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Anomalous properties of the local dynamics in polymer glasses

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We show how changes in a local, high frequency dynamic process are correlated with the macroscopic behavior of glassy polymers. Polyvinylethylenes vitrified by different chemical and thermodynamic pathways exhibit different densities in the glassy state. We find that the rate and amplitude of a high frequency relaxation mode (the Johari–Goldstein process involving local motion of segments of the chain backbone) can either correlate or anticorrelate with the density. This implies that neither the unoccupied (free) volume nor the configurational entropy governs the local dynamics in any general sense. Rather it is the magnitude of the *fluctuations* in local density that underlie these nanometer-scale motions. We show how properties of the dynamics and the density fluctuations can both be interpreted in terms of an asymmetric double well potential. Although the results herein are for polymers, the principles are expected to be generally applicable to glassy materials. [doi:10.1063/1.3223279]

I. INTRODUCTION

Polymers are fascinating molecules in which global (chain) and local (segmental) motions are convoluted, giving rise to a complex combination of behaviors and properties. As a consequence of its large size, a polymer molecule exhibits motions that span time scales ranging from nanoseconds for local segmental relaxation to years for macroscopic flow even in the liquid state. This means that a rubbery polymer exhibits many attributes of a "soft" solid, yet microscopically is indistinguishable from a liquid. The time scale of the segmental motions is extremely sensitive to proximity to the glass transition. On approaching the glass transition temperature T_g by cooling, the segmental motions slow by several orders of magnitude over a narrow temperature range, ultimately surpassing the duration of a typical experiment to become (by definition) a "glass." Various spectroscopic techniques are used to study the complicated dynamics of polymers, including mechanical measurements, nuclear magnetic resonance, light scattering, neutron scattering, and dielectric spectroscopy (DS). Among these DS has the important advantage of covering more than ten decades of time (or frequency), which is necessary to follow the multitude of relaxation processes of a polymer chain. In DS the segmental motion, comprised of correlated transitions of a couple of backbone bonds, is associated with structural (or the $\alpha-$) relaxation, characterized by a relaxation time τ_α that becomes extremely large in the glassy state. The divergence of τ_α below T_g remains the subject of debate.[1,2]

In the glassy state "secondary" processes ($\beta, \gamma, \ldots$) are observed, having an origin commonly attributed to pendant groups undergoing local, uncorrelated reorientations. (These processes also transpire above T_g but are often difficult to resolve because of their small amplitude and overlap with the high frequency part of the α process). However, as pointed out by Johari and Goldstein,[3] a secondary relaxation is observed for rigid molecules lacking side groups, which means there is a particular β relaxation, the Johari–Goldstein (JG) process, that cannot be attributed to a simple side-group motion. The JG relaxation is a universal property of glass forming liquids and polymers, but nevertheless its molecular origin remains an open question. In at least one theoretical approach,[4] the JG is treated as the precursor of the structural α-relaxation. Alternatively, the JG relaxation is analyzed as independent of the α-dynamics.[5] In energy landscape models, "whereas the primary relaxation is assumed to be intrinsically coupled to transitions among different free-energy minima, this secondary relaxation process is viewed as a *local relaxation* within a given minimum."[6] Therefore the secondary relaxation is not necessarily related to the primary (structural) relaxation, although in energy landscape models possible correlations (e.g., between activation energies) could be supposed. An assumed independence of the primary and JG dynamics contrasts with recent DS measurements under hydrostatic pressure[7,8] and NMR results[9] demonstrating a strong correlation between the JG and α relaxations, notwithstanding their very different time scales. The relationship between the JG and segmental processes is analogous to that between the segmental and chain modes of polymers—in both cases there is a difference in length and time scales, even though the same molecular units are involved in both motions. Despite a growing recognition of the strong correlation between the α and the JG dynamics, there is no model that relates the behavior of the JG to other physical properties.

