Non-Markovian Diffusion Processes in Polymers and a Stretched Exponential Relaxation Constitutive Equation

J. STASTNA,[1] D. DE KEE,[1,*] and B. HARRISON[2]

[1]Department of Chemical Engineering, University of Sherbrooke, Sherbrooke, Québec J1K 2R1, and
[2]Department of National Defence, DREO, Ottawa, Ontario K1A 0Z4, Canada

SYNOPSIS

Non-Markovian diffusion transport in polymers was studied. Applying the results of various researchers, a stretched exponential relaxation function was obtained and a linear viscoelastic constitutive equation formulated. Frequency dependent material functions, obtained from this constitutive equation were studied and the results successfully compared with experimental data for polyethylene oxide solutions. Sorption kinetics in a polymeric film were also studied. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Classical or Fickian sorption of a penetrant in a polymer membrane is described by the standard diffusion equation, taking into account appropriate boundary and initial conditions.[1]

Crank and Park[2] presented an extensive experimental characterization of Fickian sorption. The experimental quantities of interest are the amount of penetrant (M_t) associated with the polymer at time t and the equilibrium amount M_∞. A plot of M_t/M_∞ versus $t^{1/2}$ reveals a characteristic fingerprint of Fickian sorption kinetics. Such a curve is initially linear and the desorption curve is located below the corresponding absorption curve. Such features are observed for temperatures well above the glass-transition temperature (T_g) of the polymer. Below the T_g one observes non-Fickian kinetics, characterized by s-shaped plots, a large discontinuity in penetrant concentration at the advancing penetrant front as well as other features not described by classical diffusion.

Here, we draw attention to some results of a stochastic transport model[3,4] that describes the dynamics of a randomly traveling packet of walkers on a simple periodic lattice. It is not a pure microscopic model, but it provides a link between phe-

nomenological models and models based on a molecular description. Equations based on this approach have great modelling potential and can be used in various fields. The sorption kinetics of organic molecules in polymeric membranes can be described by this approach. Only the basic ideas are used in this contribution. Other studies in the literature provide more details of the theory.[3-6]

EXPERIMENTAL

Non-Markovian Transport Processes

We are interested in describing the sorption kinetics of a penetrant (gas or liquid) in a polymeric membrane, which can be thought of as an amorphous solid, that includes islands of crystalline material. From the point of view of the penetrant molecules, the polymer is a disordered system with a dispersion in the separation distances between the nearest neighbor localized sites available for the jumping molecules. There is also a dispersion in the potential barriers between these sites. Both of these variables strongly affect the jumping time; that is, the time between a molecule's arrival on successive sites. One assumes that the distribution of these jumping times, $\psi(t)$, should have a long tail.[4] This has an important effect on the transport properties of our system as we shall illustrate. The pausing time distribution function, $\psi(t)(=\alpha e^{-\alpha t})$, is representative of the walks for which an average time $\langle t \rangle$ exists between

steps. Following an induction period, a lattice walk of this class reduces to classical diffusion. A second group of walks is characterized by a distribution function $\psi(t)$ with a long tail, so that $\langle t \rangle$ becomes infinite. A pausing time distribution function with an inverse power tail, is representative for this class and is written as: $\psi(t) \approx \beta t^{-(1+\beta)}/\Gamma(1-\beta)$. In this case, the diffusion is slower and highly dispersive. It is known for example that this choice of $\psi(t)$ leads to the Williams et al. relaxation function for the frequency dependent dielectric constant for many polymeric systems.[5]

Classical theory is generally described via a Markovian transport master equation[6]

$$\frac{dG(l, t)}{dt} = -\alpha G(l, t) + \alpha \sum_{l'}{}' p(l, l') G(l', t) \quad (1)$$

where $G(l, t)$ is the probability that an investigated system is in state l at time t and $\alpha p(l, l')$ is the probability of a transition from l' to l per unit time, that is, α represents the reciprocal average time between steps. The transition probabilities are normalized:

$$\sum_{l'} p(l', l) = 1. \quad (2)$$

It is possible to interpret the states (l) as the lattice points on a periodic space lattice. The system is then a random walker on this lattice. The jumping time distribution function $\psi(t)$ is an important quantity. It is the probability density function for the time t between the arrival of a walker at a given lattice point and the start of the next step to another site. We assume all lattice points to be equivalent. That is to say: $\psi(t)$ is a universal function for the whole lattice and $p(l', l) \equiv p(l' - l)$. The function $G(l, t)$ completely specifies the propagation of the traveling packet. That is: no absorbing boundaries are considered. Also, the function $G(l, t)$ is related to the Laplace transform of $\psi(t)$, as follows[4]:

$$\mathcal{L}[\psi(t)] = \int_0^\infty e^{-ut}\psi(t)\, dt \equiv \psi^*(u) \quad (3)$$

$$G(l, t) = \mathcal{L}^{-1}\left[\frac{1 - \psi^*(u)}{u}\, \tilde{G}(l, \psi^*(u))\right] \quad (4)$$

where $\tilde{G}$ is the random walk generating function.[3]

