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Fractal Dynamic Theory of Glasses and Physical Aging: Linear and Cross-Linked Polymers

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ABSTRACT: A new statistical dynamic theory of polymeric glasses for temperatures below the glass transition is presented to address important questions in the glassy-state relaxation and physical aging. We have analyzed the hole dynamics and fluctuations on a fractal lattice and have provided a unified treatment of the KAHR (Kovacs–Aklonis–Huchinson–Ramos) equations, the KWW (Kohlrausch–Williams–Watts) function, the density of states, relaxation time, relaxation time spectrum, and the spatial-dependent local diffusivity of holes. The theory predicts that the physical aging rates of both linear and cross-linked polymers increase from zero above T_g to a constant below T_g and then decrease to zero 200 K below T_g. In contrast to all the published expressions, our calculation reveals increasingly smaller activation energies with decreasing temperature in the glassy state. As our analysis is unfolded, a theoretical justification of extending Doolittle's equation from the equilibrium liquid to nonequilibrium glassy states is also revealed.

Introduction

The fractal nature of flexible polymer chains in solution or melt has been studied extensively in recent years.[1-3] The static and dynamic properties of polymeric fractals have been discussed at least in terms of three basic fractal dimensions.[4,5] Such studies have already helped significantly the advancement in the understanding of the structure–property relationships in polymer solutions and melts. But there is no comparable theoretical development in this area of research for polymeric glasses. The lack of progress of extending polymeric fractals from the liquid to glassy states may be due to the fact that the properties of glasses are not much affected by differences in molecular weight or molecular weight distribution but depend on the short-range motion of molecular segments.[6] Therefore, different equations of motion are needed in the glassy state.

For high molecular weight polymers, the glassy-state relaxation is a result of the local configurational rearrangements of molecular segments which are described by the hole motion. In fact, free volume has played a central role in the molecular interpretation of the glassy-state relaxation and physical aging.[6-11] Besides, the Hausdorff dimension, which links the mass (total chain length) and size (radius of gyration) scaling[12] for macromolecules in solution or melt, does not even exist for holes. New scaling law and fractal dimension are therefore needed.

Since all physical properties of glasses vary slowly in time and space, we shall analyze the fractal dynamic of holes in the region of small wavenumber or large wavelength in this paper. This provides us with a useful theoretical basis to discuss the multiorder-parameter equations, relaxation function, relaxation time, relaxation time spectrum, and physical aging. The newly derived equations are then utilized to calculate the structural relaxation and physical aging behavior of linear and cross-linked polymers far below T_g.

Equation of Motion

Consider a lattice consisting of n holes and n_x polymer molecules of x monomer segments each. The total number of lattice sites is written in the form

$$N(t) = n(t) + xn_x \tag{1}$$

where $n \ll N$ and xn_x is independent of time. It is important to mention that $n(t)$ consists of both equilibrium and nonequilibrium contributions in the glassy state. For temperatures above T_g, the nonequilibrium part of n goes to zero. The change of $n(t)$ below T_g defines the glassy state. Minimizing the excess Gibbs free energy due to hole introduction with respect to the hole number, the temperature dependence of equilibrium hole fraction is given by[8]

$$\bar{f}(T) \equiv \frac{\bar{n}}{\bar{N}} = f_r \exp\left[-\frac{\epsilon}{k}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \tag{2}$$

where ϵ is the mean energy of hole formation, k is the Boltzmann constant, and the subscript r refers to the condition at $T = T_r$, which is a fixed quantity near T_g. Equation 2 reveals that holes are created by raising the temperature and are eliminated by lowering it. The "bar" refers to the equilibrium as a fully relaxed state with the nonequilibrium hole fraction

$$\delta(T,t) = \frac{n(t) - \bar{n}}{\bar{N}} = f(T,t) - \bar{f}(T) \tag{3}$$

equal to zero, where $\bar{N}$ is independent of time.

