Derivation of the Kohlrausch–Williams/Watts Decay Law from Activation-Energy Dispersion

Time-independent random walks are useful to describe conformations of disordered polymer chains in solution and bulk. Recently continuous-time random walks have been applied to very slow (>μs or so) nonexponential relaxation near and below the polymer glass transition. In particular, Glarum's defect diffusion model of dielectric relaxation was extended by Shlesinger and Montroll (SM)[1] to include the possibility that a defect's progress toward a frozen dipole might be intermittent, consisting of self-similar bursts of hopping events with intervening clusters of pauses. (Polymer defects can be high-energy backbone conformers which diffuse along or between chains.) In Glarum's original one-dimensional treatment, the nearest defect diffuses to a waiting dipole by a steady hopping motion. (A defect is pictured as carrying a packet of "free volume" so that its arrival at a dipole results in instantaneous orientation relaxation.) The rate of relaxation is governed by the flux of defects into dipoles. Intermittency results if defects get stuck, either because they wander down "dead ends" of the chain and have to find their way back or because they must wait to jump over a distribution of barriers (vide infra). The SM model yields for the Laplace transform of the defect flux $\tilde{I}(u)$[1]

$$\tilde{I}(u) = \frac{1}{[1 - \tilde{\psi}(u)]P[0,\tilde{\psi}(u)]} - 1 \qquad (1)$$

where $\tilde{\psi}(u)$ is the Laplace transform of the waiting-time density, $P(s,z)$ is the site-visitation probability generating function for the lattice, and u is the transform variable. In the case of a waiting-time density $\psi(t)$ with a long-time tail

$$\psi(t) \sim At^{-1-\alpha}, \qquad 0 < \alpha < 1 \qquad (2)$$

SM show that *asymptotically* eq 1 and 2 give for the dipole orientation survival probability $\phi(t)$

$$\phi(t) \sim e^{-c_1 t^{\alpha}} \qquad \text{(3 dimensions)} \qquad (3a)$$

$$\phi(t) \sim e^{-c_2 t^{\alpha/2}} \qquad \text{(1 dimension)} \qquad (3b)$$

where c_1 and c_2 depend on defect density, lattice structure, and the precise form of $\psi(t)$. Equation 3a is the form of the Kohlrausch–Williams/Watts (KWW) function which is widely employed to discuss glass relaxation.[2-4]

Barrier Dispersion Model of $\psi(t)$.[5] Major unresolved issues are the range of validity of the asymptotic limit, the physical interpretation of the exponent α, and its relationship to external and chemical parameters. This communication describes a familiar physical mechanism[6-14] which leads to a specific $\psi(t)$ with the required long-time behavior (i.e., eq 2). The exponent α is simply related to the dispersion of activation energies and entropies for defect hops. Dipole decay $\phi(t)$ at early times, crossover to the KWW form, and terminal behavior for this $\psi(t)$ will be discussed elsewhere.[15]

The present barrier-jump model of $\psi(t)$ assumes that the long-time tail may have the same origin discussed by Pfister and Scher for anomalous transport in semiconductors;[16] the basic transport laws contain exponential dependencies on structural parameters of the material, and distributions of such structural parameters (as occur in amorphous systems) generate power laws in transport rates. The phenomenological Eyring[17] or Kramers[18] form of a thermally activated jump rate λ in the presence of a single free energy barrier F_0^+ is

$$\lambda_0 = \lambda_\infty e^{-(F_0^+/kT)} \qquad (4)$$

where λ_∞ is the attempt frequency which depends on the potential curvatures and the effective viscosity. The barrier height F_0^+ must be several times larger than the thermal energy kT, a condition usually met in polymers. The barrier is composed of both an entropy and an energy contribution:

$$F^+ \equiv -TS^+ + E^+ = -T(S_0 + \delta S) + (E_0 + \delta E) \qquad (5)$$

where δS and δE are entropy and energy fluctuations generated by local changes in intra- and interchain conformer states. The distribution in neighbor arrangements leads to a distribution of barriers for defect hops. If the time scale of the barrier fluctuations is not much shorter than the defect waiting times, a distribution of the latter results. The simplest case occurs for a linear relationship between energy and entropy; $\delta S = \sigma\delta E$.[10] An exponential density of δE is introduced:

