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Dynamics of heterogeneous polymer networks

Thomas A. Vilgis
Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Federal Republic of Germany

Gert Heinrich
Continental AG, Werk Stöcken, Materialforschung, Postfach 169, D-30001 Hannover, Federal Republic of Germany

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This paper discusses the effect of heterogeneities in cross-link density on network dynamics. The dynamic effects of such networks are studied in two limits, i.e., at short times and at long times. It is shown that heterogeneities in cross-link density alter the chain dynamics strongly. This has several effects on the segmental motion, ruled by an additional time scale that is set mainly by fluctuations in the cross-link density. It is shown that the chains localize more strongly in the long-time limit as given in homogeneous rubbers. The localization of chains is essential for the dynamic response of networks. The collective dynamics of the whole network is investigated by the use of a Förster transfer model, which encounters the heterogeneities on larger scales. This method has not been applied to networks previously and leads to predictions on creep dynamics and long-time moduli.

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I. INTRODUCTION

The effects of heterogeneities in cross-linked polymer melts and rubbers have been recognized to be of great importance in pure academic science and in technological applications. These are generally difficult problems: First, they have been ignored in all of the classical network theories [1–3], which consider often very simple approximations and very ideal (and so unrealistic) networks, which never appear in nature. Second, it has been made evident to be of technological relevance for the ultimate properties of networks [4]. Third, it is now believed that heterogeneities have significant effects in small-angle-neutron-scattering experiments [5]. First considerations for studying the effect of heterogeneities in swollen gels seem to be very promising. Bastide, Leibler, and Prost introduced anisotropy fluctuations in swollen gels by considering "frozen blobs" [6]. Later, Onuki [7] prescribed a phenomenological theory using ideas from continuum-mechanics and thermodynamics, applied on coarse-grained scales with the additivity hypothesis for the elastic and solvent free energy, an hypothesis that is to some extent questionable [3], but often useful to find first-order results.

Attempts to predict the effects of heterogeneities for bulk networks (cross-linked melts) have been given independently by both of us [8,9], where it has been demonstrated that the elastic free energy is reduced by strong heterogeneities whereas the deformation dependence is not altered. Severe anisotropy effects can be expected if small-angle-neutron-scattering experiments are performed, leading to the so-called butterfly patterns [5]. These effects are, however, more of a fundamental nature and give detailed insight to the local structure of the networks, rather than equations of state derived from macroscopic free energies.

Another technically very important effect of heterogeneities in cross-link density is given by the strong improvement of the ultimate properties in rubber engineering. Ultimate mechanical properties of elastomers, such as tensile stress elongation on break, depends sensitively on the three-dimensional spatial distribution of cross links throughout the polymer network [4]. So far the efforts to investigate heterogeneities in cross-link density have been restricted to the case of static properties of networks. A general view of heterogeneous networks and a more detailed quantitative picture of the small-strain mechanical properties and scattering behavior is presented by the authors in Ref. [10].

It can be seen already from these introductory remarks that most of these questions are strongly related to the dynamic behavior of the networks. We mention especially the ultimate properties, such as creep experiments or dynamic stress-to-break experiments. Therefore we investigate in the present paper consequences of random heterogeneities on the dynamic behavior of the networks. We distinguish between short-time segmental dynamics of chains and cross links and the long-time dynamics. Both cases have a great physical and practical significance. It is well known that segmental dynamics affects the glass-rubber transition of bulk polymers. Obviously, a heterogeneous distribution of relaxation times caused by the cross-link distribution broadens the distribution zone [11]. A consequence of this dynamical effect is a violation of the time-temperature-superposition principle. This effect is well known if structural heterogeneities are introduced artificially when the rubber is filled by particles with random structure, e.g., carbon black. Long-time relaxation processes are typical features of elastomers and show up in stress-relaxation and creep experiments. Molecular interpretations of these effects are based on controversial assumptions which have been discussed by the authors earlier [12,13].

There exist two extreme kinds of heterogeneities: the first are heterogeneities with no scale invariance, i.e., random fractals; the second type possesses scale invariance, i.e., they are fractal at a certain length. They appear during different processes of network formation. The first type has its reasons in the dynamical processes during cross linking. This can be seen in the following example. Imagine two chains in a melt carrying functional groups at some places along the chain. Both chains obey Rouse or reptation dynamics and a diffusion constant $D \propto 1/(N^a \nu)$ $(a=1,2)$. Here ν is the monomer friction coefficient. If two functional groups react and form a cross link, the result is a branched chain with a diffusion constant $D \propto 1/(2N^a)\nu^{-1}$ that is slower. Moreover, the diffusion constant of the cross-link point is altered also to give $D_c \sim (2/f)\nu^{-1}$ where $f>2$ is the cross-link functionality. The result will be a densely cross-linked region that forms a piece of the network, in which the cross links are clustered together. This happens in all regions of the reactor and the entire sample will have a spatially varying cross-link density. This intuitive picture suggests also that heterogeneities do not disappear upon stirring, before vulcanization. Considerations on the static elastic properties of heterogeneous networks have been given in Ref. [10]. It is shown that the main effect of the random *and* fractal heterogeneities is to lower the domulus. It has been noted that the typical deformation dependence of the free energy βF is *not* altered by such heterogeneities, i.e., it is still given by the classical result [1].