Computational examples on a periodic space lattice are given by Montroll and Scher.[4] Equation (1) should not be used when dealing with nonequilib-

rium processes. For the case when all lattice points are considered equivalent, eq. (1) can be generalized as[6]:

$$\frac{dG(l, t)}{dt} = \int_0^t \phi(t - \tau)\left[-G(l, \tau)\right. $$
$$\left. + \sum_{l'}{}' p(l - l') G(l', \tau)\right] d\tau \quad (5)$$

where $\phi(t)$ is the relaxation function related to $\psi(t)$ by the following equation

$$\phi^*(u) = \frac{u\psi^*(u)}{1 - \psi^*(u)}. \quad (6)$$

For $u = i\omega$, $\phi^*(u)$ is related to the frequency dependent diffusion constant and $\phi(t)$ is the response function for a linear response theory of random walk transport.[6]

Note that an exponential form of $\psi(t)\,(=\alpha e^{-\alpha t})$ leads to:

$$\phi(t) = 2\alpha\delta(t). \quad (7)$$

Equation (5) yields then the Markovian master equation:

$$\frac{dG(l, t)}{dt} = 2\alpha\left[-G(l, t)\right.$$
$$\left. + \sum_{l'}{}' p(l - l') G(l', t)\right]. \quad (8)$$

For very small cells and considering steps to the nearest neighboring points only, one can in the continuum limit write the Markovian master equation as follows:

$$\frac{\partial G(x, t)}{\partial t} = a \frac{\partial^2 G(x, t)}{\partial x^2} + b \frac{\partial G(x, t)}{\partial x},$$
$$a, b = \text{constant.} \quad (9)$$

This is a parabolic equation that, for a homogeneous Brownian motion, represents a differential form of the Einstein–Kolmogorov equation.

If the walkers are introduced as a narrow distribution at $t = 0$ at the plane $x = 0$ [i.e., $G(x, 0) = \delta(x)$], the solution of eq. (9) is:

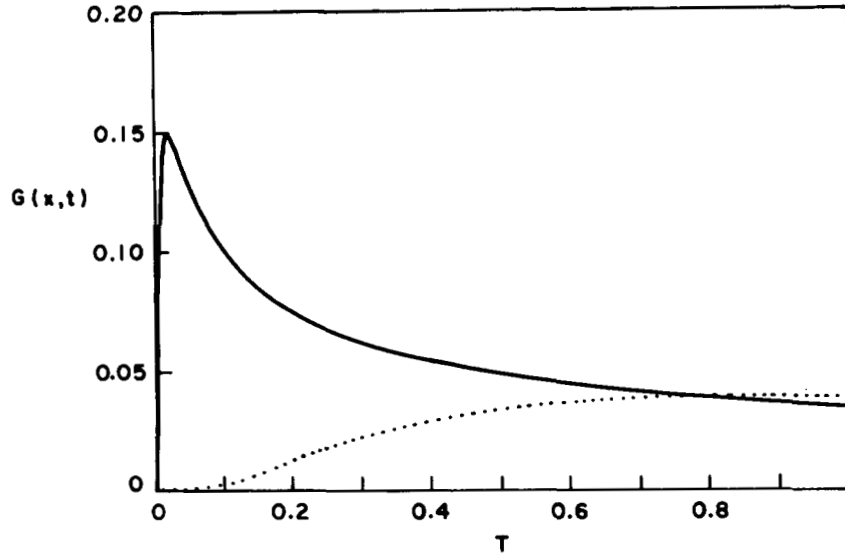$$G(x, t) = \frac{1}{2\sqrt{\pi a t}} \exp\left[\frac{b^2}{4a}t - \frac{(x + bt)^2}{4at}\right]. \quad (10)$$

Figure 1   Normalized solution of the Einstein–Kolmogorov equation. $K = b/2a = -1$; $T = 4at$. (—) $x = 0.1$ and (- - -) $x = 0.7$.

The peak is at $x_p = -bt$ and travels at a speed $dx_p/dt = -b$.

Typical predictions of equation (10) are shown in Figures 1 and 2. All moments of $G(x, t)$ given by (10) exist and are given as:

$$\langle x \rangle_n = \int_{-\infty}^{\infty} x^n G(x, t) \, dt \tag{11a}$$

$$\langle x \rangle_n = e^{b^2/4a} \left(\frac{\sqrt{at}}{i} \right)^n H_n \left(-\frac{ib\sqrt{t}}{2\sqrt{a}} \right) \tag{11b}$$

where $H_n(z)$ are Hermite polynomials.

