Molecular Theory of Physical Aging in Polymer Glasses

Kang Chen and Kenneth S. Schweizer*

Department of Materials Science, University of Illinois, 1304 West Green Street, Urbana, Illinois 61801, USA

(Received 25 January 2007; published 20 April 2007)

A molecular level theory for the physical aging of polymer glasses is proposed. The nonequilibrium time evolution of the amplitude of long wavelength density fluctuations, and its influence on activated barrier hopping, plays an essential role. The theory predicts temperature-dependent apparent power-law aging of the segmental relaxation time and logarithmic aging of thermodynamiclike properties, in good accord with experiments. A physical origin for the quantitative nonuniversal aspects based on the amplitude of quenched density fluctuations is suggested.

DOI: 10.1103/PhysRevLett.98.167802 PACS numbers: 61.25.Hq, 64.70.Pf, 81.40.Cd

The slow dynamics of glassy materials continues to be of great scientific interest and technological importance [1–3]. Theoretical activity is strongly focused on the spectacular non-Arrenhius growth of the alpha (structural) relaxation time and viscosity as the glass temperature T_g is approached. The latter signals when a liquid falls out of equilibrium due to the relaxation time exceeding the observation time scale. However, below T_g the mobility is not zero, and an ultraslow approach to equilibrium occurs characterized by a waiting or aging time (t_{age}) dependence of thermodynamic, relaxation and mechanical properties. Material properties evolve towards a more solidlike response, e.g., the alpha time or shear modulus (diffusion constant) increases (decreases) with t_{age}, ubiquitous phenomena known as physical aging [1–3]. As emphasized by McKenna [2], the shape of the time evolution is sigmoidal, although the short time response and long time (equilibrium) behavior are often not experimentally accessible. In the commonly observed intermediate regime the thermodynamic and mechanical properties increase roughly logarithmically with aging time, while relaxation times grow as an apparent power law ($\sim t_{\mathrm{age}}^{\mu}$). The aging exponent μ increases with cooling with a value of unity commonly observed for temperatures sufficiently below T_g [2,3]. For polymer glasses the aging exponent generally drops rather abruptly at a material-specific large degree of undercooling [3]. A molecular level understanding of these observations does not exist.

In principle the physical aging phenomenon occurs for all glasses including molecular, ionic, metallic, colloidal, and polymeric materials [1,3]. Generic coarse-grained phenomenological approaches based on activated barrier hopping and quenched structural disorder have been developed for soft glasses [4]. Polymer glasses are both special and particularly important since they are by far the most studied class of materials due to their use as advanced plastics at temperatures only modestly below T_g. Phenomenological approaches largely represent the state of the art for polymers, and are based on the *ad hoc* free volume concept and/or the Adams-Gibbs entropy crisis picture [1]. The modern entropy crisis based random first order phase transition theory has been applied to polymer aging [5]. For the venerable classic models empirical fitting parameters such as a fictive temperature and "nonlinearity parameter" are typically invoked in a quasithermodynamic framework [1–3]. A first order kinetic equation is postulated for the variable(s) assumed to control segmental relaxation [1]. The vast experimental work on polymers [3], and recent studies of molecular glasses [6], both suggest that barrier hopping driven aging dynamics is controlled by the alpha relaxation time and instantaneous structure. Although some polymer aging phenomena have been reproduced by phenomenological approaches [1–3], the time dependence of the alpha relaxation time has not been fundamentally addressed. The goal of this Letter is to propose a predictive theory for this basic question.