Amorphous solids are not in thermodynamic equilibrium. The departures from equilibrium for holes and bond rotations have been treated as a stochastic process. We have reported that the conformational activation energy controlling the rotational relaxation of bonds is between 1 and 2 orders of magnitude lower than the hole activation energy:[9] Δ(conformer) = 1.94 kcal/mol versus Δ(hole) = 75.3 kcal/mol for poly(vinyl acetate), in the vicinity of the glass transition. As a result, the conformer relaxes much faster than the hole. Since all physical properties of glass vary slowly in time (t), the dominant contribution to the structural relaxation and physical aging in glasses is from the hole. When the polymer is cooled from liquid to glass where the sample is annealed, the hole configurational space in the quenched and annealed glass is divided into *regions separated by barriers.* To include the spatial vector ($\mathbf{r}$) into the analysis, $n(t) - \bar{n}$ is related to the local excess of hole number density $\delta n(\mathbf{r},t)$ by integrating over the volume surrounding the individual hole

$$n(t) - \bar{n} = \int \delta n(\mathbf{r},t)\, d\mathbf{r}$$

Due to its slow varying properties, polymeric glass has been assumed[9,10] to be in a state of quasi-equilibrium. Thus, the number of holes does not change very much during

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isothermal annealing. The local configurational rearrangements of molecular segments through the hole motion are considered as the dominant mechanism[6,9] for the glassy-state relaxation and physical aging. The local excess of number density of a quenched glass relaxes by spreading slowly over the entire region and is governed by[9,10]

$$\frac{\partial \delta n(\mathbf{r},t)}{\partial t} = \int [W(\mathbf{r}|\mathbf{r}')\delta n(\mathbf{r}',t) - W(\mathbf{r}'|\mathbf{r})\delta n(\mathbf{r},\mathrm{t})]\,\mathrm{d}\mathbf{r}' \qquad (4)$$

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 the necessary condition of convergence is assumed, eq 4 can be rewritten as[9,10]

$$\frac{\partial \delta n(\mathbf{r},t)}{\partial t} = \sum_{m=1}^{\infty} \frac{1}{m!}(-\nabla)^m b_m(\mathbf{r})\delta n(\mathbf{r},t) \qquad (5)$$

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

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

Equation 5 is a partial differential equation of infinite order and cannot be solved in general. Since all properties of glass vary slowly in space and time, the left-hand side of eq 5 can be truncated, and the motion of holes in response to molecular fluctuations is then treated as an anomalous diffusion process

$$\left(\frac{\partial}{\partial t} - \nabla\cdot D\,\nabla\right)\delta n(\mathbf{r},t) = 0 \qquad (6)$$

where $D = b_2/2$ is the local diffusion constant. We have assumed here that the system is in a quasi-equilibrium state and in the absence of external field. Equation 6 reveals that the dynamics of the hole are diffusive and not vibrational. Let us assume that initially δn is nonzero only at $\mathbf{r} = 0$. When D is a constant, the solution of eq 6 displays the well-known Gaussian spreading. However, we have a spatial-dependent diffusion coefficient. Let us introduce the Fourier transform in space,

$$\delta n(\mathbf{Q},t) = \int \delta n(\mathbf{r},t)e^{-i\mathbf{Q}\cdot\mathbf{r}}\,\mathrm{d}\mathbf{r}$$

where $\mathbf{Q}$ is the wave vector of the fluctuation. Equation 6 is generalized to the form

$$\left(\frac{\partial}{\partial t} - DQ^{2+\nu}\right)\delta n(\mathbf{Q},t) = 0 \qquad (7)$$

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

$$\mathrm{Q} \sim q_\nu^{\,d}, \qquad \text{with } d = \frac{2}{2+\nu} > 0 \qquad (8)$$

Fractal is by definition a set made of parts similar to the whole.[13] Self-similarity is the basic notion in fractal structure and is also a common feature for all scaling analyses. Therefore, the fractal dimension d is introduced in accordance with the spatial scaling, eq 8. The $Q^{2+\nu}$ dependence in eq 7 is an ansatz since the $\mathbf{r}$ dependence of D in eq 6 is not known. The consequences of this ansatz are broad and far reaching. Using eqs 7 and 8, we shall be able to derive the KAHR equations (eq 14), the KWW function (eq 19), the density of states (eq 27), and the stretched exponent (eq 34) and the spatial-dependent local diffusivity (eq 35) later.

