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## Abstract

At temperatures moderately below their glass transition temperature, the properties of many glassforming materials can evolve slowly with time in a process known as physical aging whereby the thermodynamic, mechanical, and dynamic properties all drift towards their equilibrium values. In this work, we study the evolution of the thermodynamic and dynamic properties during physical aging for a model polymer glass. Specifically, we test the relationship between an estimate of the size of the cooperative rearrangements taking the form of strings and the effective structural relaxation time predicted by the Adam-Gibbs relationship for both an equilibrium supercooled liquid and the same fluid undergoing physical aging towards equilibrium after a series of temperature jumps. We find that there is apparently a close correlation between a structural feature of the fluid, the size of the string-like rearrangements, and the structural relaxation time, although the relationship for the aging fluid appears to be distinct from that of the fluid at equilibrium.

## Disciplines

Chemical Engineering

## Comments

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# Evolution of collective motion in a model glass-forming liquid during physical aging

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At temperatures moderately below their glass transition temperature, the properties of many glass-forming materials can evolve slowly with time in a process known as physical aging whereby the thermodynamic, mechanical, and dynamic properties all drift towards their equilibrium values. In this work, we study the evolution of the thermodynamic and dynamic properties during physical aging for a model polymer glass. Specifically, we test the relationship between an estimate of the size of the cooperative rearrangements taking the form of strings and the effective structural relaxation time predicted by the Adam-Gibbs relationship for both an equilibrium supercooled liquid and the same fluid undergoing physical aging towards equilibrium after a series of temperature jumps. We find that there is apparently a close correlation between a structural feature of the fluid, the size of the string-like rearrangements, and the structural relaxation time, although the relationship for the aging fluid appears to be distinct from that of the fluid at equilibrium. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4775781>]

## I. INTRODUCTION

Despite their common use in engineering applications, glasses, especially polymer glasses, remain one of the most poorly understood states of condensed matter. Many of these applications depend critically on the properties of the polymer below its glass transition temperature ( $T_g$ ). Although there has been much progress in recent years in our understanding of relaxation in equilibrium supercooled liquids above  $T_g$ ,<sup>1-4</sup> much less is known about the dynamics of glass-forming materials below  $T_g$  where non-equilibrium effects are prevalent. It is well-known that glasses undergo “physical aging,” by which we mean their properties gradually evolve their equilibrium values over time for moderate temperatures below  $T_g$  after a sufficient “aging time.” In the vicinity of  $T_g$ , this aging process is often highly prevalent; the equilibration time is typically on the order of the structural relaxation time, which can vary widely depending on the temperature of the sample. Below  $T_g$ , the necessary structural reorganization to obtain equilibrium takes progressively longer times ranging anywhere from hours to decades to reach equilibrium so that the material is intrinsically a non-equilibrium solid. This aging process is of great interest in applications where the associated property evolution can be a matter of practical concern in the end-use of the materials. For example, separations processes frequently involve polymer membranes that can exhibit significant aging effects on their permeability,<sup>5</sup> and this process has great significance for the mechanical properties of influencing end-use applications of diverse structural polymeric and glassy materials broadly.<sup>6</sup>

At temperatures near  $T_g$ , the aging process can be followed to its completion where the sample reaches equilibrium, and a number of interesting observations remain poorly understood for an aging glass. For example, it has been shown recently that different material properties can age at different rates in a glassy polymer; the time to age into equilibrium by measuring the shift factors from a linear creep experiment was found to be more than two orders of magnitude longer than the time required to age the dielectric response into equilibrium.<sup>7</sup> In addition, several experiments demonstrate that the approach to equilibrium can depend on the sign of the temperature jump employed. For samples equilibrated at a series of high temperatures and then subjected to a temperature jump to a common lower temperature, the approach to equilibrium is qualitatively different than if the samples each began at equilibrium at a lower temperature and then are subjected to a  $T$  jump to a common higher temperature.<sup>8</sup> It should be noted that molecular dynamics simulations cannot access the time scales of minutes, hours, days, and weeks relevant to many practical applications, but it is possible to perform temperature jump experiments in the supercooled regime to observe significant aging of thermodynamic and relaxation properties. This is the approach of the present paper and other recent studies of the aging effect in glass-forming materials.