Note that for $b^2/a \sim 0$ one obtains the classical result:

$$\langle x \rangle = -bt \tag{12a}$$

$$\frac{d\langle x \rangle}{dt} = -b \tag{12b}$$

$$x_p = -bt \tag{12c}$$

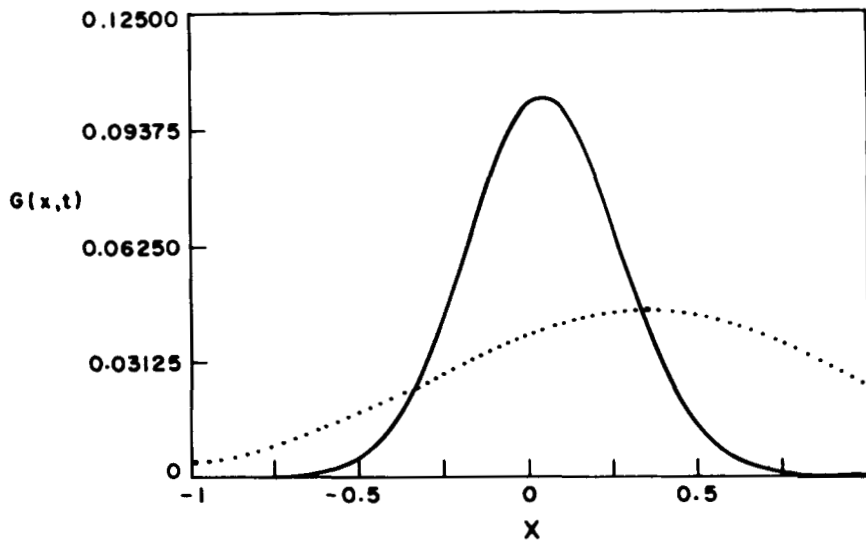$$\frac{dx_p}{dt} = -b \tag{12d}$$

Figure 2   Normalized solution of the Einstein–Kolmogorov equation. $K = b/2a = -1$; $T = 4at$. (—) $T = 0.1$ and (- - -) $T = 0.7$.

with dispersion

$$\sigma^2 = \langle x \rangle_2 - \langle x \rangle^2 \qquad (12e)$$

and

$$\frac{\sigma}{\langle x \rangle} \sim \frac{\sqrt{2a}}{b} \, t^{-1/2}. \qquad (12f)$$

Another special case is obtained when:

$$\phi(t) = \bar{A}e^{-\lambda t} \qquad (13)$$

which corresponds to $\psi(t)$ given by the difference of two exponentials.[6]

One can then differentiate eq. (5) with respect to time to generate, via the continuum limit, the following, telegraph, differential equation[5]:

$$\frac{\partial^2 G(x, t)}{\partial t^2} = \bar{A}\left[a \frac{\partial^2 G(x, t)}{\partial x^2} \right.$$
$$\left. + b \frac{\partial G(x, t)}{\partial x} \right] - \lambda \frac{\partial G(x, t)}{\partial t} \qquad (14a)$$

or

$$\frac{\partial^2 G}{\partial t^2} + \lambda \frac{\partial G}{\partial t} = \tilde{A} \frac{\partial^2 G}{\partial x^2} + \tilde{B} \frac{\partial G}{\partial x} \qquad (14b)$$

where $\tilde{A}$, $\tilde{B}$, and λ are constants.

A characteristic of the telegraph equation is that a pulse propagates initially as a wave. At later times, it behaves as a diffusion packet. Such a mechanism may be useful for studying the behavior of advancing boundaries between a swollen gel and the glassy core in glassy polymers.

The importance of the telegraph equation, when dealing with random walks has been recognized by Kenkre et al.[6]

It is possible to take advantage of eq. (6) and to combine it with the Laplace transform of eq. (5). Thus one can avoid the necessity to have an explicit expression for the relaxation function $\phi(t)$ and effectively model the process via the distribution function $\psi(t)$. Using this procedure, one can study the consequences of the choice of $\psi(t)$, especially the distribution functions with an inverse power tail. In particular, one can investigate the asymptotic behavior for long times. Next, we shall try to relate the form of $\psi(t)$ to the diffusion in polymers and to the rheological properties in polymers. The asymptotic behavior of the Laplace transform of the probability $G(x, t)$ is discussed in Appendix A.

In Appendix A, the ratio of the random walk generating functions $\tilde{G}(x, \psi^*)/\tilde{G}(0, \psi^*)$ is calculated for a free space walk (no restrictions). Before we analyze and use expression (A.17) further, it is useful to recall some results of Kenkre et al. for the case of an absorbing plane boundary. We locate the absorbing plane at $l = L$. One needs then to change the free space propagator G to the propagator P given by[6]

$$P(l, t) = G(l - l_0, t)$$
$$- \int_0^t G(l, t - \tau) F(L - l_0, \tau) \, d\tau. \qquad (15)$$

Here, we assume that initially, the walkers are injected at l_0 and $F(L - l_0, \tau)$ is the first passage-time distribution function for the transition $l_0 \rightarrow L$. $P(l, t)$ is the probability for a walker starting at l_0 at $t = 0$, to be found at l at time t. Because

$$\sum_l G(l - l_0, t) = 1 \qquad (16)$$

it is possible to calculate via eq. (15), the fraction $\varphi(t)$ of walkers surviving (not leaving the sample) until time t:

$$\varphi(t) \equiv \sum_l P(l, t) = 1 - \int_0^t F(L - l_0, \tau) \, d\tau \qquad (17)$$

that is,

$$F(l - l_0, t) = - \frac{d\varphi(t)}{dt}. \qquad (18)$$

Combining eq. (4) and (15), bearing the periodicity of the lattice in mind, one computes:

$$\frac{\tilde{G}(L - l_0, \psi^*)}{\tilde{G}(0, \psi^*)} = \mathcal{L}[F(L - l_0, t)]. \qquad (19)$$