$$\beta F = \tfrac{1}{2}\beta G \sum_{i=1}^{3} \lambda_i^2 \; . \tag{1.1}$$

This result suggests that the typical stress strain shapes are not different for heterogeneous and homogeneous networks. This has also been the result in Refs. [8,9] and is implicitly hidden in Onuki's approach [7]. It has also been found that this result holds for systems containing fractal heterogeneities. There, several scaling laws for the modulus can be predicted; see Ref. [10] for details. This could, however, be the reason that heterogeneities cannot be detected easily by static mechanic measurements, since the absolute value of the modulus is very difficult to detect experimentally.

Similar remarks hold for networks that contain fractal-type heterogeneities which result in natural percolation process, such as end-linking reactions or diffusion-limited rubber formation. The static effects of such networks have also been investigated (see Ref. [10] and references therein). We summarize the results briefly because of later connections to the dynamics. The model starts from a number of percolation clusters (made out of chains). These clusters of different sizes according to the percolation model link with each other, and the free energy of such a system is given by

$$\beta F \sim \tfrac{1}{2} M_f \sum_{i=1}^{3} \lambda_i^2 \; , \tag{1.2}$$

where M_f is the number of interfractal cluster cross-link points. This number can be estimated from the percolation model since it should be crudely proportional to the total number clusters. Above the percolation point M_f is of the order

$$M_f \sim |p-p_c|^{-(1/\sigma)(\tau-1)} \; . \tag{1.3}$$

$|p>p_c|$ is the distance from the conversation point. Since for $p \rightarrow 1$, $M_f \sim M$ in the ideal case, M_f can be estimated to be $M_f \approx M|p-p_c|^{-(1/\sigma)(\tau-1)}$, with $\sigma=\frac{1}{2}$, $\tau=\frac{5}{2}$ for the mean-field theory. Notice that $M_f \sim 0$ at $p=p_c$. The elastic modulus for the rubbers near p_c obey therefore a scaling form $G \sim M_f \sim (p-p_c)^{\nu d} \equiv \xi^d$. Also here the heterogeneities are difficult to detect, except in experiments that allow the direct access to the structure of the network and the clusters built in there.

After these introductory remarks on the static effects of heterogeneities we turn in the remainder of the paper to the single-chain and collective dynamics of such networks. The situation is different when dynamic quantities are considered, as it is demonstrated in the following in detail. We have already made simple remarks on the diffusion constant of network chains or cross links. It will be demonstrated below that many results can be derived which suggest that heterogeneities can be detected by dynamic experiments such as quasielastic neutron scattering, viscoelasticity, or NMR.

The paper is organized as follows: in the next section we study the segmental dynamics of heterogeneous networks. In Sec. III we consider in detail the long-time dynamics of heterogeneous rubbers using an analogy with the Förster transfer. For both subjects, to our knowledge, no experiments have been carried out and we will give some predications.

II. SEGMENTAL DYNAMICS OF HETEROGENEOUS NETWORKS

In the following we present consequences of random (nonfractal) heterogeneities of the dynamics in networks. The simplest idea how one can proceed is the use of the same variational model as has been given by Deam and Edwards [14]. This has been used successfully to cross-link diffusion and monomer dynamics in rubbers [15]. This simple model was able to reproduce experimental data by the Richter-Ewen group [16]. This led us to consider the effective Hamiltonian [9,15]

$$H = \frac{3}{2l^2}\int_0^N \left[\frac{\partial \mathbf{R}}{\partial s}\right]^2 ds + \tfrac{1}{6} q_0^2 l^2 \int_0^N \mathbf{R}^2(s)\,ds \; , \tag{2.1}$$

where $\mathbf{R}(s)$ is the chain segment position (s is the arc parameter), l is the Kuhn segment, and $q_0 = 6M/(Nl^2)$ is the localization parameter of a homogeneous network. The corresponding Langevin equation for the dynamics is given by [15]