By using eq 8, eq 7 is transformed to

$$\left(\frac{\partial}{\partial t} - D_\nu q_\nu^{\,2}\right)\delta n(q_\nu,t) = 0 \qquad (9)$$

where q_ν is the wavenumber on the fractal lattice, D_ν is a constant, and holes exhibit the Gaussian characteristics on the fractal lattice. The self-similarity of the fractal has dilation symmetry shown in eq 8. Using the Fourier–Laplace transformation in time

$$\delta n[q_\nu,\omega] = \int_0^\infty \delta n(q_\nu,t)e^{i\omega t}\,\mathrm{d}t$$

we obtain from eq 9

$$\delta[\omega] = \sum_{q_\nu} \frac{\delta(q_\nu,t=0)}{D_\nu q_\nu^{\,2} - i\omega} \qquad (10)$$

which solves the initial value problem and is normalized by N. Note that eq 10 is valid only for small wavenumbers or large wavelengths. Defining the local relaxation time

$$\tau_\nu = \frac{1}{D_\nu q_\nu^{\,2}} \qquad (11)$$

the Fourier–Laplace inversion of eq 10 is

$$\delta(t) = \sum_{q_\nu} \delta(q_\nu,t=0)\exp\left[-\frac{t}{\tau_\nu(q_\nu)}\right] \equiv \sum_{q_\nu} \delta(q_\nu,t) \qquad (12)$$

where the summation is carried out over the wavenumbers up to a cutoff q_m. Equation 12 reveals that $\delta(q_\nu,t)$ is the solution of

$$\frac{\mathrm{d}f_i}{\mathrm{d}t} \equiv \frac{\mathrm{d}\delta_i(t)}{\mathrm{d}t} = -\frac{\delta_i(t)}{\tau_i} \qquad (13)$$

where the subscript i is identified with a particular wavenumber on the fractal lattice. Since the index i has the meaning of a wave vector, eq 13 is a discrete version of a continuous equation. When a system is also under a temperature change such as cooling, eq 13 has to be modified by using

$$\frac{\mathrm{d}\bar{f}_i}{\mathrm{d}t} = q\,\frac{\partial \bar{f}_i}{\partial T} = q\,\frac{\epsilon_i \bar{f}_i}{kT^2}$$

Substitution of eq 13 and the above equation into the time derivative of eq 3 yields

$$\frac{\mathrm{d}\delta_i(t)}{\mathrm{d}t} = -\frac{\delta_i(t)}{\tau_i} - q\,\frac{\epsilon_i \bar{f}_i}{kT^2} \qquad (i = 1, ..., L) \qquad (14)$$

where $q = \mathrm{d}T/\mathrm{d}t$ is the cooling rate (<0) and ϵ_i and $\bar{f}_i$ are defined in the same way as those in eq 2. In addition, $\bar{f} = \sum \bar{f}_i$, $\epsilon = \sum \epsilon_i \bar{f}_i/\bar{f}$, and L is an integer which corresponds to the maximum wavenumber q_m. Equation 14 has the discrete form of the well-known KAHR (Kovacs–Aklonis–Huchinson–Ramos) equations,[14] except it is derived and expressed in terms of microscopic parameters.

Relaxation Function

For a system started from equilibrium, the solution of eq 14 has the form[8]

$$\delta(T,t) = \sum_i \delta_i = -\frac{\epsilon}{k}\int_0^t \frac{q\bar{f}}{T^2}\,\Phi(t-t')\,\mathrm{d}t' \qquad (15)$$

where Φ is the relaxation function. The $\Phi(t)$ here is basically a sum of exponential (see eq 11 in ref 8) so that there is naturally a stretched exponential present (see eq 19). Different paths of time integration describe different thermal history behavior of the glassy-state relaxation and recovery kinetics. Some typical examples of thermal history paths for eq 15 were illustrated.[8]

In accordance with the anomalous diffusion process, eq 6, one expects[9,13]

$$\langle \Delta r^2 \rangle^{1/2} \equiv R \sim t^{\beta} \qquad 0 < \beta \leq 1 \tag{16}$$