Herein we present a study of the JG relaxation in glassy polyvinylethylene (PVE), vitrified by different routes leading to different densities (three of these pathways are illustrated in Fig. 1). PVE is a judicious choice of polymer for this study because of its chemical structure—the dipoles responsible for the JG relaxation are the same as those giving rise to the α relaxation. We find unexpected and somewhat unintuitive behavior; to wit, at a given temperature and pressure, the

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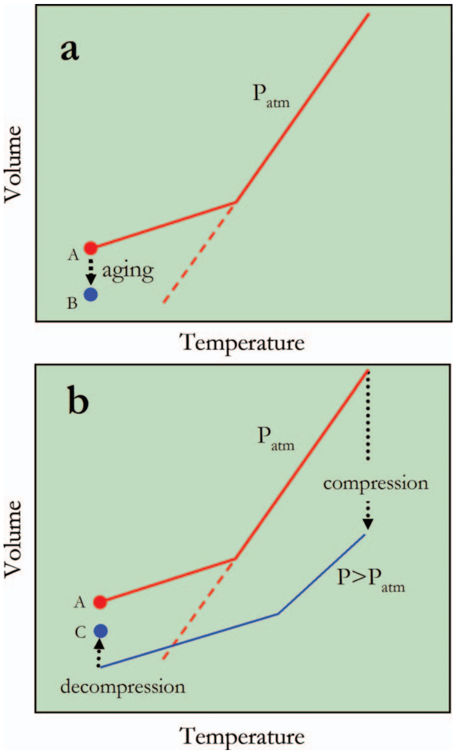

FIG. 1. Schematic of different routes to increase the density of a glassy polymer. (a) Sample A ("standard glass") was cooled at a constant rate from the equilibrium state above the glass transition; sample B ("physically aged glass") was obtained by maintaining sample A at the same temperature for a time long enough for its volume to approach the equilibrium value (dotted line). (b) Sample A was formed as above, while sample C was obtained by cooling after a compression in the melt and subsequent decompression in the glassy regime ("pressure densified glass").

JG relaxation can be slower or faster for densities greater than a "standard glass." That is, the JG dynamics can be correlated or anticorrelated with the available volume. We ascribe this behavior to the inherently heterogeneous character of the dynamics. Distinct length scales, with contributions reflected at different frequencies, respond differently and independently to volume changes. While properties such as structural relaxation in the liquid state are governed by the bulk volume, for the (very local) JG process the local distribution of the volume is paramount.

II. EXPERIMENTAL

The PVE was 96% vinyl (1,2-addition product) polybutadiene obtained from Bridgestone Americas with a weight-average molecular weight$=1.53\times 10^5$ D. Dielectric measurements employed a high precision Andeen-Hagerling 2700A bridge. The instrument has an exceptionally high resolution (loss tangent$=1.5\times 10^{-8}$) but a somewhat limited frequency range (50 Hz–20 kHz). Measurements at atmospheric pressure were done in a custom built, closed-cycle helium cryostat (Cryo Ind.) with temperature stability better than 5×10^{-2} K over a week's duration. For elevated pressure measurements the sample and electrodes were in a high pressure cell inside an environmental chamber (Tenney Co.); the experimental configuration is described more fully elsewhere.[8] Network formation (a fourth route to density modification, not shown in Fig. 1) was accomplished by reaction of the PVE with 0.67% by weight dicumyl peroxide (Varox DCP-R from R. T. Vanderbilt); details of this procedure can be found elsewhere.[10] For all cases PVE films were measured between parallel plates without spacers so that the plates could move freely in response to volume changes in the sample during the experiments. The JG relaxation time was calculated as the reciprocal of the peak frequency (in rad/s) by fitting the dielectric loss spectra using a Cole–Cole relaxation function;[11] this τ_{JG} is the most probable value.

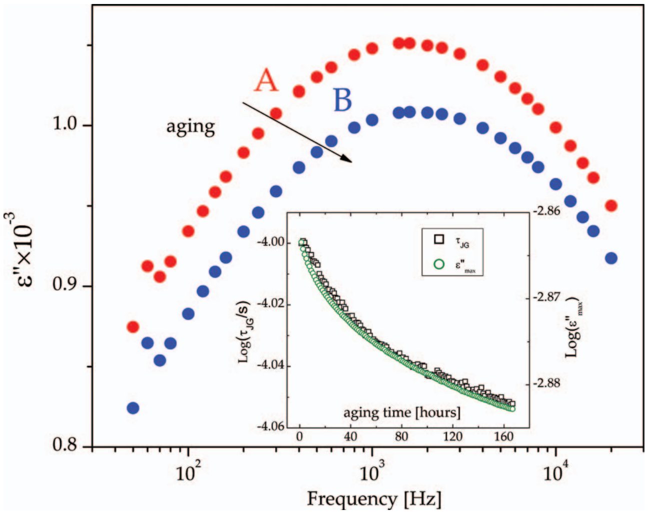

FIG. 2. Effect of physical aging on the JG-relaxation (route a). Imaginary part of the permittivity for samples cooled below the glass transition at a constant rate and then maintained at $T=240.9$ K. Curve A measured directly after cooling; curve B measured after a waiting time of 163 h at 240.9 K. Inset: variation in the JG relaxation time and the maximum in the dielectric loss during physical aging.