$$\nu \left[\frac{\partial \mathbf{R}}{\partial t}\right] + \frac{3k_B T}{l^2}\left[\frac{\partial^2 \mathbf{R}}{\partial s^2}\right] - \frac{l^2 kT}{3} q_0^2 \mathbf{R}(s,t) = \mathbf{f}(s,t) \; , \tag{2.2}$$

where $\mathbf{f}(s,t)$ is a random force with white-noise statistics and a correlation function $\langle f(s,t) f(s',t') \rangle = 2k_B T \nu \delta(t-t')\delta(s-s')$. ν is the monomer friction constant. Clearly the localization is determined by the cross-link distribution $M(\mathbf{r})$. In the case of homogeneous networks it is constant. When the cross links are distributed nonuniformly, i.e., in the sample there exist regions which are cross linked more densely compared to others, it is reasonable to assume that the localization is also nonuniform. case [9,10] we assume the q_0 to be spatially dependent, i.e., containing a random part, i.e., $q_0(\mathbf{r})=6M(\mathbf{r})/(l^2L)\equiv q_0+\delta q_0(\mathbf{r})$. The extra term stems from the nonuniform cross-link distribution $M(\mathbf{r})$. We assume further that $M(\mathbf{r})$ is of the form $M(\mathbf{r})=M+n(\mathbf{r})$ and that the extra term has simple Gaussian statistics. This assumption is reasonable since the mean cross-link number M is very large compared to the deviations $n(\mathbf{r})$. We assume a distribution

$$\langle n(\mathbf{r})n(\mathbf{r}')\rangle=\Delta(\mathbf{r}-\mathbf{r}')p(n(\mathbf{r}))$$

$$=N\exp\left\{-\frac{1}{2\Delta}\int d^3r\,n^2(\mathbf{r})\right\} \tag{2.3}$$

with the usual statistics of vanishing mean value

$$\langle n(\mathbf{r})\rangle=0 \tag{2.4}$$

and

$$\langle n(\mathbf{r})n(\mathbf{r}')\rangle=\Delta\delta(\mathbf{r}-\mathbf{r}')\ , \tag{2.5}$$

where Δ is a measure of the strength of the heterogeneity of the network. This we call in the following the Gaussian heterogeneous network (GHN). We are now in the position to continue with the study of dynamics of the GHN. The ansatz generalizes the Langevin equation that contains a second (random) term, i.e.,

$$\nu\frac{\partial\mathbf{R}}{\partial t}-\frac{3k_BT}{l^2}\left[\frac{\partial^2\mathbf{R}}{\partial s^2}\right]-\frac{l^2kT}{3}[q_0+\delta q_0(\mathbf{r})]^2\mathbf{R}(s,t)$$

$$=\mathbf{f}(s,t)\ . \tag{2.6}$$

It has to be noted that the Fourier transform used in (2.6) acts only on the arclength s on the chain. The spatial coordinate $\mathbf{r}$ itself is a coarse-grained variable that describes the disorder on a larger scale. It is assumed that the Gaussian disorder model utilized here is not sensitive on a local scale where the fluctuation of the cross-link density depends on the arclength. Here the same model is used as in the corresponding theory of the static properties of the GHN [9,10]. Such differential equations are not very simple to solve in general because its formal solution is given by

$$\mathbf{R}(q,\omega)=\frac{\mathbf{f}(q,\omega)}{i\omega\nu+\varepsilon\{q^2+[q_0+\delta q_0(\mathbf{r})]^2\}}\ ,\quad \varepsilon=\frac{3k_BT}{l^2} \tag{2.7}$$

which has to be averaged over the stochastic force $\mathbf{f}$ and the random part of the cross-link density $\delta q_0(\mathbf{r})$. In Eq. (2.7) q is the Fourier conjugate to the contour parameter s and ω is the frequency. For studying the segmental and the cross-link dynamics, correlation functions of the type

$$\langle\mathbf{R}(q,\omega)\mathbf{R}(-q,-\omega)\rangle=C(\mathrm{q}\omega[\delta q_0(\mathbf{r})])\equiv\tilde{C} \tag{2.8}$$

are needed. These still depend on the cross-link realization $\delta q_0(\mathbf{r})$ and have to be averaged after, since the randomness from $\delta q_0(\mathbf{r})$ is quenched. The average over the white-noise force $\mathbf{f}$ can be carried out simply and the correlation function $\tilde{C}$ is given by

$$\tilde{C}(q,\omega)=\frac{1}{\nu^2\omega^2+\varepsilon^2\{(q^2+q_0^2)^2+2(q^2+q_0^2)\delta q_0(\mathbf{r})+[\delta q_0(\mathbf{r})]^2\}}\ , \tag{2.9}$$

which is not simple to average over the Gaussian heterogeneity [compare Eq. (2.3)]

$$P(\delta q_0(\mathbf{r}))\sim N\exp\left\{-\int d^3r\frac{[\delta q_0(\mathbf{r})]^2}{2\Delta}\right\}\ . \tag{2.10}$$