When the random process is Gaussian, we have $\beta = 1/2$. As we mentioned earlier, there are regions of size (or length l) separated by energy barriers in an amorphous solid. This size is proportional to the time scale (λ) needed for a hole to penetrate a barrier of height (Λ)[15]

$$l \sim \lambda \sim \exp\left(\frac{\Lambda}{kT}\right) \tag{17}$$

Thus

$$\frac{R}{l} \sim \frac{t^{\beta}}{\lambda} = \left(\frac{t}{a}\right)^{\beta}, \qquad \text{with } a = \lambda^{1/\beta} \tag{18}$$

where a is the macroscopic time scale (shift factor). During isothermal annealing, the frozen-in structure of quenched glass starts to relax, and $\Phi(t)$ can be interpreted as the probability that holes have not reached their equilibrium states. The probability of a hole, in the ith wavenumber state, having reached equilibrium in a time interval t is $(n_i/n)(R/l) \approx R/Ll$.[9] Thus, we write

$$\Phi(t) \simeq \left(1 - \frac{R}{Ll}\right)^{L} \rightarrow \exp\left(-\frac{R}{l}\right), \qquad \text{as } L \rightarrow \infty$$

Combining the above equation with eq 18 yields

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \qquad 0 < \beta \leq 1 \tag{19}$$

where $\tau = \tau_r a$. The stretched exponential, eq 19, has the familiar form of the Kohlrausch–Williams–Watts (KWW) equation,[16] except that β and τ are not empirical constants in the present theory and they will be discussed in the next two sections.

Relaxation Time

In our lattice model, each lattice site occupies a single lattice cell of volume v. In view of the cooperative nature of the hole motion, the barrier energy in eq 17 is treated by a mean field average[17] and is related to the Gibbs free energy per molecule (Δg) in a system restrained to single occupancy of cells by

$$\Lambda = \frac{N}{n}\Delta g = \frac{N}{n}(\epsilon + pv - T\Delta s) \tag{20}$$

where p is pressure and is chosen to be zero in the present discussion and Δs is the configuration entropy per molecule. As we mentioned earlier, since the physical properties of glasses vary slowly in time, the system is in a quasi-equilibrium state. The entropy from hole motion can therefore be calculated approximately as[15]

$$\Delta s = k \ln\left[\frac{n(t)}{\bar{n}}\right] = k \ln\left[1 + \frac{\delta(t)}{\bar{f}}\right] \tag{21}$$

Combining eqs 2, 18, 20, and 21 yields

$$a(T, \delta) = \left(\frac{\bar{f} + \delta}{f_r}\right)^{-1/(\beta(\bar{f}+\delta))} \tag{22}$$

At $T = T_r$, we have $\delta = 0$, $\bar{f} = f_r$, and $\tau = \tau_r$ which require $a = 1$. In practice, the shift factor is measured on the logarithmic scale, and eq 12 is rewritten as

$$\ln a(T, \delta) = -\frac{1}{\beta(\bar{f} + \delta)} \ln\left(\frac{\bar{f} + \delta}{f_r}\right) = \frac{1}{\beta(\bar{f} + \delta)}\left[\left(1 - \frac{\bar{f} + \delta}{f_r}\right) + \frac{1}{2}\left(1 - \frac{\bar{f} + \delta}{f_r}\right)^2 + \ldots\right], \qquad \left|1 - \frac{\bar{f} + \delta}{f_r}\right| < 1$$

Therefore

$$\ln a(T, \delta) \simeq \frac{1}{\beta}\left(\frac{1}{\bar{f} + \delta} - \frac{1}{f_r}\right), \qquad \text{as } \frac{\bar{f} + \delta}{f_r} \rightarrow 1 \tag{23a}$$

Equation 23a may be called the "generalized" Doolittle equation. When $T \geq T_g$, we have $\delta = 0$ and eq 23a reduces to the exact form of the Doolittle[18] (or WLF (Williams–Landel–Ferry)[19]) equation. Equation 23a can also be written in the form

$$\ln a(T, \delta) \simeq -\frac{\alpha_r(T - T_r) + \delta}{\beta f_r^{\,2}} \qquad \alpha_r = \epsilon f_r / k T_r^{\,2} \tag{23b}$$

In the vicinity of T_g, eq 23 together with eqs 2, 15, and 19 has already been utilized successively in analyzing the experimental measurements of volume relaxation and recovery,[8] of yield and stress–strain behavior,[17,20] and of viscoelastic relaxation.[21,22] We shall see that eq 22 extends the range of application far below T_g.