The foundation of our work is the recently developed force-based theory for single particle dynamics in deeply supercooled polymer melts [7] which is built on naïve mode coupling [8,9], dynamic density functional [10], and activated rate concepts. The polymer melt is dynamically treated as a liquid of lightly coarse-grained "statistical segments" of size σ [7]. A closed nonlinear stochastic Langevin equation of motion for the instantaneous scalar *displacement* of a segment from its initial ($t = 0$) location, $r(t)$, has been derived [11]. The underlying "free energy" which controls the time evolution of the dynamic order parameter $r(t)$ is of a nonequilibrium origin and is given by [11]

$$\beta F_{\mathrm{eff}}(r) = -3\ln(r) - \int \frac{d\mathbf{q}}{(2\pi)^3}\rho C^2(\mathbf{q})S(\mathbf{q})[1 + S(\mathbf{q})]^{-1} \times \exp\left\{-\frac{\mathbf{q}^2 r^2}{6}[1 + S^{-1}(\mathbf{q})]\right\}, \tag{1}$$

where $\beta \equiv (k_B T)^{-1}$ and the second term quantifies interchain caging forces that favor transient localization. The stochastic Langevin theory based on Eq. (1) has been quantitatively applied in an *ab initio* manner to glassy colloidal suspensions and hard sphere fluids using microscopic structural correlation input [12]. For long Gaussian chains the site-site direct correlation function is wave vector independent $C(\mathbf{q}) = C_0$, and the density fluctuation structure factor is $S^{-1}(\mathbf{q}) = S_0^{-1} + \frac{1}{12}\mathbf{q}^2\sigma^2$ [7]. Here $S_0 \equiv S(\mathbf{q} = \mathbf{0}) = \rho k_B T \kappa = (-\rho C_0)^{-1}$ is the dimensionless compressibility which quantifies the amplitude of long wavelength density fluctuations, the statistical segment length $\sigma = \sqrt{C_\infty} l$, where l is the average backbone bond length and C_∞ is the characteristic ratio, and $\rho\sigma^3$ is a reduced segmental density of order unity [7]. The caging contribution in Eq. (1) is quantified by a *single* dimensionless, temperature-dependent material parameter, $\lambda \equiv (\rho\sigma^3 S_0^{3/2})^{-1}$, which can be computed from *experimentally measurable* static quantities thereby rendering the dynamical theory predictive.

The ideal mode coupling glass transition of the polymer theory occurs at $\lambda_c = 8.32$, corresponding to a temperature T_c that signals a crossover to non-Arrhenius activated dynamics characterized by a temperature-dependent barrier $\beta F_B \approx c(\lambda - \lambda_c)^\Delta$, $c \simeq 0.4$, $\Delta \simeq 1.3$ [7]. Noncooperative relaxation above T_c is treated in an Arrhenius manner $\tau_0(T) \equiv \tau_0 \exp(\varepsilon/k_B T)$, where $\tau_0 \approx 10^{-14\pm1}$ s is a vibrational time scale and ε is a local activation energy determined by enforcing the experimental finding of a (nearly) universal [13] dynamical crossover time $\tau_0(T_c) \simeq 10^{-7\pm1}$ s. The mean barrier hopping or segmental relaxation time is then given by the *nondivergent* form [7]

$$\tau(T) = \tau_0 \exp(\beta\varepsilon) \exp[a_c \beta F_B(T)], \tag{2}$$

where the temperature-*independent* cooperativity parameter, a_c, models the physical expectation that chain connectivity results in coordinated barrier hopping of $a_c(\sim 2\text{–}8)$ segments [7]. The glass transition temperature is determined by the kinetic criterion $\tau(T_g) = 10^x s$, $x = 2\text{–}4$. Above T_g, Eq. (2) predicts [7] temperature dependences consistent with experimental analyses based on empirical multiparameter functional forms generally involving essential singularities [1]. In all calculations in this Letter $a_c = 5$ [14].