One step is to continue by perturbation theory and a resummation, as can be seen in the following example. Expand Eq. (2.9) to second order in $\delta q_0(\mathbf{r})$ where the bare correlation function

$$C_0(q,\omega)=\frac{1}{\nu^2\omega^2+\varepsilon^2(q^2+q_0^2)^2} \tag{2.11}$$

is used. This leads to an expansion

$$\tilde{C}(q\omega)=C_0(q,\omega)(1-\{2(q^2+q_0^2)\delta q_0(r)+[dq_0(r)]\}^2)C_0(q,\omega)+4(q^2+q_0^2)^2[\delta q_0(r)]^2C_0^2(q,\omega)+(\text{higher orders})\ . \tag{2.12}$$

This series can now be averaged term by term and the result is

$$\langle\tilde{C}(q\omega)\rangle=C_0(q\omega)[1-\Delta C_0(q\omega)+4(q^2+q_0^2)^2\Delta^2C_0(q,\omega)+(\text{higher orders})]\ . \tag{2.13}$$

This can be evaluated term by term and a perturbation series of the correlation function for the segmental dynamics

$$\langle[\mathbf{R}(s,t)-\mathbf{R}(o,o)]^2\rangle+\int\frac{d\omega}{(2\pi)}\int\frac{dq}{(2\pi)}\langle\tilde{C}(q,\omega)\rangle(1-e^{-iqs-i\omega t}) \tag{2.14}$$

can be calculated, but it has to be remembered that higher orders Δ^4, Δ^6, etc., contribute. A crude resummation can be carried out and an approximate form of Eq. (2.13) is given by

$$\langle \tilde{C}(q,\omega)\rangle = C_0(q,\omega)\frac{1}{1+C_0(q,\omega)\Delta\dfrac{1}{1+4(q^2+q_0^2)^2C_0(q,\omega)\Delta}}\,, \tag{2.15}$$

which resembles the first terms of a continued-fraction expansion. This can be brought into a more appropriate form by inverting (2.15) algebraically,

$$\frac{1}{\langle \tilde{C}(q,\omega)\rangle} = \frac{1}{C_0(q,\omega)} + \frac{\Delta}{\dfrac{1}{C_0(q,\omega)}+\Delta(q^2+q_0^2)^2}\,, \tag{2.16}$$

which is a Dyson equation where the last term plays the role of the self-energy. A closer investigation of this correlation function shows that the segmental dynamics become slower by the presence of disorder. The effect of this correlation function can be worked out by finding the poles of Eqs. (2.15) or (2.16). This predicts the interpolation formula for the dynamic evolution of a segment on the chain:

$$\langle[\mathbf{R}(s,t)-\mathbf{R}(s,0)]^2\rangle \approx \left[\frac{\dfrac{\varepsilon}{\nu}t}{1+\left[1+\dfrac{4\Delta t^2}{\nu}\right]^{1/2}+q_0^2\dfrac{t\varepsilon}{\nu}}\right]^{1/2}. \tag{2.17}$$

This formula recovers all limits. For $\Delta=0$ (no heterogeneities) Eq. (2.17) reduces to the results given in Ref. [15], i.e., the short-time limit is dominated by the ordinary Rouse model for the segmental dynamics which is $R\sim t^{1/4}$. At long times the chain localizes and for $t\to\infty$ it becomes $R^2\sim q_0^{-1}$, which is the known result [15] as has been shown experimentally by Richter and Ewen [16]. It is interesting to note that the heterogeneities increase on average the localization parameter and for time scales

$$\frac{4\Delta t^2}{\nu} > 1 \tag{2.18}$$

a new effective localization parameter can be defined, i.e.,

$$q_{0\text{eff}}^2 = q_0^2+\frac{\Delta}{\varepsilon}\,. \tag{2.19}$$

However, the disorder introduces a new time scale

$$\tau_\Delta \sim \left[\frac{\nu}{\Delta}\right]^{1/2}, \tag{2.20}$$

which is proportional to the root of the monomer friction constant, where enhancement of the localization becomes relevant. Note that Eq. (2.17) can be verified experimentally directly by measuring the intermediate dynamical stricture factor $S(\mathbf{k})$, i.e.,

$$S(\mathbf{k},t)=\exp\{-\tfrac{1}{2}\mathbf{k}^2\langle[\mathbf{R}(s,t)-\mathbf{R}(s,0)]^2\rangle\}$$

in quasielastic small-angle neutron scattering.