Relaxation Time Spectrum

The parameter β of stretched exponential should be a function of local interaction, which is related to the nonzero ν mentioned in eqs 7 and 8. Let us consider the hole density–density correlation function and write Green's function

$$G(\mathbf{r},t) = \frac{\langle \delta n(\mathbf{r},t)\, \delta n(\mathbf{0},0) \rangle}{\langle \delta n^2 \rangle} \tag{24}$$

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

$$\left(\frac{\partial}{\partial t} - \nabla \cdot D \nabla\right) G(\mathbf{r},t) = \delta(\mathbf{r})\, \delta(t) \tag{25}$$

where δ is Dirac's delta function. Following the same procedure led to eq 10, except by using two-sided Fourier time transform here, we obtain the solution of eq 25

$$G(\omega) = \sum_{q_\nu} \frac{1}{D_\nu q_\nu^{\,2} - i\omega} = \int_0^{q_m} \frac{\rho(q_\nu)\, \mathrm{d}q_\nu}{D_\nu q_\nu^{\,2} - i\omega} \tag{26}$$

where ρ is the density of states. The number of modes per unit length along the hole path with wavenumber between Q and $Q + \mathrm{d}Q$ can be expressed in terms of the number of modes on the fractal lattice by using eq 8

$$\frac{\mathrm{d}Q}{2\pi} \sim \frac{d}{2\pi} q_\nu^{\,d-1}\, \mathrm{d}q_\nu$$

Using eq 11, we obtain

$$\rho(q_\nu)\, \mathrm{d}q_\nu \sim q_\nu^{\,d-1}\, \mathrm{d}q_\nu \sim \tau_\nu^{\,-d/2}\, \mathrm{d}\tau_\nu \tag{27}$$

which, due to its diffusive nature, has a different time dependence than that of vibrational fractons.[4] Substituting eq 27 into eq 26 leads to the asymptotic solution

$$G(\omega) \sim \int_\tau^\infty \frac{\tau_\nu^{\,-d/2}\, \mathrm{d}\tau_\nu}{1 - i\omega\tau_\nu} \approx \int_\tau^\infty \frac{\tau_\nu^{\,-d/2}\, \mathrm{d}\tau_\nu}{-i\omega\tau_\nu} = -\frac{2}{\mathrm{d}} \frac{\tau^{-d/2}}{i\omega}, \qquad \text{for } \omega\tau_\nu \gg 1 \tag{28}$$

where

$$\tau = \frac{1}{D_\nu q_m^{\,2}} \tag{29}$$

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 hole density fluctuations. In accordance with the method of the generalized susceptibility,[23] the viscoelastic loss modulus (E''), which measures the energy dissipation, is determined from eq 28 as

$$E''(\omega) \sim \mathrm{Im}\, G(\omega) \sim \tau^{-d/2} \tag{30}$$

In general, the viscoelastic relaxation modulus can be written in the form

$$E(t) = E_\infty + (E_0 - E_\infty)\Phi(t) \tag{31}$$

where E_0 and E_∞ are the unrelaxed and relaxed moduli, respectively. While this equation has the same form for different bulk, shear, or tensile moduli, β and a are independent of the type of stress fields applied to the system.[17,22] Substitution of eq 19 into the above equation gives the loss modulus[21]

$$\frac{E''}{E_0 - E_\infty} = \sum_{m=1}^{\infty} \frac{(-1)^{m+1}\Gamma(m\beta + 1)}{m!\,(\omega\tau)^{m\beta}} \sin(m\beta\pi/2) \tag{32}$$

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

$$E''(\omega) \sim (\omega\tau)^{-\beta}, \quad \text{for } \omega\tau \gg 1 \tag{33}$$

Comparing eqs 30 and 33 yields

$$\beta = \frac{d}{2} = \frac{1}{2 + \nu} \tag{34}$$

When we look at eqs 27 and 28, eq 34 confirms the customary way of relating β of the stretched exponential function, eq 19, to the relaxation time spectrum. The glassy-state relaxation is dominated by the part of the spectrum having longer relaxation times. Parallel to eq 8, eqs 18 and 34 give us another self-similar scaling between the relaxation time scales Λ and a. This extends the use of dilation symmetry from space to time in polymeric glasses.