The theory is extended to below T_g under the assumption that its basic structure remains valid [14]. Quantification of caging constraints requires the dimensionless amplitude of long wavelength collective density fluctuations, since the equilibrium fluctuation relation $S_0 = \langle(\delta\rho)^2\rangle\rho^{-2} = \rho k_B T \kappa$ does not hold [14]. Small angle x-ray scattering measurements [15] below T_g find initially $S_0 \propto T$, but at sufficiently low temperature it saturates at a nonzero value. The latter quantifies a frozen component of density fluctuations, $S_0(T \to 0) \equiv b S_0(T_g)$, where the polymer specific parameter $b \sim 0.4\text{–}0.75$. The experiments, and elementary landscape ideas, collectively suggest a simple additive description of the structural and phonon-like contributions [14]

$$S_0(T) \simeq b S_0(T_g) + \frac{T}{T_g}(1 - b) S_0(T_g). \tag{3}$$

Numerical results for S_0 and $\tau(T)$ based on parameters characteristic of polymethylmethacrylate (PMMA) are shown in Fig. 1. At the (modest) sub-T_g temperatures typically probed in experiment, an *effective* Arrhenius behavior is generically predicted with quantitative features in agreement with multiple measurements [14,15].

As indicated in Fig. 1, the aging process in our approach corresponds to evolution of the long wavelength amplitude of density fluctuations from its nonequilibrium value (at $t = 0$) to a smaller equilibrium value. The local fast process is taken to be unaffected by physical aging, a simplification that is not universally exact [16] but generally quite reasonable [3]. The collective barrier and mean hopping time become time-dependent via $S_0(t)$. To model this process we propose a first-order kinetic description

$$\frac{dS_0(t)}{dt} = -\frac{S_0(t) - S_{0,l}}{\tau(\lambda(t))}, \tag{4}$$

where $S_{0,l}$ is the equilibrium supercooled liquid value and $S_0(t = 0) = S_{0,g}$ is the $t = 0$ nonequilibrium value of Eq. (3). The physical idea is the rate of change of the amplitude of long wavelength density fluctuations at an aging time t is linearly proportional to how far the system is from equilibrium, and equilibration proceeds via the activated barrier hopping controlled alpha relaxation process [17]. Given $\lambda(t) \equiv [\rho\sigma^3 S_0^{3/2}(t)]^{-1}$ and Eqs. (2) and (3), Eq. (4) represents a self-consistent, highly nonlinear description of the aging dynamics of $S_0(t)$ and hence the relaxation time [18] or shift factor $a(t) \equiv \tau(t)/\tau(0)$.

Calculations of $S_0(t)$ for PMMA are shown in Fig. 2. As experimentally observed [1–3] for properties such as the density, enthalpy, and modulus, the basic shape of the aging curve is sigmoidal, with a roughly logarithmic form at intermediate times. The latter is quantified by a

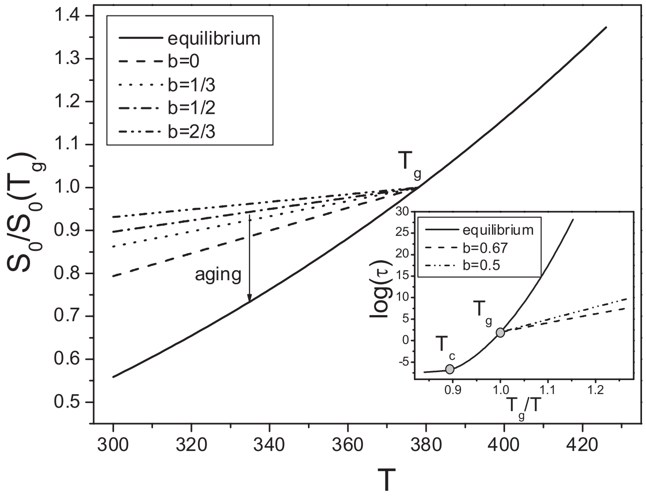

FIG. 1. Normalized $S_0(T)$ as a function of temperature (K) for material parameters relevant to PMMA [14] ($\tau(T_g) = 100$ s) and several values of b in Eq. (3). The equilibrium supercooled liquid result is also shown. The inset shows the corresponding alpha relaxation time (secs).