As a short remark we would like to mention that a more refined (and self-consistent) theory can be produced when the Martin-Siggia-Rose formalism [17] is used. In this method quenched averages can be carried out very simply. This is mentioned here because it demonstrates the complexity of this problem and that more refined theories can be produced where the simple results obtained above turn out to be only an approximate limit. The corresponding generating dynamical functional can be written as

$$Z(\{\mathbf{J},\hat{\mathbf{J}}\}\delta q_0) = \int \delta\hat{R}(q\omega)\delta R(q\omega)\exp\left\{\sum_{q,\omega}\hat{\mathbf{R}}(q\omega)\hat{\mathbf{J}}(q\omega)+\mathbf{R}(q\omega)\hat{\mathbf{J}}(q\omega) + i\sum_{q,\omega}\hat{\mathbf{R}}(q\omega)\{i\omega+\varepsilon(q^2)+[q_0+\delta q_0(\mathbf{r})]^2\}\mathbf{R}(q\omega)-\frac{1}{\nu}|\hat{\mathbf{R}}(q\omega)|^2\right\}, \tag{2.21}$$

where $\hat{\mathbf{R}}(q\omega)$ are the usual auxiliary Martin-Siggia-Rose fields. The random variable $\delta q_0(\mathbf{r})$ can now be averaged out simply since this functional has been constructed in such a way that it is normalized to $Z(\mathbf{0},\mathbf{0})=1$. The correlation function $\tilde{C}(q\omega)$ is given by

$$\tilde{C}(q,\omega)=\frac{\delta^2 Z}{\delta J(q,\omega)\delta J(-q,-\omega)}=\langle \mathbf{R}\,\mathbf{R}\rangle \tag{2.22a}$$

and the response function by the analogous expression

$$\tilde{G}(q,\omega)=i\frac{\delta^2 Z}{\delta\hat{\mathbf{J}}(q,\omega)\delta\mathbf{J}(-q,-\omega)}\equiv i\langle \hat{\mathbf{R}}\,\mathbf{R}\rangle\,. \tag{2.22b}$$

The complex nature of the problem of dynamics of heterogeneous networks is shown upon averaging over the disorder $\delta q_0(\mathbf{r})$. The averaged dynamical functional is given by

$$\begin{aligned} Z(\hat{\mathbf{J}},\mathbf{J}) &\equiv \langle Z(\{\hat{\mathbf{J}},\mathbf{J}\};\delta q_0)\rangle_{\delta q_0} \\ &= \int \delta\hat{\mathbf{R}}(q,\omega)\int \delta\mathbf{R}(q,\omega) e^{\sum_{q,\omega}\hat{\mathbf{R}}(q,\omega)\hat{\mathbf{J}}(q,\omega)+\mathbf{R}(q,\omega)\mathbf{J}(q,\omega)} \\ &\quad\times\exp\left\{\sum_{q,\omega} i\hat{\mathbf{R}}(q,\omega)(i\omega+q^2+q_0^2)\mathbf{R}(q,\omega) - \frac{q_0^2}{\frac{1}{\Delta}+\sum_{p,z}\hat{\mathbf{R}}(pz)\mathbf{R}(-p-z)}\sum_{\substack{q,\omega\\ p,\Omega}}\hat{\mathbf{R}}(q,\omega)\hat{\mathbf{R}}(p,\Omega)\mathbf{R}(-q,\omega)\mathbf{R}(-p,-\Omega)\right\}, \end{aligned} \tag{2.23}$$

be solved self-consistently, leading to four coupled integrodifferential equations for the correlation and response function. This will be analyzed in detail in a separate work, since it is beyond the scope of this study. In the following section we proceed with the long-time relaxation effects of heterogeneities.

III. LONG-TIME DYNAMICS OF (NONFRACTAL) HETEROGENEOUS NETWORKS

So far we have discussed the segmental dynamics of chains and cross links embedded in a heterogeneous network. In this section the long-time dynamics of the ensemble of chains is discussed. This is especially important when relaxation experiments are performed, which measure the dynamic behavior of the modulus. It is well known that the modulus can be written as $G(t)=G_0\Phi(t)$ in general, as long as the cross-link points are constant during the experiment. The total number of cross-link points determines G_0, which is the static modulus mentioned in the Introduction. For the purpose of studying dynamic behavior of the modulus, it is enough to concentrate on the time-dependent relaxation function $\Phi(t)$. In a previous paper we had demonstrated that using a simple model, the empirical Thirrion-Chasset law [13], can be derived [12]. This was given by a power-law decay of the relaxation function, i.e.,

$$\Phi(t)\sim t^{-n_e}, \tag{3.1}$$

where n_e can be related to the tube diameter, i.e., $n_e \approx (l/a)^2$, where l is the Kuhn length and a the tube diameter. Note that the ration $n_e \approx (l/a)^2$ appears naturally "everywhere" in polymer dynamics and rubber theory [18,1–5] and is experimentally accessible. To derive Eq. (3.1) we used a uniform cross-link density. In the following we extend this work to heterogeneous networks.