III. RESULTS AND DISCUSSION

The choice of PVE facilitates investigation of the JG relaxation, since its dielectric spectra show a resolved, and thus unambiguous, JG secondary relaxation peak.[12,13] Polymers generally are well suited for studies of vitrification since crystallization is slow or, in the case of the atactic PVE, nonexistent. Figure 1 illustrates three routes used to obtain glassy PVE, each resulting in a different density at the same T and P. The first (sample A) consists of isobaric cooling at a constant rate (2 K/min) from above T_g to a temperature well below the PVE glass transition temperature [$T_g=272.5$ K (Ref. 14)]. Since the pressure is one atmosphere, this material is referred to as the "standard" PVE glass. The polymer is in a nonequilibrated state, having a volume in excess of the equilibrium value (indicated by the dotted line in Fig. 1). The dielectric loss spectrum for sample A is shown in Fig. 2. Only the JG process is observed because structural relaxation is too slow ($\tau_\alpha > 10^4$ s) to contribute in the available frequency window. As the sample is maintained under isobaric and isothermal conditions, the volume slowly relaxes toward thermodynamic equilibrium, yielding a progressively denser material (sample B); this process is called "physical aging." Dielectric loss spectra recorded at different aging times (Fig. 2) show a clear decrease in amplitude of the dispersion, along with a shift to *higher frequency*. The inset of Fig. 2 shows the change in the JG relaxation time versus aging time. It is remarkable that the increased density during aging (estimated to be about 0.04%) causes the JG process to *speed up*; that is, at constant T τ_{JG} becomes *smaller* with decreasing volume. The amplitude of the JG peak also decreases during aging, as reported previously by several authors.[15–18] A few prior studies of small molecules rather than polymers found that the JG-relaxation time (as well as for some non-JG secondary processes) could be affected by physical aging well below T_g.[17–21] In these experiments, either no appreciable change in τ_{JG} was observed, an expected consequence if the temperature is sufficiently below T_g that physical aging is extremely slow,[15,18] or τ_{JG} was reported to decrease. We note that the decrease herein of the JG amplitude with density is also counterintuitive, since a denser material has a larger concentration of dipoles. And indeed, a larger value of the relaxed part $(f \gg \tau_{\mathrm{JG}^{-1}})$ of the real part of the permittivity is observed. The decrease in the amplitude of the dielectric loss peak means that there is a decrease in the average reorientation. An analysis of the time evolution of the τ_{JG} was presented previously.[22]

Another route to glassy PVE makes use of hydrostatic pressure. It is known that cooling at high pressure to below T_g, followed by release to ambient pressure, produces a denser polymeric glass.[23–25] In the present case the PVE is first pressurized to 350 MPa at 60K above T_g, with glass formation taking place during subsequent isobaric cooling. In the glassy state at constant temperature (242.8 K), the pressure is then reduced to ambient. This material (sample C in Fig. 1), known as "pressure-densified" glass, has a larger density (by about 1% as estimated from the change in ε' at the highest frequency) than the glass formed conventionally by cooling at atmospheric pressure (sample A).

Comparing the dielectric loss spectra of samples A and C at atmospheric pressure and $T=242.8$ K (Fig. 3), the JG relaxation for the latter has a larger amplitude and occurs at lower frequency than the peak for sample A. Thus, pressure densification, which increases the density, causes the expected changes in the JG process—slower with concomitantly larger amplitude. Over the range of temperatures up through T_g, the JG relaxation time of sample C remains longer than τ_{JG} for A (Fig. 3 inset). The JG activation energy E_{JG} of C is slightly smaller than for A ($E_{\mathrm{JG}}^{A}=46\pm2$ kJ mole^{-1}; $E_{\mathrm{JG}}^{C}=42\pm2$ kJ mole^{-1}), while a substantial difference is observed in the high temperature limiting values of τ_{JG} ($\log(\tau_{\mathrm{JG}}^{A})=-14.1\pm0.3$; $\log(\tau_{\mathrm{JG}}^{C})=-12.8\pm0.2$). Note that physical aging during the course of the measurements themselves was negligible. These changes in the JG process for PVE are consistent with previous observations for molecular liquids.[26,27] At the length scales relevant to glassy dynamics, the chain character of polymers is largely irrelevant.