Although less common than the extensive work investigating relaxation in equilibrium supercooled liquids, several simulation studies have investigated the dynamics of model glass-formers during physical aging. Mossa and Sciotino have reproduced the so-called “Kovacs effect”<sup>9</sup> in a simulation study of ortho-terphenyl (OTP).<sup>10</sup> The Kovacs effect occurs when a glass-former is quenched to a low temperature and is subjected to a temperature increase, and under

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the appropriate conditions the thermodynamic properties follow a non-monotonic approach towards equilibrium. That is, the density or the enthalpy can pass through and overshoot the equilibrium value before returning to equilibrium. Rottler and Robbins have shown how aging a polymer glass affects its yielding behaviors.<sup>11</sup> Additionally, Warren and Rottler<sup>12-14</sup> have provided a detailed analysis of the dynamics and creep response of an aging polymer glass. By providing a detailed analysis of the characteristic times of particle displacement in a polymer glass, they have shown how the mean of the distribution of hop times is divergent for an aging polymer, and the application of stress changes the shape of the distributions such that the mean hopping time becomes finite and relaxation is possible.

In equilibrium supercooled liquids, there is both experimental<sup>15</sup> and computational evidence<sup>16-18</sup> of a growing dynamical length scale on the approach to the glass transition, and we take these equilibrium fluid studies as the starting point of our work. The Adam-Gibbs theory<sup>4</sup> of glass formation leads one to expect the growth of the activation energy in glass-forming liquids to be governed by the growth of dynamic clusters or “cooperatively rearranging regions” (CRRs). Recently, the identification of string-like clusters of cooperative rearrangement has been quantitatively tested using molecular dynamics simulations in a series of supercooled polymer nanocomposites by determining the average size of the string-like collective rearrangements as a function of temperature.<sup>17</sup> For the time scales accessible to molecular dynamics, it was found that the Adam-Gibbs relationship collapsed the relaxation time data very well when the strings are directly identified with the CRRs. Given this success for equilibrium fluids, here we explore whether the changes in the relaxation time under physical aging conditions can be understood from the evolution of the strings under non-equilibrium conditions. A previous study by Zhang *et al.*<sup>19</sup> has examined the evolution of string-like collective motion in Ni nanoparticles undergoing melting and freezing, where it was found that there was a peak in the prevalence of the cooperative dynamics during melting. Furthermore, on the surface of the nanoparticle string-like rearrangements were prevalent and their equilibrium size changed following step changes in temperature.<sup>20</sup> Therefore, there is good reason to expect that the string-like collective motion in our glass-forming liquids can be defined under non-equilibrium conditions. If validated, this approach would provide a direct structural parameter in the glass-forming liquid to identify with physical aging.

In this study, we examine physical aging in a model polymer glass-forming liquid studied previously under equilibrium conditions and here we study the same fluid under a variety of thermal histories and non-equilibrium conditions. Inspired by the classic Kovacs experimental studies, we first perform two-step temperature jumps:  $T$  is first decreased to a temperature just above  $T_g$ , and our glasses are allowed to age into equilibrium before they are subsequently jumped to a higher temperature. In the second series of simulations, our supercooled polymers are equilibrated at various temperatures in the supercooled regime, and each system subsequently experiences a temperature jump to a common, central temperature. In other words, we examine the response of our

system to a symmetric temperature jump to a common, intermediate temperature. During these calculations, we monitor the time evolution of the density, internal energy, the relaxation time, and a measure of the collective motion (i.e., the string length). We find that we can understand many of the observed trends in our aging data from the evolution of the strings in the course of the system equilibration.