To do this we adopt a model that is often used to study relaxation phenomena in disordered systems: the Förster transfer [19]. The idea for its application to polymer networks with inhomogeneities can be summarized as follows: We consider the network on a simple lattice where all sites are occupied with polymer units or with a cross-linking unit. The probability p that a lattice site is occupied by a cross-linking point reads

$$p=N_c^{-1},$$

where $N_c(\gg 1)$ is the number of units per network chains. The network chains are highly interpenetrated, i.e., each coil contains many other chains. The spatial distance between a test junction and a spatial neighbor is smaller than the average distance between two topological neighbors that are connected via a network strand. The spatial path crosses a large number of cross links and is therefore longer than the contour length between topological neighbors. In [12] we argued that, after a distortion of the sample, a cooperative relaxation in the rearrangement of the cross-link positions takes place that leads to the typical anomalous long-time relaxation behavior. We assume therefore that a characteristic single relaxation time $\tau(\mathbf{R}_i)$ of the rearrangement between a test junction and the spatial neighbor depends on the spatial distance $\mathbf{R}_i$. The corresponding single relaxation function is then

$$\Phi_i(t)\sim e^{-t/[\tau(\mathbf{R}_i)]}. \tag{3.2}$$

For a fixed configuration $\{R_i\}$ of the cross-link positions we obtain the total relaxation

$$\tilde{\Phi}(\{\mathbf{R}_i\},t)=\prod_{i=1} e^{-t/[\tau(\mathbf{R}_i)]}, \tag{3.3}$$

where the product excludes the test junction. The average overall configurations of the statistically distributed cross links give with $p \ll 1$ the expression [20,21]

$$\begin{aligned} \tilde{\Phi}(t) &\equiv \langle \Phi(\{\mathbf{R}_i\},t)\rangle_{\{\mathbf{R}_i\}} \\ &\simeq \Phi_0 \exp\left\{-p\sum_i \left[1-e^{-t/[\tau(\mathbf{R}_1)]}\right]\right\}. \end{aligned} \tag{3.4}$$

Introducing the cross-link density

$$m(\mathbf{R})\equiv\frac{M(\mathbf{R})}{V}=\sum_i \delta(\mathbf{R}-\mathbf{R}_i) \tag{3.5}$$

leads to the overall relaxation functional for a given cross-link density $m(\mathbf{R})$:

$$\tilde{\Phi}(t)=\Phi_0 \exp\left\{-p\int d^3\mathbf{R}\, m(\mathbf{R})(1-e^{-t/[\tau(\mathbf{R})]})\right\} . \tag{3.6}$$

We introduce now a fluctuation $n(\mathbf{R})$ in the cross-link density for heterogeneous networks, i.e., $M(\mathbf{R})=M+n(\mathbf{R})$ as before. In the following it is convenient to use cross-link densities, which are denoted by lowercase symbols, e.g., for the mean cross-link density $m_0=M/V$, etc., where V is the volume of the sample. Applying the Gaussian distribution, Eqs. (2.3)–(2.9), leads to the observable relaxation

$$\Phi(t)=\int \delta(n(\mathbf{R}))\tilde{\Phi}(t,\{n(\mathbf{R})\})p(\{n(\mathbf{R})\}) . \tag{3.7}$$

Performing the functional integral yields the following separation:

$$\Phi(t)=\Phi_1(t)\varphi(t) , \tag{3.8a}$$

where

$$\begin{aligned}\Phi_1(t)&=\Phi_0 \exp\left\{-pm_0\int d^3\mathbf{R}(1-e^{-t/[\tau(\mathbf{R})]})\right\} ,\\ \varphi(t)&=\exp\left\{\frac{\Delta p^2}{2}\int d^3\mathbf{R}(1-e^{-t/[\tau(\mathbf{R})]})^2\right\} .\end{aligned} \tag{3.8b}$$