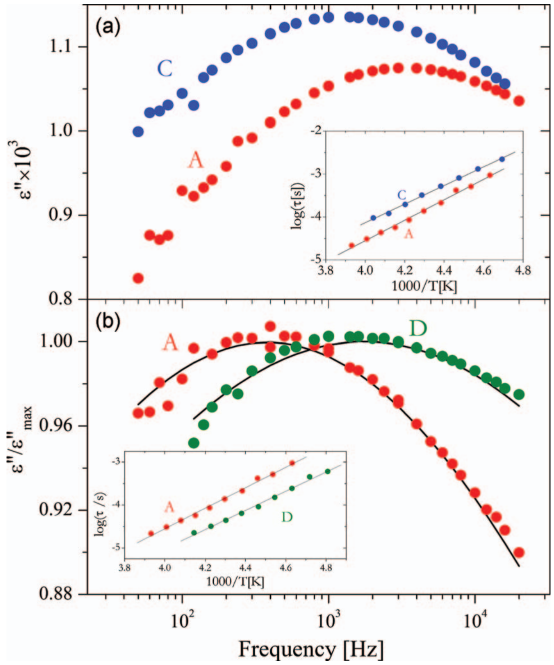

FIG. 3. (a) Effect of high pressure on the JG relaxation (route b). Imaginary part of the permittivity at atmospheric pressure and $T=242.8$ K. Sample A was vitrified at atmospheric pressure [Fig. 1(b)], while C was pressure densified (glass formation under high pressure) [Fig. 1(b)]. Inset: comparison of the temperature dependence of the JG relaxation time. (b) Effect of chemical cross-linking on JG relaxation. Imaginary part of the permittivity at atmospheric pressure and $T=224$ K for the (a) linear and the (d) cross-linked PVE. Both samples were cooled from the equilibrium state at the same rate (2 K/min). Inset: comparison of the temperature dependence of the JG process.

An example of the physical aging for the pressure densified glass is reported in Fig. 4. In this case a glass formed at 350 MPa was then kept at the same conditions of P and T ($P=83$ MPa and $T=252.6$ K) for about 10 days. The effect of aging is similar to that of a normal glass, observed as a decrease in ε'' of about 7% and an increase in τ of 25%, while the density (estimated from the change in ε' at the highest frequency) increases by $\sim$0.3%. Interestingly this indicates that the pressure densified glass will become even denser in the evolution toward equilibrium.

Thermodynamic models would account for the slowing down of the JG relaxation in sample C in terms of a reduction in either the free volume or the configurational entropy. These are the common explanations of the equilibrium dy-

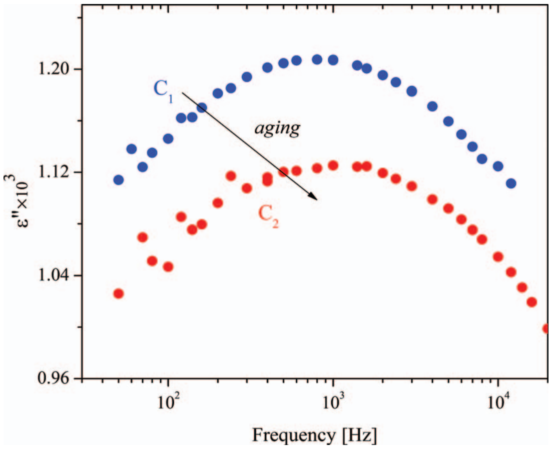

FIG. 4. Effect of physical aging on the JG relaxation for glass formed at high pressure. Imaginary part of the permittivity at $P=83$ MPa and $T=252.6$ K. Spectrum C_1 was measured after pressure densification (glass formation under high pressure) [Fig. 1(b)] at P $\sim$ 350 MPa. Spectrum C_2 was measured for the same sample after a waiting time of about 240 h at the same conditions of P and T ($P=83$ MPa and $T=252.6$ K). The aging of a pressure densified sample is similar to that of a normal glass (Fig. 2).