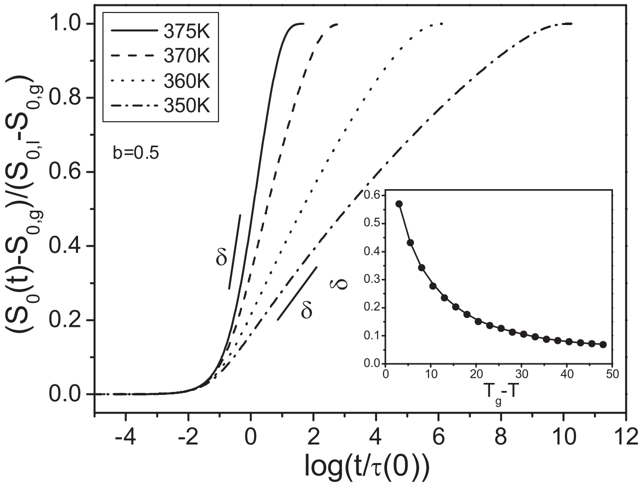

FIG. 2. Normalized differential amplitude of density fluctuations as a function of aging time reduced by the initial nonequilibrium relaxation time for PMMA with $b = 0.5$. The inset shows the numerically determined slope parameter (extracted as schematically indicated in the main panel) as a function of the degree of cooling below T_g.

slope, δ, extracted from the early stages of the intermediate aging regime (Fig. 2 inset), which decreases in a strongly nonlinear manner with cooling. Figure 3 shows the corresponding results for the relaxation time shift factor. Again a sigmoidal shape is found, and good power law behavior occurs at intermediate times. This allows an apparent aging exponent, $\mu = d\ln[\tau(t)]/d\ln(t)$, to be accurately determined. Note the time axis in Fig. 3 is scaled by the initial relaxation time, and μ is extracted under the assumption all time scales are accessible. The equilibration time (long time plateaus in Figs. 2 and 3) increases extremely rapidly with cooling, and roughly equals the alpha relaxation time of the supercooled melt. The inset of Fig. 3 shows the aging exponent (shift rate) as a function of a temperature difference variable. The effective exponent initially increases sharply with cooling below T_g, and then slowly approaches unity for $T_g - T \sim 50$ K. The theoretical results depend weakly on the frozen density fluctuation parameter b. Given the compressibility and segmental density parameters of many polymers are quite similar [7], we also expect a weak dependence on these material-specific aspects which are largely subsumed in specification of T_g.

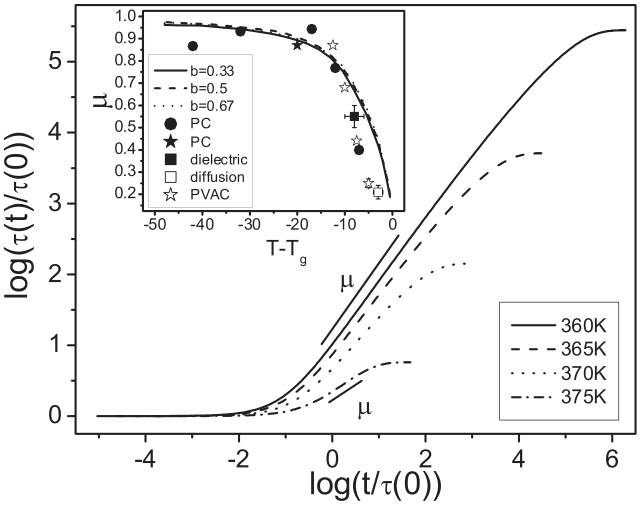

FIG. 3. Logarithmic shift factor as a function of normalized aging time for the same system as in Fig. 2. The inset shows the aging exponent as a function of the degree of undercooling for three values of b. Data is given for mechanical [polycarbonate (circle [19], solid star [20]), polyvinylacetate (open star [21])], dielectric relaxation (solid square [23]), and tracer diffusion (open square [22]) experiments.

Our aging exponent calculations are compared in Fig. 3 with experimental results for several polymers and different properties (mechanical [19–21], diffusion [22], dielectric relaxation [23]). The modest data scatter likely reflects both real quantitative differences associated with the aging of different properties and/or materials, and statistical errors in extracting an apparent power law exponent. To within these uncertainties, the calculations are in good agreement with the measurements.

