Fractal dynamics in polymeric glasses

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We have analyzed the hole dynamics on a fractal lattice, and have obtained a spectral dimension (d) for the state density. This is the only independent fractal dimension needed in the discussions of the self-similar connectivity of hole motions, and the fluctuation-dissipation relationship controlling the glass relaxation and stretched exponential. The glass relaxation is a result of the local configurational rearrangements of molecular segments that is described by the hole motion. In contrast to polymeric fractals of flexible chains in solution or melt, we find that d decreases as the system is changed from linear to cross-linked polymers.

The fractal nature of flexible polymer chains in solution or melt has been studied extensively in recent years [1–4]. The static and dynamic properties of polymeric fractals have been discussed at least in terms of three basic fractal dimensions [5,6]. One of them is the Hausdorff dimension (d_f), which provides the mass, or the total chain length, and radius (of gyration) scaling [7]. In the glassy state, the viscoelastic properties of polymers are dominated by the short-range motion of molecular segments, and are not much affected by differences in molecular weight or molecular weight distribution [8], except when molecular weight is very small, which we shall not consider in this paper. The concept of the hole (free volume) has been used to describe segmental mobility [8–10]. There are important differences between the hole dynamics in the glassy state and chain dynamics in the liquid or molten states. Holes do not have the fractal or Hausdorff dimension d_f, because the well-known mass-size scaling for polymer chains does not exist for holes. In addition, the motion of holes is governed by different equations.

In this paper, we analyze the spatial and time-dependent hole density-density correlation function, and produce a fractal dimension (d), which is independent of the spatial configuration. This intrinsic parameter allows us to discuss the self-similar connectivity of hole motion, and the spectra for the hole density of states and for the relaxation times, without having to know the Hausdorff dimension beforehand. The viscoelastic loss modulus is then calculated as a result of energy dissipation caused by the nonequilibrium hole density fluctuations in glassy polymers. This leads to the determination of the parameter β of the stretched exponential function. Finally, the important difference between the hole and chain connectivities in an ideal phantom network is discussed.

Amorphous solids are not in thermodynamic equilibrium. The departures from equilibrium for holes and bond rotations have been treated as a random stochastic process. We have reported that the conformational activation energy controlling the rotational relaxation of bonds is between one and two orders of magnitude lower than the hole activation energy [10]. As a result, the conform-er relaxes much faster than the hole. Since the physical properties of glasses vary slowly in time (t), the dominant contribution to the structural relaxation and physical aging in glasses is from the hole. The hole configurational space in a quenched and annealed glass is divided into regions separated by barriers. The local excess of hole number density from the equilibrium value of the hole number density $\langle n \rangle$ within a region is

$$\delta n(\mathbf{r},t) = n(\mathbf{r},t) - \langle n \rangle . \tag{1}$$

Consider that a polymer is cooled from liquid to glass, where the sample is annealed. During isothermal annealing, the number of holes is close to a conserved quantity. The local excess of number density (δn) cannot disappear locally but can only relax by spreading slowly over the entire region and is governed by

$$\frac{\partial \delta n(\mathbf{r},t)}{\partial t} = \int [W(\mathbf{r}|\mathbf{r}')\delta n(\mathbf{r}',t) - W(\mathbf{r}'|\mathbf{r})\delta n(\mathbf{r},t)]d\mathbf{r}' , \tag{2}$$

where $W(\mathbf{r}|\mathbf{r}')$ is the transition probability per unit time jumping from $\mathbf{r}'$ to $\mathbf{r}$, and the integration is over the space. When necessary condition of convergence is assumed, Eq. (2) can be rewritten as [10]

$$\frac{\partial \delta n(\mathbf{r},t)}{\partial t} = \sum_{m=1}^{\infty} \frac{1}{m!} (-\nabla)^m b_m(\mathbf{r})\delta n(\mathbf{r},t) , \tag{3}$$

where b_m is the mth moment of the transition rate $W(\mathbf{r}'|\mathbf{r})$:

$$b_m(\mathbf{r}) = \int (\mathbf{r}'-\mathbf{r})^m W(\mathbf{r}'|\mathbf{r})d\mathbf{r}' .$$

Equation (3) is a partial differential equation of infinite order and cannot be solved in general. When all the properties of glass vary slowly in space and time, the left-hand side of Eq. (3) can be truncated,

$$\sum_{m=1}^{\infty} \frac{1}{m!} (-\nabla)^m b_m(\mathbf{r})\delta n(\mathbf{r},t) \simeq \nabla \cdot D \nabla \delta n(\mathbf{r},t) + \cdots ,$$

where $D = b_2/2$ is the local diffusion coefficient. We have assumed here that the system is in a quasiequilibrium state and in the absence of an external field. This reveals that the dynamics of the hole are diffusive and not vibrational. We shall see that the use of the hole density-density correlation function is extremely useful in the present study of the space- and time-dependent cooperative phenomenon. The Green's function can be defined as

$$G(\mathbf{r},t) = \frac{\langle \delta n(\mathbf{r},t)\delta n(0,0) \rangle}{\langle \delta n^2 \rangle} . \tag{4}$$