The fractal dynamics of holes are diffusive, and the diffusivity depends strongly on the tenuous structure in fractal lattices. Using eqs 16 and 34, we obtain the dependence of the local diffusion coefficient (D) on the diffusion length (R) as

$$D = \frac{R^2}{2t} \sim R^{-\nu} \tag{35}$$

The physics behind the divergence of the diffusivity in eq 35 at $R = 0$ for $\nu > 0$ was revealed when the fractal dimension had been introduced in eq 7 together with a spatial scale transformation, eq 8. For linear polymers, the diffusion coefficient is spatially independent and $\beta = 0.5$. In cross-linked polymers, the connectivity of hole motions decreases significantly because holes encounter many dead ends and the diffusion coefficient decreases rapidly with distance. Matching the motion of holes and the chain motions in terms of the segmental mobility (or diffusivity) of an ideal phantom network, we find[10] that $\nu = 4$ ($\beta = 1/6$). We have also shown in ref 10 that the spectral dimension of this chain network is 4/3, which corresponds to percolation on the infinite cluster. Our theoretical predictions compare well with $\beta = 0.48$ and 0.19 obtained from fitting experimental data of linear[8,17,22a] and highly cross-linked[20b,21] polymers, respectively.

Physical Aging

The new equations, eqs 22 and 34, together with eqs 2, 15, and 19 provide the basic theoretical relationships for the prediction of the structural relaxation and physical aging of polymeric glasses far below T_g. There are five parameters (ϵ, β, f_r, τ_r, T_r) in these equations. Let us consider the case where both linear and cross-linked polymers have the same T_r and τ_r and have the theoretical β obtained in the last section. The hole energy ϵ is related to T_r by $\epsilon/kT_r = c$,[24] where c is chosen to be 4.8 for a linear polymer like polystyrene. Since the value of c increases with an increase in the lattice coordinate number,[24] a larger c is expected for cross-linked system like epoxy resins. As a result of stronger cooperative interaction among holes (larger ν or smaller β) in cross-linked polymers, the cooling process contributes more free volume frozen-in near the glass transition[21] (larger f_r). These effects on ϵ and f_r are included in Table I.

Table I
Input Parameters for Theoretical Calculations

polymers	linear	X-linked
T_r, K	373	373
τ_r, min	30	30
β	1/2	1/6
ϵ, kcal/mol	$4.8\,kT_r = 3.554$	$1.2\epsilon_{\mathrm{linear}} = 4.265$
f_r	1/30	$3f_{r,\mathrm{linear}} = 1/10$

When polymer is cooled from liquid to glass, the departure from a Doolittle–WLF dependence to an eq 22 type of relaxation time scale is as shown in Figure 1. To evaluate the thermal history dependent integral, eq 15, $\mathrm{d}t'$ is replaced by $\mathrm{d}T'/q$, f/T^2 is treated as a function of T', and $t - t' = (T - T')/q$ in the cooling step.[17] The cooling rate is 1 K/min. The integration starts at $t = 0$ where the cooling step begins at an elevated liquid temperature $T_0 \geq T_r + 10$ K. The calculated transitions in ln a in the vicinity of T_g are consistent with those reported observations for linear and cross-linked systems.[21,22]

Following eq 22, we obtain the activation energy

$$\Delta H = k\frac{\mathrm{d}(\ln a)}{\mathrm{d}(1/T)} = \frac{\epsilon\bar{f}}{\beta(\bar{f} + \delta)^2}\left(1 + \frac{1}{\alpha}\frac{\mathrm{d}\delta}{\mathrm{d}T}\right)\left[1 - \ln\left(\frac{\bar{f} + \delta}{f_r}\right)\right] \tag{36}$$

where $\alpha = \epsilon\bar{f}/kT^2$. In contrast to all the published expressions[18,19,25] which are developed for $T > T_g$, the present theory shown in Figure 2 reveals that the activation energy controlling the relaxation process decreases with a decrease in temperature. Interestingly, ΔH drops to less than 10 kcal/mol at low temperatures, which is consistent with observed sub-T_g relaxations. Further discussions will be published elsewhere. We also see in Figure 2 that the cooling rate has little effect on ΔH in the glassy state, and its main effect is related to the kinetic shift of T_g.

