber Elasticity* (Clarendon, Oxford, 1975).

[8] Yu. Ya. Gotlib and K. M. Salikhov, Akust. Zh. **9**, 301 (1963).

[9] A. J. Chompff and J. A. Duiser, J. Chem. Phys. **45**, 1505 (1966).

[10] A. J. Chompff and W. J. Prins, J. Chem. Phys. **48**, 235 (1968).

[11] N. R. Langley, Macromolecules **1**, 348 (1968).

[12] S. F. Edwards, J. Phys. A **7**, 318 (1974).

[13] P. J. Flory, Proc. R. Soc. London, Ser. A **351**, 351 (1976).

[14] G. Ronca and G. Allegra, J. Chem. Phys. **63**, 4990 (1975).

[15] R. T. Deam and S. F. Edwards, Philos. Trans. R. Soc. London, Ser. A **280**, 317 (1976).

[16] G. Marrucci, Rheol. Acta **18**, 193 (1979).

[17] B. Erman and P. J. Flory, J. Chem. Phys. **68**, 5363 (1978).

[18] P. J. Flory and B. Erman, Macromolecules **15**, 800 (1982).

[19] D. S. Pearson and W. W. Graessley, Macromolecules **11**, 528 (1978).

[20] L. M. Dossin and W. W. Graessley, Macromolecules **12**, 123 (1979).

[21] W. W. Graessley, Macromolecules **13**, 372 (1980).

[22] B. E. Eichinger and J. E. Martin, J. Chem. Phys. **69**, 4595 (1978).

[23] W. W. Graessley, Adv. Polym. Sci. **47**, 68 (1982).

[24] J. E. Mark, Adv. Polym. Sci. **44**, 1 (1982).

[25] A. J. Stavermann, Adv. Polym. Sci. **44**, 73 (1982).

[26] R. C. Ball, M. Doi, S. F. Edwards, and M. Waner, Polymer **22**, 1010 (1981).

[27] Yu. Ya. Gotlib, Pure Appl. Chem. **53**, 1531 (1981).

[28] S. F. Edwards, Br. Polym. J. **17**, 123 (1985).

[29] A. Kloczkowski, J. E. Mark, and H. L. Frisch, Macromolecules **23**, 3481 (1990).

[30] T. A. Vilgis and F. Boué, J. Polym. Sci., Polym. Phys. Ed. **26**, 2291 (1988).

[31] G. Heinrich and T. A. Vilgis, Macromolecules **25**, 404 (1992).

[32] Yu. Gotlib and G. Golovachev, J. Non-Cryst. Solids **172**, 850 (1994).

[33] *Elastomeric Polymer Networks*, edited by J. E. Mark and B. Erman (Prentice-Hall, Englewood Cliffs, NJ, 1992).

[34] Y.-K. Leung and B. E. Eichinger, J. Chem. Phys. **80**, 3877 (1984); **80**, 3885 (1984).

[35] L. Y. Shy and B. E. Eichinger, J. Chem. Phys. **90**, 5179 (1989).

[36] J. Gao and J. H. Weiner, Macromolecules **20**, 2520 (1987); **20**, 2525 (1987).

[37] E. R. Duering, K. Kremer, and G. Grest, Phys. Rev. Lett. **67**, 3531 (1991).

[38] E. R. Duering, K. Kremer, and G. Grest, J. Chem. Phys. **101**, 8169 (1994).

[39] H. L. Trautenberg, J. U. Sommer, and D. Goritz, J. Chem. Soc., Faraday Trans. **91**, 2649 (1995).

[40] F. A. Escobedo and J. J. de Pablo, J. Chem. Phys. **104**, 4788 (1996); **106**, 793 (1997).

[41] N. R. Kenkare, S. W. Smith, C. K. Hall, and S. A. Khan, Macromolecules **31**, 5861 (1998).

[42] N. R. Kenkare, C. K. Hall, and S. A. Khan, J. Chem. Phys. **110**, 7556 (1999).

[43] S. Lay, J.-U. Sommer, and A. Blumen, J. Chem. Phys. **110**, 12173 (1999).

[44] R. W. Brotzman and B. E. Eichinger, Macromolecules **14**, 1445 (1981).

[45] N. A. Neuburger and B. E. Eichinger, Macromolecules **21**, 3060 (1988).

[46] Y. Zhao and B. E. Eichinger, Macromolecules **21**, 6988 (1992).

[47] M. Gottlieb and R. J. Gaylord, Macromolecules **17**, 2024 (1984).

[48] G. B. McKenna, K. M. Flynn, and Y.-H. Chen, Macromolecules **22**, 4507 (1989).