Next we assume that we are studying desorption kinetics via the following simple experiment. At time $t = 0$, a narrow packet of diffusant is injected into a polymeric membrane of thickness h. Both lateral sides of the membrane are "washed" by an external medium that collects the penetrant molecules arriving at the boundary planes. That is to say, we are dealing with absorbing boundaries, where penetrant molecules disappear. By monitoring the amount of penetrant, $Q(t)$, present at time t in the membrane, we can write:

$$\varphi(t) = \frac{Q(t)}{Q(0)}. \qquad (20)$$

Assuming that the model of propagating packets discussed earlier can be applied to this case, we have:

$$F(L - l_0, t) = - \frac{1}{Q(0)} \frac{dQ(t)}{dt} \qquad (21)$$

which, combined with eq. (19), yields:

$$Q(t) = Q(0) \mathcal{L}^{-1} \left[u^{-1} - \frac{\tilde{G}(h - x_0, \psi^*)}{u\tilde{G}(0, \psi^*)} \right]. \qquad (22)$$

Using the asymptotic form (A.22), one can write:

$$\left. \frac{Q(t)}{Q(0)} \right|_{t \to \infty} \approx \frac{\bar{K}_a}{b^2} \sinh \frac{b\bar{x}t^{-(\beta+k-1)}}{2a\Gamma(2 - \beta - k)} \qquad (23)$$

where $\lim_{t \to \infty} Q(t) = 0$.

Thus for the jumping time distribution function $\psi(t)$ which has an inverse power tail, that is,

$$\psi(t) \approx [Ct^{(1+\beta)}\Gamma(1 - \beta)]^{-1},$$

one can write the following asymptotic form for $Q(t)$:

$$Q(t) \approx t^{-(\beta+k-1)} \qquad (24)$$

for $t \to \infty$.

Even though no data are available for such an idealized experiment, there is evidence supporting the fractional exponential behavior of $Q(t)$. A standard gravimetric desorption experiment, described by Saleem et al.,[7] has been performed, using a low density polyethylene (LDPE) film at 298 K. The degree of crystallinity was estimated at 50%. The amount of penetrant was measured with a Cahn 2000 electrorecording balance, and the desorption kinetics were studied for various organic penetrants.

Analyzing these experiments, one notices a similar character in all the desorption curves. Immediately after the onset of desorption, the amount of penetrant decreases. Then there is a region of slower decrease, followed finally by a tail region. Figure 3 illustrates normalized desorption curves for several hydrocarbons in LDPE at 25°C. The onset of the tail region defines the transit time $\bar{t}$. $Q(t)$ has been normalized to $Q(\bar{t})$ and the time is measured in relative units of $\bar{t}$. The log–log plot of Figure 4 shows the similarity of the desorption curves more clearly. One observes that for $t > \bar{t}$, $Q(t) \approx t^{-m}$, which is the type of qualitative behavior predicted by eq. (24). It is difficult to find a reasonable explanation for such a behavior without a detailed knowledge of
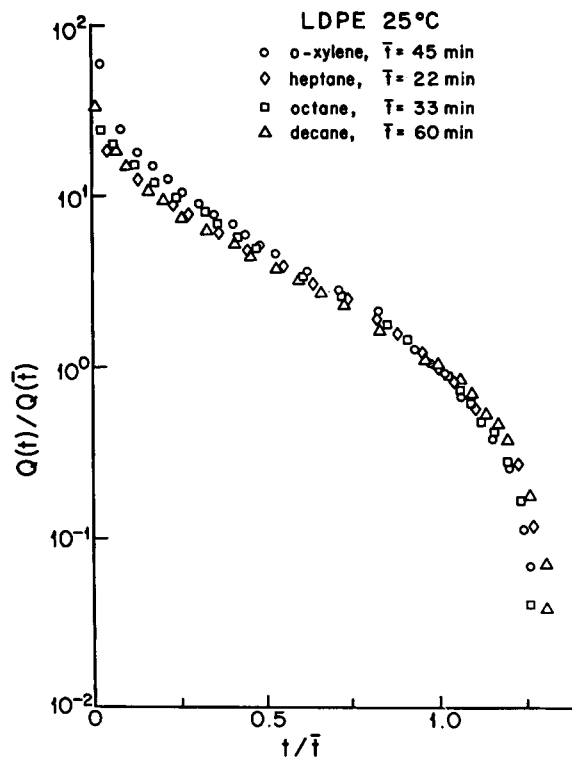

Figure 3 Normalized desorption curves for hydrocarbons in LDPE at 25°C.

the structural properties of the polymer film. One can only speculate that crystallinity and molecular weight distribution are some of the reasons for this unusual transport mechanism.