## II. METHODS

We have employed a coarse-grained polymer model that has been extensively characterized in the literature,<sup>21-24</sup> for completeness, we recount the main details here. Each polymer chain consists of  $N = 500$  Lennard-Jones (LJ) monomers connected by very stiff harmonic bonds. The LJ potential is cut at  $r_{cut} = 2.5\sigma$ , and the energy is shifted such that it goes smoothly to zero at the cut-off distance. The force constant employed in the harmonic bonding potential  $U_{bond}(r_{ij}) = k(r_{ij} - r_0)^2/2$  is  $k = 2000$ , and the equilibrium bond length  $r_0 = 1.0$ . Our simulation box contains 81 polymer chains, giving a total number of sites  $N_T = 40\,500$ . All results presented below are in LJ units reduced by the properties of the polymer monomers (e.g.,  $T = T^* k_B/\epsilon$ , where  $T^*$  is the temperature in laboratory units), and all of our calculations were performed using the LAMMPS simulation package.<sup>25</sup>

We begin by carefully equilibrating our systems at a temperature that is well above the glass transition temperature ( $T = 1.5$ ) using a combination of connectivity-altering Monte Carlo moves<sup>26-28</sup> and molecular dynamics (MD) in the NPT ensemble. Equilibration was justified by ensuring that the monomers had diffused multiple times the average end-to-end distance,  $R_E$ , and by requiring that the statistics of the entanglement network no longer changed with further equilibration.<sup>29-31</sup> Three independent configurations were generated, and all results presented below are averaged over these configurations; the uncertainties represent the standard error of the properties calculated in each independent configuration.

After equilibration at  $T = 1.5$ , our systems are cooled to lower temperatures of interest at a rate of  $\Delta T/\delta t = 5 \times 10^{-5}$  in the NPT ensemble with  $P = 0$ ;  $T = 0.84$  is close to the onset of supercooled behavior where the dynamic properties first take on a super-Arrhenius temperature dependence for this model, and the characteristic temperatures and glass-forming nature of a closely related polymer model has been characterized in detail in the literature.<sup>22,32</sup> We point out that there are some small differences in the characteristic temperatures in the present model due to the use of a force-shifted Lennard-Jones potential in the previous work.

Each of our temperature jumps discussed below are performed as instantaneous changes in the set temperature of the simulation; these correspond to infinitely fast temperature changes, and we observe how the system reaches equilibrium after such step changes. We note that the temperature, which is controlled with the Nosé-Hoover thermostat,<sup>33</sup> stabilizes at the new set point within a time less than approximately  $t = \tau_{LJ}$  (approximately 500 MD time steps with a step size  $\delta t = 0.002$ ). The physical aging process occurs on times much longer than this relatively short time scale. We identify the

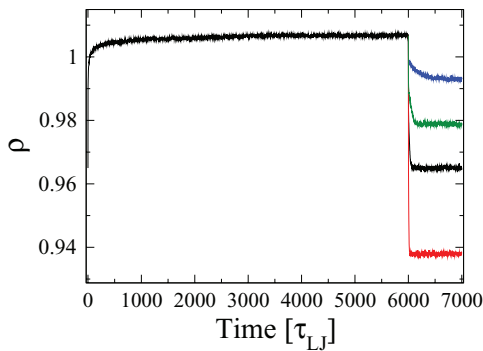


FIG. 1. Evolution of the system density with time after two successive temperature jumps: first, at time  $t = 0$ ,  $T$  is decreased from 0.6 to 0.45. Second, at  $t = 6000$ , the temperature is increased to  $T = 0.5$  (blue), 0.55 (green), 0.6 (black), or 0.7 (red).

glass transition temperature  $T_g$  as the temperature where our sample falls out of equilibrium upon cooling at a fixed cooling rate, and  $T_g$  for this model when cooled at  $\Delta T/\delta t = 5 \times 10^{-3}$  from  $T = 0.8$  to  $T = 0.2$  is found to be  $T_g = 0.437 \pm 0.004$ . This estimate of  $T_g$  was made by identifying the location where a plot of  $\ln(v)$  versus  $T$  changes slope, indicating a change in the coefficient of thermal expansion that is commonly associated with the glass transition. It is possible for us to age into an apparent equilibrium for our polymer glass down to  $T \approx 0.43$ .