Struik has introduced an exponent (μ) to characterize the physical aging observed in his isothermal creep experiments.[25]

$$a(T,t) \sim t^{\mu} \tag{37}$$

at long aging time t. To calculate the aging exponent μ, in addition to cooling step mentioned earlier, the relaxation function in eq 15 is written in the form: $\Phi(t - t') = \Phi[(T - T')/q\tau + (t - t_1)/\tau]$ in the annealing step, where $t_1 = (T - T_0)/q$ and $t - t'$ ranges in logarithmic time scale (in h) from −1 to 2.[9,17] Noting[17]

$$\beta f_r^{\,2}\mathrm{d}(\ln t) = \alpha_r\,\mathrm{d}T$$

we obtain the temperature dependence of physical aging rate

$$\mu = -\frac{1}{\alpha_r}\left[1 - \ln\left(\frac{\bar{f} + \delta}{f_r}\right)\right]\left(\frac{f_r}{\bar{f} + \delta}\right)^2\frac{\mathrm{d}\delta}{\mathrm{d}T} \tag{38}$$

In the vicinity of glass transition ($T \rightarrow T_r$), eq 38 approaches

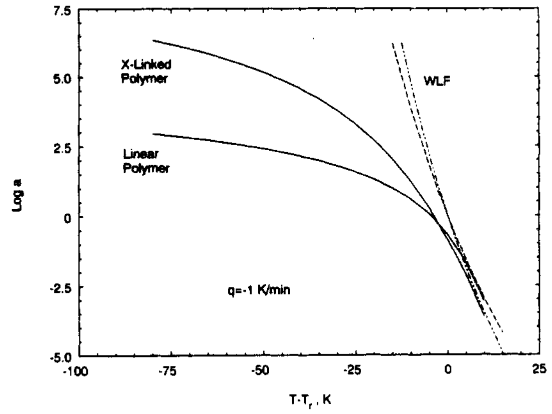

Figure 1. Calculated shift factors (solid curves) of linear and cross-linked polymers as a function of temperature.

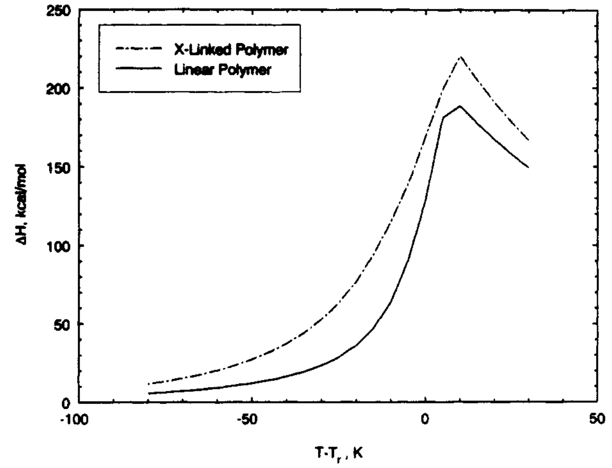

Figure 2. Prediction of increasingly smaller activation energies for linear and cross-linked polymers with decreasing temperature in the glassy state.

an earlier reported expression[17,21,22]

$$\mu \simeq -\frac{1}{\alpha_r}\frac{\mathrm{d}\delta}{\mathrm{d}T} \tag{39}$$

which goes to zero for $T > T_g$, and eq 36 becomes

$$\Delta H \simeq \frac{\epsilon}{\beta f_r}(1-\mu) \tag{40}$$

which provides a simple relationship between ΔH and μ for interpreting the transition of the relaxation time near T_g as mentioned in Figure 1. The dependence of the physical aging rate on temperature for the linear and cross-linked polymers is shown in Figure 3. The calculation reveals that the Struik exponent (μ) increases from zero above T_g to a constant less than 1 below T_g and then decreases to zero 200 K below T_g. The two polymers all show a similar type of temperature dependence of physical aging rate. The reported data (see Figure 15 of ref 25) on μ of linear polymers compare very well with our theoretical prediction. There is no experimental data for cross-linked polymers.

Conclusions

A fractal dynamic theory of hole motion and fluctuations in polymeric glasses for temperatures below T_g is developed. Using the ansatz eq 7 and the spatial scale transformation eq 8, we have derived the KAHR equations, the KWW function, the density of states, the stretched exponential, and the spatial-dependent local diffusivity of holes. A unified physical picture to relate them has emerged.