The angular brackets denote an equilibrium ensemble average. $G(\mathbf{r},t)$ is invariant under translations of $\mathbf{r}$ and t, and vanishes when r and/or t are very large. We look for the solution of the equation:

$$\left[\frac{\partial}{\partial t} - \nabla \cdot D\nabla \right] G(\mathbf{r},t) = \delta(\mathbf{r})\delta(t) , \tag{5}$$

where δ is Dirac's delta function. When D is a constant, the solution of Eq. (5) displays the well-known Gaussian spreading. However, we have a spatial dependent diffusion coefficient. Let us introduce the Fourier transform in space,

$$G(\mathbf{q},t) = \int G(\mathbf{r},t)e^{-i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r} ,$$

where $\mathbf{q}$ is the wave vector of the fluctuation. Equation (5) can be generalized to the form

$$\left[\frac{\partial}{\partial t} - Dq^{2+\nu} \right] G(\mathbf{q},t) = \delta(t) , \tag{6}$$

where ν produces the fractal dimension d, which defines a self-similar scaling between wave numbers:

$$q \sim q_\nu^d \quad \text{with } d = \frac{2}{2+\nu} > 0 . \tag{7}$$

Either d or ν is the only independent exponent in this paper. By using Eq. (7), Eq. (6) is transformed to

$$\left[\frac{\partial}{\partial t} - D_\nu q_\nu^2 \right] G(q_\nu,t) = \delta(t) . \tag{8}$$

On the fractal lattice, D_ν is a constant, and the holes exhibit Gaussian characteristics. The self-similarity of the fractal has the dilation symmetry shown in Eq. (7). Using the Fourier transformation in time,

$$G(q_\nu,\omega) = \int_{-\infty}^{\infty} G(q_\nu,t)e^{i\omega t}dt ,$$

we obtain the solution of Eq. (8),

$$G(\omega) = \sum_{q_\nu} \frac{1}{D_\nu q_\nu^2 - i\omega} = \int_0^{q_m} \frac{\rho(q_\nu)dq_\nu}{D_\nu q_\nu^2 - i\omega} , \tag{9}$$

where ρ is the state density. An approximation has been made here that the hole number spectrum is extended up to the maximum value q_m. This is consistent with the truncation made on the left-hand side of Eq. (3). In Eq. (9), we have [7]

$$\tau_\nu = \frac{1}{D_\nu q_\nu^2} \tag{10}$$

as a local relaxation time. Equation (9) shows that the density of states does not carry as much information about the structures of the states of the system as does the Green's function. The direction of preferential orientation for the hole motion in an amorphous polymer is completely arbitrary. In the absence of an external field, the lattice exerts no orienting influence of the hole dynamics. The number of modes per unit length along the hole path with a wave number between q and $q+dq$ can be expressed in terms of the number of modes on the fractal lattice by using Eqs. (7):

$$\frac{dq}{2\pi} \sim \frac{d}{2\pi} q_\nu^{d-1} dq_\nu .$$

Using Eq. (10), we obtain

$$\rho(q_\nu)dq_\nu \sim q_\nu^{d-1} dq_\nu \sim \tau_\nu^{-d/2} d\tau_\nu , \tag{11}$$

which, due to its diffusive nature, has different time dependence than that of vibrational fractons [5]. Substituting Eq. (11) into Eq. (9) leads to the asymptotic solution

$$G(\omega) \sim \int_\tau^\infty \frac{\tau_\nu^{-d/2} d\tau_\nu}{1 - i\omega\tau_\nu} \approx \int_\tau^\infty \frac{\tau_\nu^{-d/2} d\tau_\nu}{-i\omega\tau_\nu} = -\frac{2}{d} \frac{\tau^{-d/2}}{i\omega}$$

$$\text{for } \omega\tau_\nu \gg 1 , \tag{12}$$

where

$$\tau = \frac{1}{D_\nu q_m^2} \tag{13}$$

is the macroscopic relaxation time. The change in the state of glass during isothermal annealing is accompanied by dissipation (absorption) of energy, which is related to the density fluctuations of the hole from its equilibrium value defined in Eq. (4). In accordance with the method of generalized susceptibility [11], the viscoelastic loss modulus (E''), which measures the energy dissipation, is determined from Eq. (12) as

$$E''(\omega) \sim \mathrm{Im} G(\omega) \sim \tau^{-d/2} . \tag{14}$$

Phenomenologically, the viscoelastic relaxation modulus can be written as [12–14]

$$E(t) = E_\infty + (E_0 - E_\infty)\exp\left[-\left[\frac{t}{\tau} \right]^\beta \right] , \quad 0 < \beta \le 1 , \tag{15}$$

where E_0 and E_∞ are the unrelaxed and relaxed moduli, respectively. While this equation is valid for the bulk, shear, or tensile modulus, β and τ are independent of the type of stress fields applied to the system [13]. The above equation gives the loss modulus [14]

$$\frac{E''}{E_0 - E_\infty} = \sum_{m=1}^\infty \frac{(-1)^{m+1}\Gamma(m\beta+1)}{m!(\omega\tau)^{m\beta}}\sin(m\beta\pi/2) , \tag{16}$$

where Γ is the gamma function. The leading term provides a useful asymptotic expression in the glassy state

$$E''(\omega) \sim (\omega\tau)^{-\beta} \quad \text{for } \omega\tau \gg 1 \ . \tag{17}$$

Comparing Eqs. (14) and (17) yields

$$\beta = \frac{d}{2} = \frac{1}{2+v} \ . \tag{18}$$

By looking at Eqs. (11) and (12), Eq. (18) confirms the customary way of relating β of the stretched exponential function, Eq. (15), to the relaxation-time spectrum. The glassy-state relaxation is dominated by the part of the spectrum having longer relaxation times.