We measure our effective relaxation times during “time windows” as our systems undergo physical aging to equilibrium following approaches used in previous non-equilibrium simulations of the same polymer glass.<sup>34–36</sup> Briefly, we divide our simulation trajectory into overlapping windows of fixed widths in time  $\delta t_{win} = 200 \tau_{LJ}$ . In each window, we calculate  $F_s(q, t)$  at  $q = 7.14$ , which is approximately the location of the first peak in the static structure factor for this system at equilibrium. Each calculation of  $F_s(q, t)$  is averaged over a moving time origin that is restricted to the current time window, and the effective structural relaxation time,  $\tau_{eff}$  is calculated by fitting the piece of  $F_s(q, t)$  calculated in each time window to a KWW stretched exponential,  $F_s(q, t) = a_0 \exp[-(t/\tau)^\beta]$  and integrating to obtain  $\tau_{eff} = a_0 \tau \Gamma(1/\beta)/\beta$ .  $\Gamma(x)$  is the Gamma function.

The average string length is calculated in the same time windows as  $F_s(q, t)$ . We calculate the string length as a func-

tion of observation time  $\delta t$ , and at all temperatures investigated here the time windows of length  $200 \tau_{LJ}$  are sufficient to observe the maximum in the string length. The 5% most mobile particles were considered for string formation, and two particles  $i$  and  $j$  were taken as part of the same string if they satisfied

$$\min[|\mathbf{r}_i(t) - \mathbf{r}_j(0)|, |\mathbf{r}_j(t) - \mathbf{r}_i(0)|] < 0.6 \sigma. \quad (1)$$

We have verified that the results presented below are not sensitive to considering higher fractions of mobile particles or more restrictive definitions for considering mobile particles to be part of the same string (e.g., using  $0.55 \sigma$  rather than  $0.6 \sigma$  in Eq. (1)).

### III. RESULTS

#### A. Aging of thermodynamic properties

We begin by showing how the density ( $\rho$ ) changes after two sequential changes in  $T$ : a large  $T$  decrease followed by aging into equilibrium and a subsequent  $T$  increase. Figure 1 shows the evolution of  $\rho$  when a system is quenched from  $T = 0.6$  at time  $t = 0$  to  $T = 0.45$ . After approximately  $3000 \tau_{LJ}$ , the density has reached its equilibrium value, and further simulation time does not change  $\rho$  further. At  $t = 6000 \tau_{LJ}$ ,  $T$  is increased to one of several values ( $T = 0.5, 0.55, 0.6$ , or  $0.7$ ). For the larger  $T$  jumps to higher temperatures, the polymer equilibrates very quickly while for the jump to  $T = 0.5$ , equilibration is noticeably slower due to the slow equilibrium dynamics at  $T = 0.5$ .

#### B. Aging of structural relaxation

We calculate a variety of dynamic properties and monitor their time dependence on the approach to equilibrium. Figure 2 shows the evolution of the effective relaxation time  $\tau_{eff}$  after the temperature jumps described in Fig. 1. When the temperature is decreased at  $t = 0$ , the effective relaxation time immediately begins to increase, and it experiences a net change of nearly two orders of magnitude before settling to its equilibrium value at  $t \approx 3000$ , which is approximately the same as the time required for the density to reach equilibrium. Following the subsequent temperature increases, the time required for  $\tau_{eff}$  to reach its plateau value depends strongly on