The glassy-state relaxation is dominated by the part of the spectrum having longer relaxation times. A new equation, eq 22, is derived to describe the dependence of relaxation time on temperature far below T_g. This equation provides a theoretical justification of extending Doolittle's equation from the equilibrium liquid to non-equilibrium glassy states.

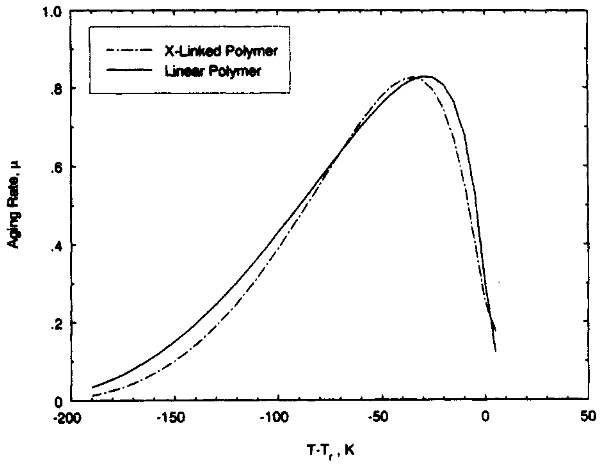

Figure 3. Calculated dependence of physical aging rate on temperature for linear and cross-linked polymers.

All the new equations are finally used in the calculation of the low-temperature structural relaxation and physical aging of linear and cross-linked polymers. In contrast to all the published expressions, the present new theory predicts that the activation energy controlling the structural relaxation and physical aging decreases with decreasing temperature in the glassy state. Our calculation also reveals that the physical aging rates of both linear and highly cross-linked polymers increase from zero above T_g to a constant below T_g and then decrease to zero 200 K below T_g.

References and Notes

(1) Cates, M. E. *Phys. Rev. Lett.* **1984**, *53*, 926; *J. Phys. (Paris)* **1985**, *46*, 1059.
(2) Vilgis, T. A. *Phys. Rev. A* **1987**, *36*, 1506.
(3) Hess, W.; Vilgis, T. A.; Winter, H. H. *Macromolecules* **1988**, *21*, 1536.
(4) Alexander, S.; Orbach, R. *J. Phys. (Paris)* **1982**, *43*, L625.
(5) Rammal, R.; Toulouse, G. *J. Phys. (Paris)* **1983**, *44*, L13.
(6) Ferry, J. D. *Viscoelastic properties of Polymers*, 3rd ed.; John Wiley & Sons: New York, 1980.
(7) Cohen, M. H.; Grest, G. S. *Phys. Rev.* **1979**, *B20*, 1077.
(8) Chow, T. S. *Macromolecules* **1984**, *17*, 2336.
(9) Chow, T. S. *Macromolecules* **1989**, *22*, 701.
(10) Chow, T. S. *Phys. Rev. A* In press.
(11) Robertson, R. E.; Simha, R.; Curro, J. G. *Macromolecules* **1984**, *17*, 911.
(12) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell Univ. Press: Ithaca, NY, 1979.
(13) Mandelbrot, B. B. *The Fractal Geometry of Nature*, Freeman: San Francisco, 1982.
(14) Kovacs, A. J.; Aklonis, J. J.; Huchinson, J. M.; Ramos, A. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1097.
(15) Ma, S. K. *Statistical Mechanics*; World Scientific: Philadelphia, 1985; Chapter 25.
(16) Kohlrausch, R. *Ann. Phys. (Leipzig)* **1847**, *21*, 393. Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.
(17) Chow, T. S. *J. Polym. Sci.* **1987**, *B25*, 137.
(18) Doolittle, A. K. *J. Appl. Phys.* **1951**, *22*, 1471.
(19) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.
(20) Chow, T. S. (*a*) *Macromolecules* **1990**, *23*, 4648; (b) *Polymer* **1991**, *32*, 29.
(21) Chow, T. S. *Polymer* **1988**, *29*, 1447.
(22) (a) Chow, T. S. *J. Mater. Sci.* **1990**, *25*, 957. (b) Chow, T. S.; Van Laeken, A. C. *Polymer* **1991**, *32*, 1798.
(23) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*, 2nd ed.; Pergamon Press: Oxford, 1969; Chapter 12.
(24) Chow, T. S. *Macromolecules* **1989**, *22*, 698.
(25) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, 1978.