Mechanical Relaxation

The diffusion of large penetrant molecules through a glassy polymer may have another interesting effect. During the permeation through a polymeric membrane, the diffusing molecules can generate various local conformational abnormalities (a field of local strains) into the system of polymer chains. When a penetrant molecule vacates the site of such a local disturbance, it will cause a disturbance at some other site of the network. After some time, the neighborhood of the disturbed segment will relax, as the system returns to equilibrium. According to this picture, the migration of penetrant molecules may cause a mechanical relaxation in the sample. The fraction of segments surviving the "attack" of diffusing molecules can be estimated from the continuous time random walk model. If a typical unperturbed segment is at the origin of a periodic space lattice, we need to know the flux of walkers at the origin. Let $p(r, t)$ be the probability density, at time t, that a
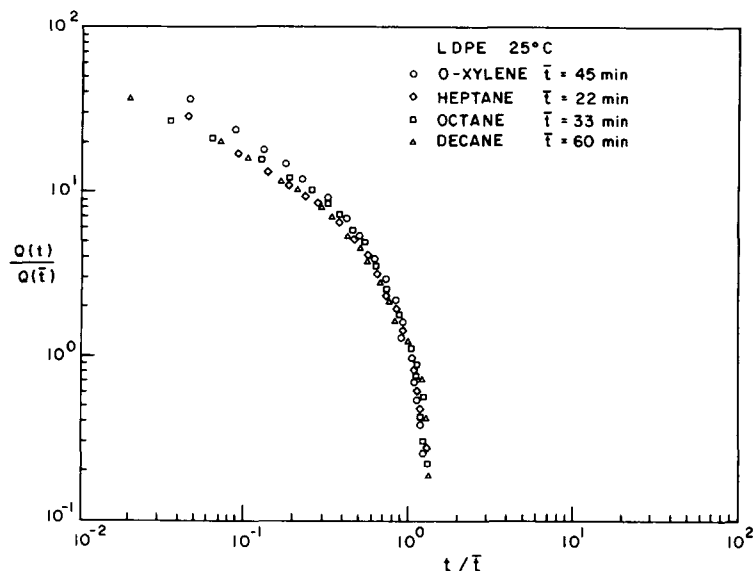
Figure 4 Normalized desorption curves (log–log plot) of the systems shown in Figure 3.

walker originally at r reaches the origin for the first time. The probability that the walker has not reached the origin during the time interval $(0, t)$ is then: $1 - \int_0^t p(r, t') \, dt'$. The probability that none of the n walkers has reached the origin is the survival probability $\bar{P}(t)$ of undisturbed segments. This quantity is given by:

$$\bar{P}(t) = \sum_{r_1, r_2, \ldots r_n = 1}^{N} \prod_{i=1}^{n} \left[1 - \int_0^t p(r_i, t') \, dt' \right]$$
$$\times \bar{p}(r_1, \ldots, r_n) \quad (25)$$

where n is the number of walkers, N is the number of lattice points, and $\bar{p}(r_1, \ldots, r_n)$ is the initial probability density function of walker positions. If:

$$\bar{p} = N^{-n} \quad (26)$$

(randomly distributed walkers at the start of the process), n and N are large and

$$c = \frac{n}{N}. \quad (27)$$

Equation (25) then yields:

$$\bar{P}(t) = \exp\left[-c \int_0^t J(t') \, dt' \right] \quad (28)$$

where the flux of walkers $J(t)$ is given by:

$$J(t) = \sum_{r \neq 0} p(r, t). \quad (29)$$

The relaxation modulus, $G(t)$, should be proportional to the rate of change of the survival probability $\bar{P}(t)$ of the undisturbed segments. Writing:

$$G(t) = -k \frac{d\bar{P}(t)}{dt} = , \quad k \equiv \text{constant} \quad (30)$$

one observes that:

$$G(t) = ckJ(t) \exp\left[-c \int_0^t J(t') \, dt' \right] \quad (31)$$

and

$$J(t) = \frac{G(t)}{c \left[k - \int_0^t G(t') \, dt' \right]}. \quad (32)$$

Shlesinger and Montroll[8] showed that for a jumping time distribution function $\psi(t)$ proportional to $\beta t^{-(1+\beta)} / \Gamma(1 - \beta)$, as in eq. (A.18), the asymptotic form for $J(t)$ is given by:

$$J(t) \approx \begin{cases} B_3 t^{\beta-1} / \Gamma(\beta) - \text{cubic lattice} \\ B_1 t^{(\beta/2)-1} / \Gamma\left(\dfrac{\beta}{2}\right) - \text{linear chain} \end{cases} \quad (33)$$