$$g(\delta E) = qe^{-q\delta E} \qquad (\delta E > 0) \qquad (6)$$

For a single barrier (with no memory betwen hops), one has a Poisson density of waiting times:

$$\psi(t) = \lambda_0 e^{-\lambda_0 t} \qquad (7)$$

For a distribution of barriers this becomes

$$\psi(t) = \int_0^\infty \lambda e^{-\lambda t}\rho(\lambda)\, d\lambda \qquad (8)$$

where the density ρ of rates is given by $\rho(\lambda) = g(\delta E)\, d\delta E/d\lambda$. Using eq 4–6 one finds

$$\rho(\lambda) = \frac{\alpha}{\lambda}\left(\frac{\lambda}{\lambda_0}\right)^{\alpha}, \qquad 0 \le \lambda \le \lambda_0 \qquad (9)$$

with $kTq/(1 - \sigma T) \equiv \alpha$. Equation 9 and eq 8 give

$$\psi_\alpha(t) = \left(\frac{\alpha}{\lambda_0^{\alpha}}\right)\int_0^{\lambda_0} e^{-\lambda t}\lambda^{\alpha}\, d\lambda \qquad (10)$$

A change of variable allows ψ_α to be written as an incomplete Γ function:

$$\psi_\alpha(t) = \left(\frac{\alpha}{\lambda_0^{\alpha}}\right)t^{-1-\alpha}\int_0^{\lambda_0 t} e^{-y}y^{\alpha}\, dy = \left(\frac{\alpha}{\lambda_0^{\alpha}}\right)t^{-1-\alpha}\gamma(\alpha + 1,\lambda_0 t) \qquad (11)$$

and as $t \to \infty$, $\psi_\alpha(t) \sim [\alpha\Gamma(1 + \alpha)/\lambda_0^{\alpha}]t^{-1-\alpha}$, which is exactly the form of eq 2.

Discussion. The model $\psi(t)$ of eq 10 goes to a constant $[\alpha\lambda_0/(1 + \alpha)]$ at short time $\lambda_0 t < 1$ and to the power-law decay of eq 2 at long time $\lambda_0 t \gg 1$. The crossover is temperature dependent through eq 4. The early-time $\psi(t)$ results in exponential dipole decay $\phi(t)$ at early times (before KWW) for any lattice.[15]

The basic assumption of the calculation is the exponential form of the barrier density in eq 6.[10,16] This is an idealization and barrier densities deduced from protein binding studies[19] appear rounded at the low end, perhaps like a Γ density $E^{*}e^{-q\delta E}$. The important difference between eq 6 and Wagner's Gaussian model[6] is the asymmetry which is reasonable if the dilute solution value of the barrier is a lower bound. Van der Ziel's "box distribution" of barriers[8,9] still plays a role in the theory of $1/f$ noise. Macdonald[10] has made an extensive study of the exponential density, eq 6, for the dielectric problem.

The special assumption of activation energy–entropy correlation is made for simplicity and to illustrate that even

0024-9297/85/2218-0591$01.50/0

if the dispersion parameter q is constant, the exponent α could display nonlinear temperature dependence. Other choices are possible[10] and would alter the temperature behavior. The proposed barrier dispersion mechanism might play a role outside of the glass region, and there is evidence for power laws in "high-temperature" elastomers.[20]

Acknowledgment. We thank Dr. George H. Weiss for many valuable comments and discussions. Thanks are due to Professor Robert Zwanzig and Professor G. Williams for each asking about early-time KWW, which led to this calculation.