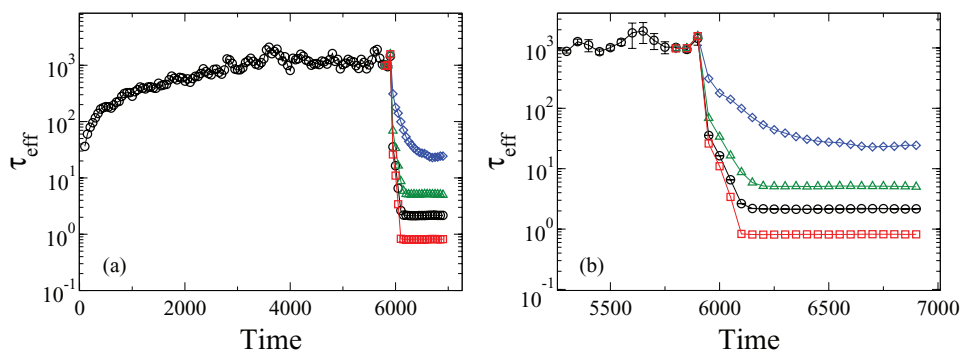


FIG. 2. (a) Evolution of the effective relaxation time after the temperature jumps described in Fig. 1. (b) Close-up of the region where the temperature is increased, and error bars are shown on the low temperature data where our statistical uncertainties are the largest.

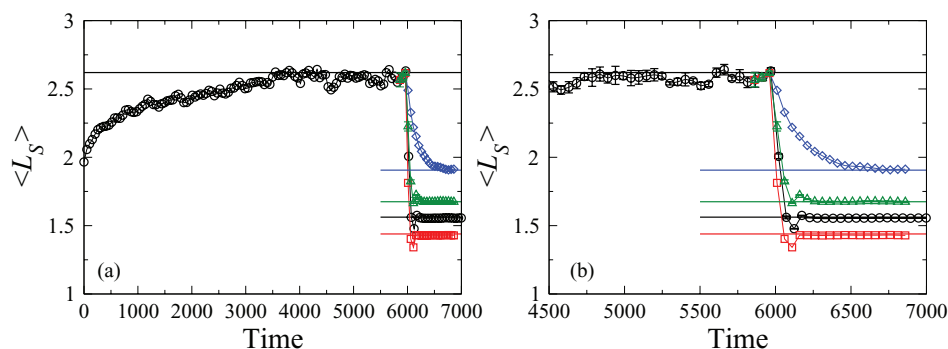


FIG. 3. (a) Evolution of the average string length after the temperature jumps described in Figs. 1 and 2. (b) Close-up view of the region where the temperature is increased, and the horizontal lines indicate the equilibrium value of  $L_S$  at the new set point temperature.

the magnitude of the  $T$  jump. For the smaller  $T$  increase to  $T = 0.5$ , the system does not reach its new equilibrium until  $t \approx 6700$ , while the larger  $T$  increases equilibrate almost immediately.

Figure 3 shows how the string length evolves after each temperature jump. After the decrease in  $T$  to  $T = 0.45$  at  $t = 0$ , the average string length  $L_S$  monotonically decreases to the equilibrium value, much like the density and structural relaxation time above. However, upon heating the system to the higher temperatures, a new trend emerges. For the larger temperature increases, the time evolution of  $L_S$  after  $T$  is increased proceeds non-monotonically to the equilibrium value. For a modest  $T$  jump to  $T = 0.55$ , there is an intermittent slight increase in  $L_S$ . As the magnitude of the temperature jump is further increased, we find that  $L_S$  overshoots the equilibrium value very briefly before returning at longer times. The subtle non-monotonic behavior in  $L_S$  are not observed in other properties of our system. This overshoot phenomenon is reminiscent of the large increase in string length near the point of nanoparticle melting,<sup>20</sup> which is likewise a point of significant particle rearrangement to accommodate this structural transition.