[49] J. M. Crissman and G. B. McKenna, Polym. Mater. Sci. Eng. **67**, 487 (1992).
[50] G. B. McKenna and J. M. Crissman, Polym. Mater. Sci. Eng. **68**, 280 (1993).
[51] J. Bastide, L. Leibler, and J. Prost, Macromolecules **23**, 1821 (1990).
[52] E. Mendes, P. Lindner, M. Buzier, F. Boué, and J. Bastide, Phys. Rev. Lett. **66**, 1595 (1991).
[53] N. Weiss, T. van Vliet, and A. Silberberg, J. Polym. Sci., Polym. Phys. Ed. **19**, 1505 (1981).
[54] K. L. Wun and W. Prins, J. Polym. Sci., Polym. Phys. Ed. **12**, 533 (1974).
[55] A. M. Hecht, R. Duplessix, and E. Geissler, Macromolecules **18**, 2167 (1985).
[56] B. Lindemann, U. P. Schröder, and W. Oppermann, Macromolecules **30**, 4073 (1997).
[57] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
[58] R. Kohlrausch, Ann. Phys. (Leipzig) **12**, 393 (1847).
[59] G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).
[60] J. C. Phillips, Rep. Prog. Phys. **59**, 1133 (1996).
[61] M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996).
[62] K. L. Ngai, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994), p. 89.
[63] P. Grassberger and I. Procaccia, J. Chem. Phys. **77**, 6281 (1982).
[64] J. C. Rasaiah, J. Zhu, J. B. Hubbard, and R. J. Rubin, J. Chem. Phys. **93**, 5768 (1990).
[65] J. E. Martin and J. P. Wilcoxon, Phys. Rev. Lett. **61**, 373 (1988).
[66] J. E. Martin, J. Wilcoxon, and J. Odinek, Phys. Rev. A **43**, 858 (1991).
[67] S. Z. Ren, W. F. Shi, W. B. Zwang, and C. M. Sorensen, Phys. Rev. A **45**, 2416 (1992).
[68] S. Z. Ren and C. M. Sorensen, Phys. Rev. Lett. **70**, 1727 (1993).
[69] A. H. Krall and D. A. Weitz, Phys. Rev. Lett. **80**, 778 (1998).
[70] E. K. Hobbie and A. D. Stewart, Phys. Rev. E **61**, 5540 (2000).
[71] A. Heuer and K. Okun, J. Chem. Phys. **106**, 6176 (1997).
[72] G. Iori, E. Marinari, and G. Parisi, Europhys. Lett. **25**, 491 (1994).
[73] J. S. Shafer, J. Chem. Phys. **103**, 761 (1995).
[74] P. Kaatz, P. Prêtre, U. Meier, U. Stalder, C. Bosshard, P. Günter, B. Zysset, M. Stähelin, M. Ahlheim, and F. Lehr, Macromolecules **29**, 1666 (1996).
[75] G. I. Nixon and G. W. Slater, Phys. Rev. E **60**, 3170 (1999).
[76] J. P. Kemp and Z. Y. Chen, Phys. Rev. E **60**, 2994 (1999).
[77] V. Degiorgio, T. Bellini, R. Piazza, F. Mantegazza, and R. E. Goldstein, Phys. Rev. Lett. **64**, 1043 (1990).
[78] B. J. Cherayil, J. Chem. Phys. **97**, 2090 (1992).
[79] J. Colmenero, A. Arbe, and A. Alegría, Phys. Rev. Lett. **71**, 2603 (1993).
[80] J. Colmenero, A. Arbe, G. Coddens, B. Frick, C. Mijangos, and H. Reinecke, Phys. Rev. Lett. **78**, 1928 (1997).
[81] A. Arbe, J. Colmenero, M. Monkenbusch, and D. Richter, Phys. Rev. Lett. **81**, 590 (1998).
[82] E. W. Montroll and J. T. Bendler, J. Stat. Phys. **34**, 129 (1984).
[83] J. T. Bendler and M. F. Shlesinger, Macromolecules **18**, 591 (1985).
[84] Yu. Ya. Gotlib, Doctoral thesis, IMC, St. Petersburg, 1970.
[85] M. L. Mansfield, J. Polym. Sci., Polym. Phys. Ed. **21**, 773 (1983).
[86] Yu. Ya. Gotlib, A. A. Darinskii, and Yu. E. Svetlov, *Physical Kinetics of Macromolecules* (Khimiya, Leningrad, 1986).
[87] J. E. Shore and R. Zwanzig, J. Chem. Phys. **63**, 5445 (1975).
[88] J. L. Skinner, J. Chem. Phys. **79**, 1955 (1983).