Equation (31) then yields:

$$G(t) = \frac{k\beta}{\lambda}\left(\frac{t}{\lambda}\right)^{\beta-1} e^{-(t/\lambda)^\beta} \qquad (34)$$

where

$$\lambda^{-\beta} = cB_3/\beta\Gamma(\beta). \qquad (35)$$

The memory function

$$m(t) = -dG/dt \qquad (36)$$

associated with G, given by eq. (34) has the form:

$$m(t) = -\frac{k\beta}{\lambda^\beta} t^{\beta-2} e^{-(t/\lambda)^\beta}\left[(\beta-1) - t^\beta \frac{\beta}{\lambda^\beta}\right]. \qquad (37)$$

Note that for $\beta = \frac{1}{2}$, eq. (37) reduces to Wagner's memory function.[9] Stastna et al.[10] simulated various material functions using the quantities defined by eqs. (34) or (37). For example, the relaxation modulus $G(t)$ is related to the complex viscosity function $\eta^*(\omega)$ via the Fourier transform (F)

$$G(t) = F^{-1}[\eta^*(\omega)]. \qquad (38)$$

Introducing the zero shear rate viscosity

$$\eta_0 = k\beta\Gamma(\beta) \qquad (39)$$

one computes via eq. (34), the following expressions for the components of $\eta^*(=\eta' - i\eta'')$:

$$\eta'(\omega) = \eta_0\left[1 - \omega \int_0^\infty e^{-(t/\lambda)^\beta}\sin \omega t \, dt\right] \qquad (40)$$

$$\eta''(\omega) = \eta_0\omega \int_0^\infty e^{-(t/\lambda)^\beta}\cos \omega t \, dt. \qquad (41)$$

This type of expressions for η' and η'' can be approximated by the following equation for η^*,

$$\eta^*(\omega) = \frac{\eta_0}{(1 + i\omega\bar\lambda)^\alpha}. \qquad (42)$$

Predictions of eqs. (40)–(42) successfully compare with experimental data, for polymer melts, and even for polymer solutions.[10] Figures 5 and 6 illustrate such a comparison in the case of polyethylene oxide solutions. The figures illustrate surprisingly good agreement for both η' and η''. It is possible to obtain an analytic form for the corresponding linear viscoelastic constitutive equation via eq. (42). Using the Fourier transform

$$F\left[U(t)e^{-t/\bar\lambda} \frac{t^{\alpha-1}}{\Gamma(\alpha)}\right] = \bar\lambda^\alpha \frac{1}{(1 + i\omega\bar\lambda)^\alpha} \qquad (43)$$

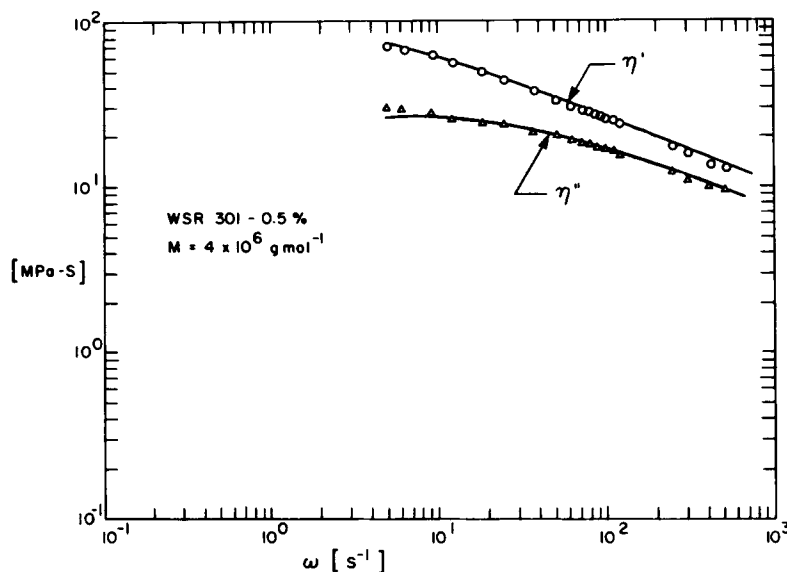where $U(t)$ is the unit step function, and the general form of the linear viscoelastic constitutive equation

Figure 5 Model predictions of η' and η'' data on a 0.5% polyethylene oxide (PEO) WSR 301 (Union Carbide) solution. The parameters are: (—) eqs. (40), (41): $\eta_0 = 110$ MPa·s; $\beta = 0.44$; $\lambda = 0.1$ s.
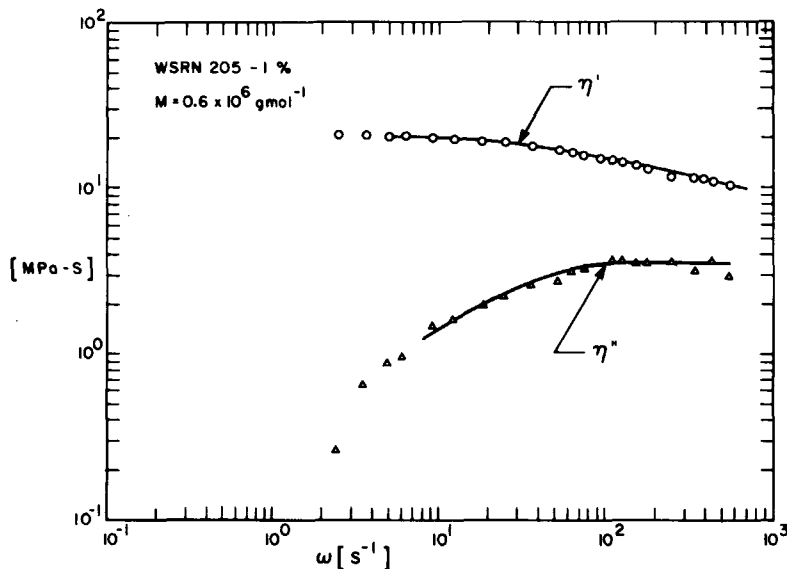
Figure 6 Model predictions of η' and η'' data on a 1% PEO WSR 205, (Union Carbide) solution. The parameters are: (—) eqs. (40), (41): η_0 = 19.64 MPa·s; β = 0.33; λ = 0.002 s.