### C. Asymmetric approach to equilibrium

Next, we consider a different temperature history and subsequent aging evolution: we perform a series of temperature jumps to a common target temperature ( $T = 0.5$ ) for

systems equilibrated both above and below the target temperature. We consider temperature jumps of  $\Delta T = \pm 0.05$  and  $\pm 0.025$ , and we take the time of the temperature change as  $t = 0$ . First, the time evolution of the molar volume  $v = 1/\rho$  and the potential energy is shown in Figures 4(a) and 4(b), respectively. We plot our data as relative deviations from the long-time equilibrium value of the molar volume  $v_{eq}$  and potential energy  $E_{eq}$  at  $T = 0.5$ . We can clearly see in this figure that the approach to equilibrium is asymmetric: when the temperature is decreased to  $T = 0.5$  ( $\Delta T < 0$ ), the two curves corresponding to  $\Delta T = -0.25$  and  $\Delta T = -0.5$  quickly join each other and approach the equilibrium value together. This trend is observed in both the time evolution of the density and the potential energy. In contrast, when the temperature is increased to  $T = 0.5$  ( $\Delta T > 0$ ), the approach to equilibrium is distinct for the two different  $\Delta T$  jumps; the systems that were previously at a lower temperature approach the new equilibrium more slowly.

We also find a similar asymmetry in the time evolution of  $\tau_{eff}$  and  $L_S$ , as shown in Figures 5(a) and 5(b). For the two temperature decreases, we find that  $\tau_{eff}$  and  $L_S$  have essentially merged by  $t = 100 \tau_{LJ}$ ; the two curves then approach equilibrium together. However, after a temperature increase, neither  $\tau_{eff}$  nor  $L_S$  ever merge with each other until they reach equilibrium; they apparently approach equilibrium independently. The evolution of the average string length following a downward temperature jump is very similar in form to that found in the self-assembly of equilibrium

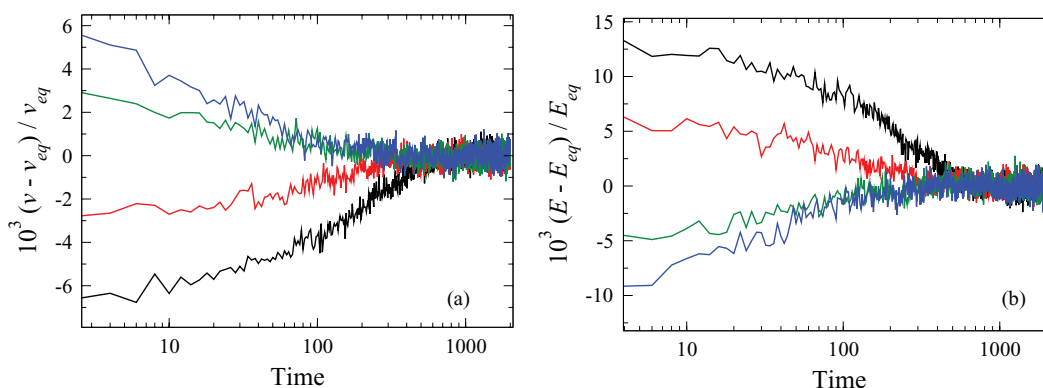


FIG. 4. Evolution of the system density (a) and potential energy (b) after  $T$  jumps from above and below to a common intermediate temperature,  $T = 0.5$ . The black, red, green, and blue curves each represent temperature jumps of  $\Delta = 0.05, 0.025, -0.025,$  and  $-0.05$ , respectively.

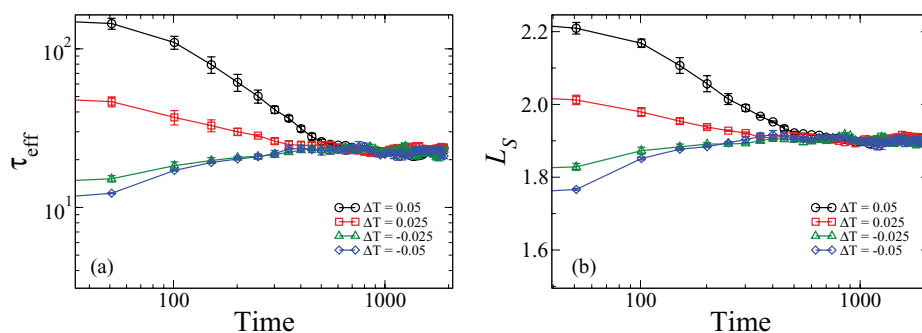


FIG. 5. (a) Effective relaxation times and (b) average string length after the symmetric temperature jumps described in Fig. 4. As with the density in Fig. 4(a), after a temperature decrease, the curves representing the properties quickly merge and drift to the equilibrium value together, while after a temperature increase the curves approach equilibrium at different rates.