Our predictions for the aging exponent follow from the fact that $\mu = d[\beta a_c\{F_B(\lambda(t)) - F_B(\lambda(0))\}]/d\ln(t)$ is controlled by the time dependence of the barrier. The latter is determined by the magnitude and time evolution of $S_0(t)$. If $S_0(t) \propto \ln(t)$, then $d[dS_0(t)/d\ln(t)]/dt \approx 0$ over an intermediate time interval where the relaxation time grows as a power law with aging time. Using the latter condition, Eq. (4), and the definition of the aging exponent, one can easily show $\mu = 1 - [t/\tau(t)]$ *evaluated* in the intermediate time (plateau) regime where $[t/\tau(t)]$ is roughly constant. Hence μ is bounded from above by unity in our simple model, although we do not know of a fundamental reason that $\mu \leq 1$. Its specific value follows from the near "plateau level" of $[t/\tau(t)]$ which decreases with cooling resulting in a monotonic increase of μ.

The power law aging of the mechanical response time scale of polymer glasses (stress relaxation or creep) often exhibits [3] a material-specific intermediate temperature interval where $\mu \sim 1$, followed by a rather sharp downturn at lower temperatures. As a first attempt to address the downturn behavior, Fig. 4 presents model calculations of the aging exponent for several values of the frozen density fluctuation parameter that span the experimental range [15]. Apparent exponents (now defined locally) are computed at two specific, but different, (long) *absolute* aging times typical of experimental studies. Two interesting, *experimentally testable*, predictions emerge. (i) The initial growth of the aging exponent below T_g is insensitive to the nonuniversal material aspects. One interpretation relevant to experiment is that $\mu \rightarrow 0$ as $T \rightarrow T_g$ is a practical consequence of a minimum observable time scale and the sigmoidal form of the aging curve. (ii) The breadth of the approximate plateau of $\mu(T)$ and onset of the downturn are sensitive to b and observation time scale. The decrease of

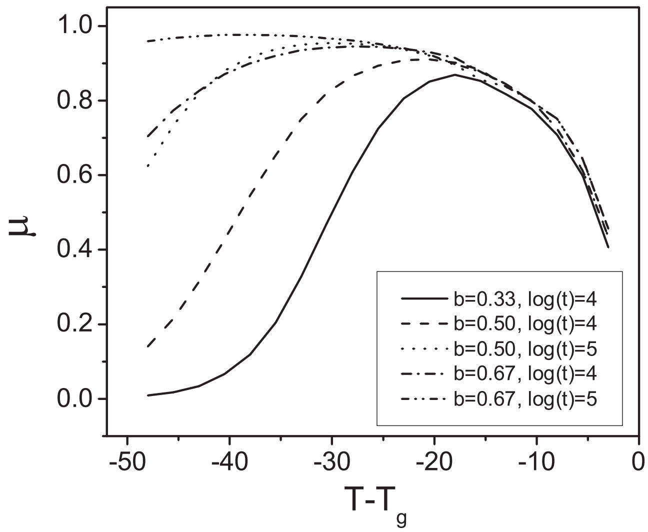

FIG. 4. Apparent value of the local aging exponent for PMMA as a function of degree of undercooling evaluated at two aging times (10^4, 10^5 s) and three values of b.

the apparent aging exponent at low temperatures is thus suggested to be a consequence of the power law intermediate regime (see Fig. 3) being shifted to unobservably long times. The breadth of the $\mu \sim 1$ nearly constant intermediate temperature behavior is enhanced as b increases and/or observation time lengthens. The former trend is a consequence of $\tau(0)$ decreasing with increasing b [20], which implies the intermediate power law regime emerges at shorter absolute time for larger values of the frozen in density fluctuation amplitude. The latter trend reflects the fundamentally sigmoidal form of the full aging response (Fig. 3). The model calculations in Fig. 4 qualitatively capture the diversity of experimental observations by Struik [3], and to the best of our knowledge represent the first molecular level theoretical description of this generic aging behavior of polymer glasses. Our calculations also suggest a clear possible origin for the quantitative nonuniversality of $\mu(T)$.