namic behavior[28,29] but they cannot explain the opposite effect that density has on sample B and on the aged sample C (e.g. sample C2 in Fig. 4). The implication is that samples C and B are different, not only in terms of their macroscopic density but also in their microscopic structure. For this reason a description of the dynamics based on macroscopic thermodynamical quantities fails. Moreover, the sensitivity to local structure confirms the untenability of the conventional picture that the JG process is a simple, noncooperative relaxation. There must be a number of segments involved (or molecules in the case of simple liquids), depending on the particular conditions under which the glass is formed. The fact that the local distribution of volume, rather than the macroscopic volume, governs the JG relaxation means this process can be used to probe the local structure of a glass, which is important for macroscopic properties, as we now describe.

Previous studies comparing physically aged and pressure-densified glassy polymers found interesting differences in their mechanical properties. In particular, physical aging confers brittleness while pressure densification increases the material's ductility.[30–32] In some cases the increased brittleness of aged glassy polymers can be removed ("rejuvenation") by mechanical stress.[32,33] Interesting insight into the differences between glasses formed by different pathways is gleaned from x-ray scattering measurements on polystyrene.[34] Large scale density fluctuations were found to correlate with the macroscopic density, irrespective of the method used to vitrify the material; however, density fluctuations occurring over a smaller scale (<0.5 nm) varied substantially depending on the pathway to the glass. Independent of the macroscopic density, physical aging increased local ordering. On the other hand, pressure densification had the opposite effect, with the reduction in local order correlated with improved mechanical properties, producing in particular a more ductile glass. Thus, there is an interesting connection between macroscopic and (subnanometer) microscopic properties.

If we assume that the motions giving rise to local density fluctuations in a glassy polymer are related to the same reorientational motions comprising the JG relaxation, certain behaviors can be anticipated. First, since the probability of a fluctuation is related to the minimum energy E_0 needed to carry out reversibly a given change in density,[35] a system having larger fluctuations is characterized by a smaller value of E_0. If E_0 is related to the energy barrier that needs to be overcome to orient dipoles, then larger fluctuations correspond to a larger amplitude of the dielectric loss (and vice versa).

An interpretation of both the density fluctuations and their influence on the dielectric loss can be obtained using the asymmetric double well potential (ADWP)[5,36–38] model. Indeed, a physical justification for and derivation of structural relaxation behavior from the ADWP has recently been proposed.[39] Previously Dyre and Olsen[5,40] used a "minimal" version of the ADWP model to analyze JG relaxations in small molecule glass formers; it is this form that we discuss herein (mADWP). The mADWP is described in terms of two quantities, the energy barrier U and the asymmetry Δ (see inset of Fig. 4). The relaxation time and the height of the dielectric loss peak $\varepsilon''_{\max}$ are given by[5,36]

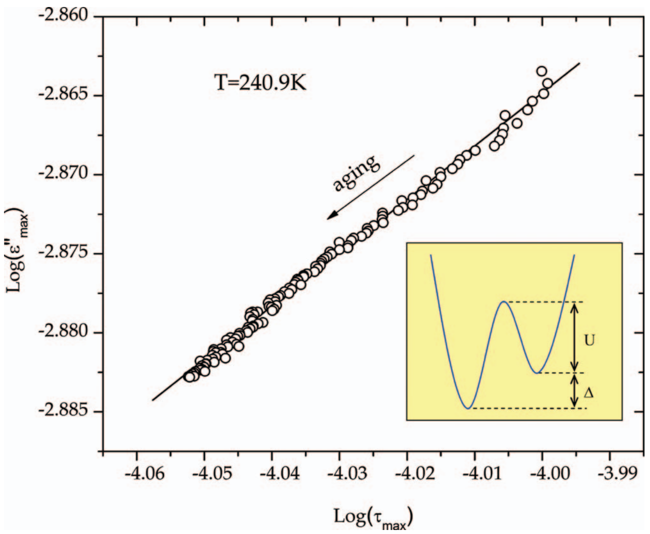

FIG. 5. Test of mADWP model. Double logarithmic plot of the amplitude of the dielectric loss vs the JG relaxation time during isothermal aging. The solid line is a linear fit with a slope=0.34. This power-law behavior, $\varepsilon''_{\max}\tau_{\max}^{-0.34}$=const, is consistent with the results of Olsen *et al.* (Ref. 19), interpreted using the mADWP (shown schematically in the inset) (Ref. 5). From Eq. (1) with the approximation that the sum $2U+\Delta$ does not change with aging (since U increases while Δ decreases), the slope should be 0.5. A linear coefficient smaller than 0.5 implies a decrease in $2U+\Delta$ with aging.