associating linear polymers,<sup>37</sup> which is consistent with understanding strings in glass-forming liquids as a kind of self-assembly phenomenon.<sup>38</sup> We now examine the extent to which we can understand the changes in relaxation that we observe in aging fluid based on a dynamical extension of the Adam-Gibbs theory where the evolving magnitude of the string length,  $L(t)$ , is incorporated into the description.

#### D. Non-equilibrium relationship between $\tau_{eff}$ and $L_S$

From the Adam-Gibbs theory of glass-formation, we would expect that the activation energy for relaxation should grow exponentially as the size of the cooperative rearrangements increases,  $\log \tau \propto L_S/T$ . This relationship has recently proven robust for a series of model polymer systems of varying fragilities,<sup>17</sup> and so it is of interest to test whether this relationship also holds even for systems out of equilibrium. First, it is instructive to briefly review the trends of  $\tau_\alpha$  with  $L_S$  as a function of temperature at equilibrium. This analysis has never been performed on the present model glass-forming polymer, although the model considered in Ref. 17 is closely related. Figure 6(a) shows an Arrhenius plot of  $\tau_\alpha$ , and the inset to Fig. 6(a) shows the equilibrium temperature dependence of the average string length,  $L_S$ . As expected, both  $\tau_\alpha$  and  $L_S$  sharply increase as the temperature is reduced. Figure 6(b) tests the Adam-Gibbs relationship by plotting  $\tau_\alpha$  vs.  $L_S/T$  on a semi-log scale calculated from equilibrium simulations in the

supercooled regime. The Adam-Gibbs relationship suggests a linear relationship, and we verify this expected trend to a good approximation. By fitting the data shown in Fig. 6(b), we can extrapolate the value of  $L_S$  at a “laboratory”  $T_g$ , which is typically defined where  $\tau_\alpha \approx 100$  s. We fit the structural relaxation time data in Fig. 6(a) to the commonly used VFTH equation, and extrapolate our fit to obtain an extrapolated  $T_g$ , yielding  $T_g^{ext} = 0.381$ . Subsequently, we linearly fit the data in Fig. 6(b), and we estimate that the string length value  $L_S$  which corresponds to our extrapolated  $T_g$  is approximately  $L_S = 6.75$ .

Figure 7 tests the connection between the relaxation time and the size of the cooperative rearrangements for systems out of equilibrium that have experienced the symmetric temperature jumps to a common intermediate temperature,  $T = 0.5$ . A value of  $T = 0.5$  was used for the aging configurations since the set point temperature is reached on time scales much shorter than the characteristic time associated with the string-like rearrangements. Even for systems out of equilibrium, there is apparently a close connection between the relaxation time and the CRRs. The relationship clearly falls off of the equilibrium line, yet  $\log \tau$  remains approximately linear in  $L_S/T$ . It is worth noting that the structural relaxation time measured using the time window approach does not necessarily account for the full decay of  $F_s(q, t)$  to the equilibrium value. This procedure neglects the change of the stretching exponent  $\beta$  which definitely can be a complication to our