Only $\varphi_1(t)$ contains the effects of heterogeneities. $\varphi_1(t)$ is similar to the relaxation function in the Förster transfer [20]. The final form of the relaxation function depends on the form of the single relaxation time $\tau(\mathbf{R})$. We consider the two limiting cases of power-law and exponential decay:

$$\tau(\mathbf{R})=\tau_0\left[\frac{R}{l}\right]^{d_w}\sim N^{d_2/2} , \tag{3.9a}$$

$$\tau(\mathbf{R})=\tau_0 e^{\gamma(R/l)}\sim e^{\gamma\sqrt{N}} , \tag{3.9b}$$

where N is here the number of Kuhn segments between two neighbors along the spatial path. These two limiting cases have a neat physical reason. Equation (3.9a) corresponds to the local segmental dynamics that is relevant for time scales where the chain segment is not affected by cross-link constraint. It is simply the diffusion law for a segment. d_w is the corresponding dynamical exponent (or walk dimension) for the "defect" motion along the polymer chain, i.e., $d_w=8,4,3$ for reptation, Rouse dynamics, or dynamics including hydrodynamic interaction in swollen gels, respectively. The maximum time of the validity of Eq. (3.9a) is given by $\tau_{\max}\sim N$, i.e., where translational motion starts. This time $\tau_{\max}$ determines also the crossover time where Eq. (3.9b) starts to become important. The exponential increase of the typical relaxation time is due to the cross-link constraint and has been used successfully in Ref. [12], and has a similar origin as in star-branched molecules [22].

Performing the integrals in Eq. (3.8) we obtain for $t/\tau\gg 1$ the following results: For Eq. (3.9a),

$$\Phi_1(t)=\Phi_0 \exp\left\{-\alpha_1\left[\frac{t}{\tau_0}\right]^{3/d_w}\right\} , \tag{3.10a}$$

$$\varphi(t)=\exp\left\{+\alpha_1\frac{\Delta p}{m_0}\left[\frac{t}{\tau_0}\right]^{3/d_w}\right\} , \tag{3.10b}$$

where the constant α_1 is given by

$$\alpha_1=\frac{4\pi}{3}pm_0\Gamma\left[1-\frac{3}{d_w}\right](1-2^{(3/d_w)-1})^2, \quad d_w\geq 3 \tag{3.10c}$$

[$\Gamma(x)$ being the gamma function]. Similarly we find for the second case [Eq. (3.9b)]

$$\Phi_1(t)=\Phi_0 \exp\left\{-\beta_1 \ln^3\left[\frac{t}{\tau_0}\right]\right\} , \tag{3.11a}$$

$$\varphi(t)=\exp\left\{+\beta_1\frac{\Delta p}{2m_0}\ln^3\left[\frac{t}{\tau_0}\right]\right\} , \tag{3.11b}$$

$$\beta_1=r\pi\frac{pm_0}{\gamma^3} . \tag{3.11c}$$

The anomalous decay function Φ_1 was also found in the Förster transfer model describing defect relaxation in solids [21]. Equations (3.10b) and (3.11b) indicate that the form of the time dependence of the long-time relaxation is not altered by heterogeneities. Hence, Eqs. (3.10a) and (3.10b), and (3.11a) and (3.11b), can be summarized and give for the first case [Eq. (3.9a)]

$$\Phi_1(t)=\Phi_0 \exp\left\{-\alpha\left[\frac{t}{\tau_0}\right]^{3/d_w}\right\} , \tag{3.12a}$$

with

$$\alpha=\alpha_1\left[1-x\frac{f}{4}\frac{\Delta}{n_s}\right] , \tag{3.12b}$$

and $x=2(1-2^{(3/d_w)-1})$, i.e., $0\leq x<1$ and $x=0$ for $d_w=3$ and $x\to 1$ for $q\to\infty$. For the second case [Eq. (3.9b)]

$$\Phi(t)=\Phi_0 \exp\left\{-\beta\ln^3\left[\frac{t}{\tau_0}\right]\right\} , \tag{3.13a}$$

$$\beta=\beta_1\left[1-\frac{f}{4}\frac{\Delta}{n_s}\right] \tag{3.13b}$$

for the number of network chains and therefore $p/(2m_0)=f/(4n_s)$, where n_s is the constant segment number density of the network. The relations $\alpha,\beta>0$ and $\alpha<\alpha_1$, $\beta<\beta_1$ are always fulfilled for realistic networks because $\Delta/n_s\ll 1$ in all cases. Fluctuations in cross-link density are always smaller than the average segment density. Equations (3.12a) and (3.13a) predict a slowing down of the long-time relaxation behavior.