$$\tau = \int_0^\infty G(s)\dot{\gamma}(t-s)\,ds \tag{44}$$

where τ is the extra-stress tensor and $\dot{\gamma}$ is the rate of deformation tensor, one obtains

$$\tau(t) = \frac{\eta_0}{\lambda^\alpha \Gamma(\alpha)} \int_0^\infty e^{-s/\lambda} s^{\alpha-1} \dot{\gamma}(t-s)\,ds. \tag{45}$$

This constitutive equation approximates the equation corresponding to the relaxation modulus of eq. (34): the stretched exponential relaxation.

CONCLUSIONS

In the study of nonclassical effects of diffusion in polymers by the method of continuous time random walk, we observe that non-Markovian processes, characterized by the jumping-time distribution function ψ, can lead to various nonstandard forms of diffusion characteristics. For a small dispersion in jumping times, the process becomes Gaussian with increasing time. On the other hand, for $\psi(t) \approx t^{-(1+\beta)}$, $t \geq \bar{t}$, the transport process is non-Gaussian. If the penetrating molecules are such that they generate various local conformational abnormalities in the system of polymer chains, nonclassical transport might generate stretched exponential relaxation in the polymer. There are known rheological models of this type that describe linear viscoelastic behavior of melts and of solutions.

The stretched exponential relaxation was in fact proposed by Kohlrausch in 1863.[11] Recently, many such relaxation phenomena in disordered systems (dielectric, magnetic, thermal, optical) have been found. The universality of this stretched exponential law is most striking. It seems that atomic or molecular structure is not essential; spatial and energetic disorder is.

APPENDIX A: ASYMPTOTIC BEHAVIOR

By taking the Laplace transform of eq. (5) and using the continuum limit, one obtains the following equation for $\mathcal{L}[G] \equiv G^*$:

$$uG^*(x, u) - G(x, o)$$
$$= \phi^*(u)[aG^*_{xx}(x, u) + bG^*_x(x, u)]. \tag{A.1}$$

With

$$G(x, o) = \delta(x), \tag{A.2}$$

defining

$$A = a\phi^*, \tag{A.3}$$

and

$$B = b\phi^* \tag{A.4}$$

we obtain the following nonhomogeneous differential equation for $G^*(x, u)$ where u is fixed.

$$AG_{xx}^* + B_x^* - uG^* = -\delta(x). \qquad (A.5)$$

The solution of the homogeneous equation can be written as

$$G_{\text{hom}}^*(x, u)$$
$$= c_1(u)e^{[\alpha+\lambda(u)]x} + c_2(u)e^{[\alpha-\lambda(u)]x} \qquad (A.6)$$

where

$$\alpha = -\frac{b}{2a} \qquad (A.7)$$

and

$$\lambda(u) = \left(\frac{b^2}{4a^2} + \frac{u}{a\phi^*}\right)^{1/2} \qquad (A.8)$$

where $c_1(u)$ and $c_2(u)$ are arbitrary functions of the Laplace transform parameter u. We choose the particular solution of eq. (A.5) together with the following conditions:

$$G^*(0, u) = 0 \qquad (A.9)$$

$$G_x^*(0, u) = 0 \qquad (A.10)$$

as a solution of the free space problem.
Via the space Laplace transform $[\bar{G}^*(s) \equiv \mathcal{L}_x(G^*)]$, we find

$$\bar{G}^*(s) = -\frac{1}{A} \frac{1}{\left[s - \left(-\frac{B}{2A}\right)\right]^2 - \left[\left(\frac{u}{A} + \frac{B^2}{4A^2}\right)^{1/2}\right]^2} . \qquad (A.11)$$