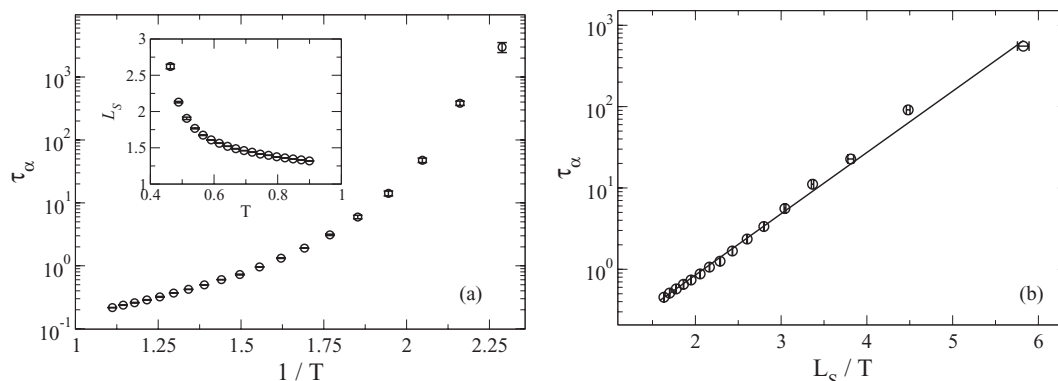


FIG. 6. (a) Structural relaxation normalized by  $T_g$ , with the inset representing the average string length; (b) test of the Adam-Gibbs relationship for this model polymer glass at equilibrium. The relaxation times  $\tau_\alpha$  and average string length  $L_S$  are calculated as a function of temperature for systems at equilibrium in the supercooled regime ( $0.825 > T > 0.45$ ); the line is merely a guide to the eye.  $\tau_\alpha$  is calculated at equilibrium as the time for  $F_s(q, t)$  to decay to 0.2.

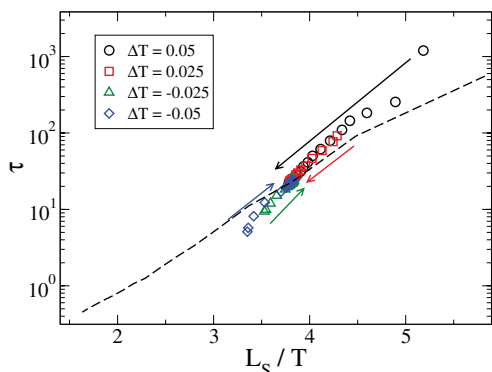


FIG. 7. Test of the connection between  $\tau_{eff}$  and the ratio  $L_s/T$  for systems out of equilibrium. The dashed black line represents the equilibrium results in the supercooled regime, and the various sets of points are from the non-equilibrium, symmetric temperature jump simulations described in Figures 4 and 5 above. Each data set represents a distinct temperature jump, and the arrows indicate the time evolution of the relaxation time and string length.

non-equilibrium relaxation analysis. The forms of the relaxation functions as well as  $\tau$  can be expected to change somewhat under aging conditions, although the experiments of Lee and McKenna<sup>39</sup> on model epoxy materials have indicated that the evolution of  $\beta$  under aging conditions can be small near  $T_g$ . Despite this complication in the analysis, we find that we qualitatively understand the evolution of the relaxation time in a system out of equilibrium from the evolution in the scale of collective rearrangement motion,  $L$ .

#### IV. SUMMARY

In summary, we have examined the evolution of some basic thermodynamic and dynamic properties of a model coarse-grained glass-forming polymer subjected to a variety of temperature jumps. We find that the approach to equilibrium depends on the sign of the temperature step  $\Delta T$ ; following a temperature decrease of varying magnitude to a common lower temperature, properties approach equilibrium at approximately the same rate. After a temperature increase, the approach to equilibrium depends on the magnitude of the temperature jump. Finally, we have explored whether the Adam-Gibbs model with the strings identified as the CRRs can describe the dynamics of our model supercooled liquid under aging conditions. While we find that there is apparently a correlation between the size of the cooperative rearrangements (strings) and the effective relaxation time, the relationship is apparently distinct from that found at equilibrium. While very encouraging for providing a direct structural basis for understanding aging in glass-forming materials, the observed deviations imply that we must better understand the nature of the cooperative motion and structural relaxation under aging conditions. It would also be useful to calculate the configurational entropy  $S_c$  as function of time as determined by Saika-Voivod and Sciortino<sup>40</sup> to see if this quantity scales inversely with  $L_s(t)$ , providing another important test of the Adam-Gibbs framework.

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