We finally note that the Thirrion-Chasset law (3.1) is only a special case of the Förster transfer model for the case (3.9b). It can be derived under the assumption that the single relaxation time depends on the topological distance $R=lN_c^{1/2}$ between the test junction and its topological neighbors [21]. Again we point out that these results can be compared to experiments, since the creep modulus is directly proportional to these correlation functions $\Phi(t)$, which are calculated above.

IV. DYNAMICS OF NETWORKS CONTAINING FRACTAL HETEROGENEITIES

The dynamics of fractal structures has become a very active field [20]. The dynamic scaling of critical gels in particular has developed quite far [18,23]. It has been shown that a viscoelastic scaling exponent

$$\sigma = \frac{d_f}{d_f + 2} \tag{4.1}$$

describes the frequency dependence of the modulus

$$G(\omega) \sim kT\omega^{\sigma} \tag{4.2}$$

and that an Einstein relation of the form

$$\eta = G\tau_z \tag{4.3}$$

can be established, where τ_z is the longest time in the system.

When we studied the mechanical properties of fractal-containing networks we showed that the static scaling relation

$$G \sim \frac{kT}{\xi^d} \sim (p - p_c)^{d\nu} \tag{4.4}$$

holds, by employing the percolation model and showing that only the interfractal connecting cross links contribute to the elasticity (at least in the low-deformation regime). For the dynamic scaling we expect similar results as given in Refs. [23,24] at scales less than the correlation length and ξ_f where the system is fractal. This will take place at times where a "defect," i.e., a dynamic excitation, will have explored the fractal heterogeneity of size τ_z. But the heterogeneity is collapsed, i.e., saturated, and forms a ball of size $\xi^d \sim m$, where m is the total number of monomers in the heterogeneity. The time involved is here just given by the dimension $d_w = 2d_f/d_s$ where d_s is the spectral dimension (or connectivity dimension [25–27] with an upper bond given by $d_w = 4.5$. For longer times the connectivity of the fractals matters and assuming a "tennis net" where the net elements are the fractal heterogeneities one returns to the classical behavior $G(\omega) \sim \omega^2$. Thus we expect frequency behavior of the modulus that is ruled by $\sigma \approx 0.6$ for times less than $\tau_d \sim \xi_4^{4.5}$ are classical Rouse behavior for time $t > \tau_d$. Again these predictions can be checked experimentally by a frequency sweep in a mechanical spectrometer.

V. DISCUSSION AND FINAL REMARKS

We have discussed several possibilities of how heterogeneities in cross-linked polymer melts can affect dynamic properties. Local methods such as neutron scattering in statics and NMR, dielectric, or mechanical spectroscopy in dynamics are well suited for the determination of heterogeneity effects on a dynamical experiment. It is also important to distinguish between two kinds of heterogeneities: fractal and random inhomogeneities. Both behave substantially differently and some completely different methods have to be used. Let us summarize both typical results on their physical consequences.

In Sec. II we have shown the significant effect of random heterogeneities on the segmental dynamics. The main result is given in Eq. (2.17). It can be summarized by

$$\langle [\mathbf{R}(s,t) - \mathbf{R}(s,0)]^2 \rangle \approx \left[\frac{at}{1 + \sqrt{1 + \Delta b t^2 + q_0^2 a t}} \right]^{1/2} .$$

This result contains all known cases. For example, if the disorder is not important, i.e., $\Delta = 0$, the chain segment follows Rouse dynamics for short times ($aq_0^2 t < 1$) and becomes localized for larger times. For heterogeneous samples the disorder is relevant. The disorder introduces a new characteristic time

$$\tau_\Delta \propto \frac{1}{\Delta} .$$

It is an intermediate time scale, relevant for the time interval

$$\frac{1}{a} < t < \frac{1}{q_0^2 a} .$$

Again, the localization takes place at later times. Such results can be checked experimentally by quasielastic small-angle neutron scattering, NMR, or light scattering. Section III used the Förster transfer to study the dynamic behavior of the modulus. Such considerations are of importance when creep measurements are performed. By Fourier transform of the decay function $\Phi(t)$ the mechanical spectrum of the modulus can be compared to mechanical data from dynamic mechanic measurements. Such Fourier transforms are naturally very hard when slow relaxation such as stretched exponentials or logarithms in the exponents are dominating the dynamics. Nevertheless it is known that such decay functions broaden the relaxation significantly, comparable to the nonexponential decay in glass-forming liquids (see, for example, [28] for the latest review collection). Fractal heterogeneities can be detected along the same lines by mechanical spectroscopy. Whether one can distinguish between scaling function of fractal nature and those occurring from random heterogeneities by such experiments alone has to be questionable. We expect that different information about the cross-linking process and scattering data has to be taken into account.

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