[89] A. K. Roy and A. Blumen, J. Chem. Phys. **91**, 4353 (1989).
[90] R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984).
[91] R. Richert and A. Blumen, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994), p. 1.
[92] M. T. Cicerone and M. D. Ediger, J. Chem. Phys. **103**, 5684 (1995).
[93] S. C. Kuebler, A. Hueur, and H. W. Spiess, Phys. Rev. E **56**, 741 (1997).
[94] R. Richert, J. Phys. Chem. B **101**, 6323 (1997).
[95] Yu. Ya. Gotlib and A. A. Gurtovenko, Macromol. Theory Simul. **6**, 523 (1997).
[96] A. A. Gurtovenko and Yu. Ya. Gotlib, Macromolecules **33**, 6578 (2000).
[97] T. Jr. Alfrey, *Mechanical Behaviour of High Polymers* (Interscience, New York, 1948).
[98] J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed. (Wiley, New York, 1980).
[99] F. Chambon and H. H. Winter, J. Rheol. **31**, 683 (1987).
[100] H. H. Winter, P. Morganelli, and F. Chambon, Macromolecules **21**, 532 (1988).
[101] C. Friedrich and L. Heymann, J. Rheol. **32**, 235 (1988).
[102] K. te Nijenhuis and H. H. Winter, Macromolecules **22**, 411 (1989).
[103] J. C. Scanlan and H. H. Winter, Macromolecules **24**, 47 (1991).
[104] A. Izuka, H. H. Winter, and T. Hashimoto, Macromolecules **25**, 2422 (1992); **27**, 6883 (1994).
[105] N. V. Pogodina and H. H. Winter, Macromolecules **31**, 8164 (1998).
[106] T. Alfrey and P. Doty, J. Appl. Phys. **16**, 700 (1945).
[107] E. T. Copson, *Asymptotic Expansions* (Cambridge University Press, Cambridge, 1965).
[108] M. H. Cohen and G. S. Grest, Phys. Rev. B **24**, 4091 (1981).
[109] A. Bunde, S. Havlin, J. Klafter, G. Gräff, and A. Shehter, Phys. Rev. Lett. **78**, 3338 (1997).
[110] J.-U. Sommer, J. Chem. Phys. **95**, 1316 (1991).
[111] P. E. Rouse, J. Chem. Phys. **21**, 1272 (1953).
[112] G. Glatting, R. G. Winkler, and P. Reineker, Macromolecules **28**, 5906 (1995).
[113] M. Schultz and J.-U. Sommer, J. Chem. Phys. **96**, 7102 (1992).
[114] P. Thirion and R. Chasset, Rev. Gen. Caout. Plast. **45**, 859 (1968).
[115] G. B. McKenna and R. J. Gaylord, Polymer **29**, 2027 (1988).
[116] A. A. Gurtovenko and Yu. Ya. Gotlib, Macromolecules **31**, 5756 (1998).
[117] A. A. Gurtovenko, Yu. Ya. Gotlib, and H.-G. Kilian, Macromol. Theory Simul. **9**, 388 (2000).
[118] Yu. Ya. Gotlib and A. A. Gurtovenko, Macromol. Symposia **171**, 69 (2001).
[119] H. G. Kilian, B. Zink, and R. Metzler, J. Chem. Phys. **107**, 8697 (1997).
[120] H. G. Kilian, W. Oppermann, B. Zink, and O. Marti, Comput. Theor. Polym. Sci. **8**, 99 (1998).
[121] M. Köpf and H. G. Kilian, Acta Polym. **50**, 109 (1999).
[122] G. Ronca and G. Allegra, J. Chem. Phys. **63**, 4104 (1975).
[123] Yu. Ya. Gotlib and A. A. Gurtovenko, Macromol. Theory Simul. **9**, 407 (2000).
[124] A. A. Gurtovenko and Yu. Ya. Gotlib, Macromol. Theory Simul. **9**, 416 (2000).
[125] R. B. Blizard, J. Appl. Phys. **22**, 730 (1951).
[126] H. Schiessel and A. Blumen, Macromolecules **28**, 4013 (1995).
[127] H. Schiessel and A. Blumen, J. Phys. A **26**, 5057 (1993).
[128] N. W. Tschoegl, *The Phenomenological Theory of Linear Viscoelastic Behavior* (Springer, Berlin, 1989).
[129] A. A. Gurtovenko and A. Blumen, J. Chem. Phys. **115**, 4924 (2001).