Inverting eq. (A.11) and using solution (A.6), one obtains:

$$G^*(x, u) = c_1(u)\exp\left[-\frac{b}{2a} + \left(\frac{b^2}{4a^2} + \frac{u}{a\phi^*}\right)^{1/2}\right]x$$

$$+ c_2(u)\exp\left[-\frac{b}{2a} - \left(\frac{b^2}{4a^2} + \frac{u}{a\phi^*}\right)^{1/2}\right]x$$

$$- \frac{1}{a\phi^*} \frac{e^{-(b/2a)x}\sinh\left(\frac{u}{a\phi^*} + \frac{b^2}{4a^2}\right)^{1/2}x}{\left(\frac{u}{a\phi^*} + \frac{b^2}{4a^2}\right)^{1/2}} . \qquad (A.12)$$

It is now possible [see eqs. (4) and (6)] to express the generating function $\tilde{G}(x, \psi^*)$, using $G^*(x, u)$ and the continuum limit, as follows.
First

$$\frac{\phi^*}{u + \phi^*} = \psi^* \qquad (A.13)$$

and

$$\frac{u}{\phi^*} = \frac{1 - \psi^*}{\psi^*} . \qquad (A.14)$$

Then

$$\frac{\tilde{G}(x, \psi^*)}{\frac{u}{1 - \psi^*}} = G^*(x, u). \qquad (A.15)$$

Also

$$\frac{1 - \psi^*}{u} \tilde{G}(0, \psi^*) = c_1(u) + c_2(u) \qquad (A.16)$$

and finally we have:

$$\frac{\tilde{G}(x, \psi^*)}{\tilde{G}(0, \psi^*)} = \frac{c_1(u)}{c_1(u) + c_2(u)}$$

$$\times \exp\left[-\frac{b}{2a} + \left(\frac{b^2}{4a^2} + \frac{(1 - \psi^*)}{a\psi^*}\right)^{1/2}\right]x$$

$$+ \frac{c_2(u)}{c_1(u) + c_2(u)} \exp\left[-\frac{b}{2a} - \frac{b^2}{4a^2} + \frac{(1 - \psi^*)}{a\psi^*}\right)^{1/2}\right]x$$

$$- \frac{1}{c_1(u) + c_2(u)} \frac{1 - \psi^*}{ua\psi^*}$$

$$\times \frac{e^{-(b/2a)x}\sinh\left[\frac{b^2}{4a^2} + \frac{(1 - \psi^*)}{a\psi^*}\right]^{1/2}x}{\frac{b^2}{4a^2} + \frac{(1 - \psi^*)}{a\psi^*}} . \qquad (A.17)$$

A complete analytic study is possible only if the functions $c_1(u)$ and $c_2(u)$ are known. Such information can be obtained via detailed experimental work. It is however possible to study the impact of various models of $c_i(u)$. To study the asymptotic behavior, we use the modelling potential of the jumping time distribution function $\psi(t)$. Assume now that $\psi(t)$ has an inverse power tail for long times, that is, its Laplace transform can be approximated as follows:

$$\psi^*(u) \sim 1 - Cu^\beta \qquad (A.18)$$

for $u \to 0$ and $\beta > 0$.

We can write:

$$\frac{\tilde{G}(x\,\psi^*)}{u\tilde{G}(0,\psi^*)} = \frac{c_1(u)}{u[c_1(u) + c_2(u)]}\left(1 + \frac{2a}{b}Cxu^\beta\right)$$

$$+ \frac{c_2(u)e^{-(b/a)x}}{u[c_1(u) + c_2(u)]}\left(1 - \frac{2a}{b^2}Cxu^\beta\right)$$

$$- \frac{Ce^{-(b/2a)x}}{a[c_1(u) + c_2(u)]}$$

$$\times \frac{\sinh\dfrac{b}{2a}x + \dfrac{C}{b}\times\left(\cosh\dfrac{b}{2a}x\right)u^\beta}{\dfrac{b^2}{4a^2}u^2 + \dfrac{C}{a}u^{\beta+2}}. \qquad (A.19)$$

Assuming that:

$$\lim_{u\to 0}c_1(u) = \lim_{u\to 0}c_2(u) \qquad (A.20)$$

and that

$$c_1(u) + c_2(u) \sim Ku^{-k}, \qquad (A.21)$$

for $u \to \infty$ and $k \in (0, 1)$.

Such a choice guarantees that the probability $G(0, t)$ decreases to 0 with time. Using our assumptions, we can write the following asymptotic expression:

$$\mathcal{L}^{-1}\left[u^{-1} - \frac{\tilde{G}(\bar{x}, \psi^*)}{u\tilde{G}(0, \psi^*)}\right]$$

$$\approx \frac{1 - e^{-b\bar{x}/2a}}{2} - \frac{a}{b^2}\bar{C}\bar{x}(1 - e^{-b\bar{x}/a})\frac{t^{-\beta}}{\Gamma(1-\beta)}$$

$$+ \bar{K}\frac{a}{b^2}e^{-b\bar{x}/2a}\sinh\frac{b\bar{x}}{2a}\frac{t^{-[(\beta+k)-1]}}{\Gamma[2 - (\beta + k)]} \qquad (A.22)$$

as $t \to \infty$, where

$$\bar{x} = h - x_0 \qquad (A.23)$$

and $0 < k < 1; 0 < \beta < 1; 1 < \beta + k < 2$.

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