In conclusion, we have proposed a dynamical theory for the physical aging of polymer glasses based on the premise that long wavelength density fluctuations are the critical collective dynamic order parameter. The present work provides a foundation for treating more complex phenomena such as the coupling of aging and mechanical deformation which results in stress-induced "rejuvenation" [2,3]. We have considered only the generic aspects of the classic "down-jump" aging experiment [3]; generalization to treat memory or asymmetric aging experiments, and property dependence of aging time scales [2], is possible. By combining our approach with recent ideas for treating the nonlinear mechanical response of glassy particle systems [24], predictive theories for the influence of deformation on the alpha process and rate-dependent nonlinear mechanical properties can be constructed.

This work was supported by the National Science Foundation as NIRT Project No. 0505840. We thank Greg McKenna for stimulating discussions and correspondence.

*Electronic address: kschweiz@uiuc.edu

[1] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).
[2] G. B. McKenna, J. Phys. Condens. Matter **15**, S737 (2003).
[3] L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, Amsterdam, 1978).
[4] P. Sollich, F. Lequeux, P. Hebraud, and M. E. Cates, Phys. Rev. Lett. **78**, 2020 (1997).
[5] V. Lubchenko and P. G. Wolynes, J. Chem. Phys. **121**, 2852 (2004).
[6] P. Lunkenheimer, R. Wehn, U. Schneider, and A. Loidl, Phys. Rev. Lett. **95**, 055702 (2005).
[7] K. S. Schweizer and E. J. Saltzman, J. Chem. Phys. **121**, 1984 (2004).
[8] T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. A **35**, 3072 (1987).
[9] W. Gotze and L. Sjogren, Rep. Prog. Phys. **55**, 241 (1992).
[10] A. J. Archer and M. Rauscher, J. Phys. A **37**, 9325 (2004).
[11] K. S. Schweizer, J. Chem. Phys. **123**, 244501 (2005).
[12] K. S. Schweizer and E. J. Saltzman, J. Chem. Phys. **119**, 1181 (2003); E. J. Saltzman and K. S. Schweizer, Phys. Rev. E **74**, 061501 (2006).
[13] V. N. Novikov and A. P. Sokolov, Phys. Rev. E **67**, 031507 (2003).
[14] K. Chen and K. S. Schweizer, J. Chem. Phys. **126**, 014904 (2007).
[15] See Ref. [14] for a detailed summary of the experimental measurements of $S_0(T)$ and the change in apparent activation energy across T_g of many polymer glasses.
[16] M. L. Cerrada and G. B. McKenna, Macromolecules **33**, 3065 (2000), and refs. cited therein.
[17] The explicit factor of density in λ should also be time dependent, but this is a weak effect compared to dependence of the barrier on S_0 and is neglected for simplicity.
[18] The alternative theoretical model $S_0(t) = S_{0,g} + (S_{0,l} - S_{0,g})(1 - e^{-t/\tau(t)})$ has also been investigated. This ansatz is motivated by a recent experimental dielectric study [6] where it was shown to represent the observations very well. Calculations based on this model agree in all essential aspects with the predictions based on Eq. (4).
[19] P. A. O'Connell and G. B. McKenna, J. Chem. Phys. **110**, 11 054 (1999).
[20] J. M. Hutchinson, S. Smith, B. Horne, and G. M. Gourlay, Macromolecules **32**, 5046 (1999).
[21] M. Delin, R. Rychwalski, J. Kubat, C. Klason, and J. M. Hutchinson, Polym. Eng. Sci. **36**, 2955 (1996).
[22] C. T. Thurau and M. D. Ediger, J. Chem. Phys. **116**, 9089 (2002).
[23] A. Alegria, L. Goitiandia, I. Telleria, and J. Colmenero, Macromolecules **30**, 3881 (1997).
[24] V. Kobelev and K. S. Schweizer, Phys. Rev. E **71**, 021401 (2005).