In accordance with Eqs. (6) and (18), one finds the diffusion length

$$\langle \Delta r^2 \rangle^{1/2} \equiv R \sim t^{\beta} \tag{19}$$

and the local diffusion coefficient

$$D = \frac{R^2}{2t} \sim R^{-v} \ . \tag{20}$$

The divergence of the diffusivity in Eq. (20) at $R = 0$ for $v > 0$ was the main reason behind the fractal dimension that was introduced in Eq. (6) together with a spatial scale transformation, Eq. (7). For linear polymers, $d = 1$, Eqs. (18) and (20) show that the diffusion coefficient is spatially independent because the spreading of excess holes is Gaussian ($v = 0$). The theoretical $\beta = 0.5$ is found to be in good agreement with the measured [13] $\beta = 0.48$. When $0 < d < 1$, we have $\beta < \frac{1}{2}$ and $v > 0$; the random motion of holes slows down as the local diffusion coefficient in Euclidean space decreases with distance. If $-1 \le v < 0$ which implies $\frac{1}{2} < \beta \le 1$, Eq. (20) reveals that a hole moves faster as it travels, because the diffusion coefficient increases with distance. Such a motion is more like hopping than diffusion. Since these hops must occur on all length scales due to the self-similarity in fractal structure, the explanation is related to a long-range interaction which affects the local environment of the system. It has an effect equivalent to an external field, i.e., the presence of the b_1 term in Eq. (3). However, in the study of linear and cross-linked polymers, the interesting range is for $v \ge 0$.

According to recent reports on polymeric fractals, which describe the dynamics of flexible chain macromolecules in solution or melt, the spectral dimension (d_s) is related to the static Hausdorff dimension (d_f) by [1,2]

$$d_s = \frac{2d_f}{2+\theta} \ , \tag{21}$$

where θ is the exponent in the power-law relationship between the local chain diffusivity (D_s) and diffusion length (R_s):

$$D_s \sim R_s^{-\theta} \ . \tag{22}$$

The spectral dimension has the range $1 < d_s \le 2$, which

TABLE I. Comparison of the spectrum dimensions (connectivities) of chain (d_s) and of hole (d).

	Chain [1]	Hole[a]
Formula	$d_s = 2d_f/(2+\theta)$	$d = 2/(2+v)$
Range	$1 < d_s \le 2$	$0 < d \le 1$[b]
Linear ($\theta = 0$)	$d_s = d_f = 1$	$d = 1$
Phantom ($\theta = 4$)	$d_s = \frac{4}{3}$ ($d_f = 4$)	$d = \frac{1}{3}$

[a] There is no "d_f" for holes.
[b] The range of anomalous diffusion.

differs from that for the hole mentioned earlier. For an ideal phantom network, the fractal dimensions are [1]

$$d_f = 4 \ , \quad d_s = \frac{4}{3} \ , \tag{23}$$

which give $\theta = 4$, in accordance with Eq. (21). When an amorphous melt is quenched from liquid to solid, the glass is assumed to have the frozen-in polymer structure. Matching the motion of holes and the chain motions in terms of the segmental mobility and using Eqs. (20) and (22) yields

$$v = \theta \ . \tag{24}$$

The important differences between the hole and chain connectivities are summarized in Table I. In contrast to d_s in polymeric fractals, we find that the fractal dimension d decreases as the system is changed from linear to cross-linked polymers. This is due to the tenuous structure in cross-linked polymers, and the random motion of holes encounters many dead ends and is forced to return. The hole path gets longer and the number density gets smaller. As a result, the connectivity of hole motion decreases significantly and the diffusion coefficient decreases rapidly with distance. Using Eq. (18), we obtain $\beta = \frac{1}{6} \simeq 0.17$, which compares well with the measured $\beta = 0.19$ for cross-linked polymers [14].

In conclusion, we have analyzed the Green's function of collective hole fluctuations in the region of a small wave number or large wavelength where a large number of holes is involved in the glassy state. A fractal dimension (d) combined with a spatial scale transformation is obtained to describe the self-similar connectivity of hole motions, the relaxation spectrum, and the parameter β of the stretched exponential. The fractal dynamics of holes are diffusive, and the diffusivity depends strongly on the tenuous structure in fractal lattices. The connectivity of hole motions decreases as the system is changed from linear to cross-linked polymers, which also results in a smaller value for β.

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