References and Notes

(1) M. F. Shlesinger and E. W. Montroll, *Proc. Natl. Acad. Sci. (U.S.A.)*, **81**, 1280 (1984). Some history and references are in J. T. Bendler, *J. Stat. Phys.*, **36**, 625 (1984).
(2) G. Williams and D. C. Watts, *Trans. Faraday Soc.*, **66**, 80 (1970).
(3) J. E. Shore and R. Zwanzig, *J. Chem. Phys.*, **63**, 5445 (1975).
(4) K. L. Ngai and C. T. White, *Phys. Rev.*, **B20**, 2475 (1979).
(5) Presented in part at the American Physical Society Meeting, Detroit, MI, Mar 1983.
(6) K. W. Wagner, *Ann. Phys.*, **40**, 817 (1913). Probably the first use of a Gauss barrier density for dielectrics, though Wiechert (E. Wiechert, *ibid.*, **50**, 335, 546 (1893)) made a similar approximation for the elastic aftereffect.
(7) Yager (W. A. Yager, *Physics*, **7**, 434 (1936)) computed the spectral density for the Gaussian model and showed the symmetric loss peak.
(8) A. Van der Ziel, *Physica*, **6**, 359 (1950).
(9) H. Frohlich, "Theory of Dielectrics", Clarendon Press, Oxford, 1958, pp 92–98.
(10) (a) J. R. Macdonald, *J. Appl. Phys.*, **34**, 538 (1963); (b) *J. Chem. Phys.*, **36**, 345 (1962); (c) *Physica*, **28**, 485 (1962). These papers contain many of our results (sometimes in more general form) for the dipole relaxation $\phi(t)$ and not for defect hopping $\psi(t)$. Macdonald discusses the energy–entropy correlation question, solves other cases, and gives references to Nowick and Berry (A. S. Nowick and B. S. Berry, *IBM J. Res. Develop. S*, 297 (1961)), who undertook analogous calculations for Wagner's Gaussian barrier model. Macdonald avoids the weak singularity at the origin in eq 9 by introducing a cutoff in eq 6.
(11) U. T. Hochli, *Phys. Rev. Lett.*, **48**, 1494 (1982).
(12) H. Frauenfelder, G. A. Petsko, and D. Tsernoglu, *Nature (London)* **280**, 558 (1979).
(13) R. D. Young and S. F. Bowne, *J. Chem. Phys.*, **81**, 3730 (1984).
(14) N. Agmon and J. J. Hopfield, *J. Chem. Phys.*, **79**, 2042 (1983).
(15) M. F. Shlesinger and J. T. Bendler, *Phys. Rev. Lett.*, to be submitted.
(16) G. Pfister and H. Scher, *Adv. Phys.*, **27**, 795 (1978). The calculation in this paper is an extension of Pfister and Schers' concept of a distribution of electron traps, and we were not originally familiar with the parallel ideas in ref 6–14 above.
(17) H. Eyring, *Chem. Rev.*, **17**, 65 (1935).
(18) H. A. Kramers, *Physica*, **7**, 284 (1940).
(19) P. G. Debrunner and H. Frauenfelder, *Annu. Rev. Phys. Chem.*, **33**, 283 (1982), Figure 3.
(20) R. J. Gaylord, B. Joss, J. T. Bendler, and E. A. DiMarzio, *Br. Polym. J.*, in press.

John T. Bendler*
Polymer Physics and Engineering Branch
General Electric Corporate Research and Development
Schenectady, New York 12301

Michael F. Shlesinger
Physics Division
Office of Naval Research
Arlington, Virginia 22217

Received November 28, 1984

CORRECTIONS

Michael Eisele and Walther Burchard*: Slow-Mode Diffusion of Poly(vinylpyrrolidone) in the Semidilute Regime. Volume 17, Number 8, August 1984, p 1636.

Equation 6 was wrongly cited. According to de Gennes[1] the self-diffusion follows the relationship

$$D_{self} \sim N^{-2}c^{-1.75} \tag{C1}$$

If scaling with respect to the overlap concentration c^* is desired the chain length dependence of c^* has to be taken into account, which is

$$c^* \sim N/R^3 \approx 1/[\eta] \sim N^{-4/5} \tag{C2}$$

Thus in a good solvent one has

$$D_{self} \sim N^{-3/5}(c/c^*)^{-1.75} \tag{C3}$$

which replaces eq 6 of the original paper. The error has no effect on the conclusions drawn in that paper since the chain length dependence was not studied.

(1) de Gennes, P.-G. *Nature (London)* **1979**, *282*, 367.