$$\tau_{\mathrm{JG}} = \tau_0 \exp\left(\frac{2U+\Delta}{2k_BT}\right)\cosh^{-1}\left(\frac{\Delta}{2k_BT}\right),$$
$$\varepsilon''_{\max} = \varepsilon''_0(T)\cosh^{-2}\left(\frac{\Delta}{2k_BT}\right). \tag{1}$$

The parameter τ_0 is independent of both structure and temperature, while ε''_0 is independent of structure but varies inversely with temperature. The free energy differences U and Δ are structure dependent and it is this dependence that can be related to the fictive temperature T_f, characterizing the nonequilibrium glass:[5] As T_f decreases, U decreases and Δ increases.

The mADWP model predicts at least qualitatively the observed behavior. During isothermal aging T_f decreases with aging time; therefore, Δ increases and U decreases. Consequently, according to Eq. (1), $\varepsilon''_{\max}$ and τ_{JG} both decrease (inset of Fig. 2). As discussed by Dyre and Olsen[5] the mADWP model gives a description of the quasilinear relationship between $\log(\varepsilon''_{\max})$ and $\log(\tau_{\mathrm{JG}})$ shown in Fig. 5. From Eq. (1) it is easy to see that the changes in $\varepsilon''_{\max}$ and τ_{JG} between the aging times t_1 and t_2 are related as

$$\ln\left(\frac{\tau_{\mathrm{JG}}^{t_1}}{\tau_{\mathrm{JG}}^{t_2}}\right) = \frac{2(U^{t_1}-U^{t_2})+\Delta^{t_1}-\Delta^{t_2}}{2kT} + 2\ln\left(\frac{\varepsilon''_{\max}{}^{t_1}}{\varepsilon''_{\max}{}^{t_2}}\right), \tag{2}$$

from which it follows that when the sum $2U+\Delta$ remains constant during aging (which is roughly true since U and Δ have opposite behavior), the two quantities should exhibit a power-law relationship with an exponent equal to 0.5. As seen in Fig. 5, we obtain $d\log(\varepsilon''_{\max})/d\log(\tau_{\mathrm{JG}}) = \sim 0.34$.

The lower experimental value can be attributed to a decrease in $2U+\Delta$ during aging. The change in the potential energy barriers during aging can be calculated from Eq. (1) as

$$\begin{aligned} \Delta^{t_1} - \Delta^{t_2} &\cong -kT \ln({\varepsilon''_{\max}}^{t_1}/{\varepsilon''_{\max}}^{t_2}), \\ U^{t_1} - U^{t_2} &\cong kT\left[\ln(\tau_{\mathrm{JG}}^{t_1}/\tau_{\mathrm{JG}}^{t_2}) - \tfrac{3}{2}\ln({\varepsilon''_{\max}}^{t_1}/{\varepsilon''_{\max}}^{t_2})\right]. \end{aligned} \tag{3}$$

Using these equations we calculate that the changes in the spectra in Fig. 2 correspond to $U^B - U^A = -0.32$ kJ mole^{-1} and $\Delta^B - \Delta^A = 0.15$ kJ mole^{-1}. Thus, during aging the energy barrier decreases, the potential becomes more asymmetric, and $2U+\Delta$ decreases.

The ADWP model can also be applied to the behavior observed during pressure densification. For sample C formed at higher pressure, since T_g increases with pressure, its T_f is higher than for the standard glass A. Consequently, Δ is smaller and U is larger than for A, which means that $\varepsilon''_{\max}$ and τ_{JG} are larger for sample C than for A. This is exactly the experimental results seen in Fig. 3. Using Eq. (1) we calculate for the changes in the spectra $U^C - U^A = 2.4$ kJ mole^{-1} and $\Delta^C - \Delta^A = -0.8$ kJ mole^{-1}. The pressure densified sample has a more symmetric potential with larger energy barrier.

It is reasonable to expect that local fluctuations are controlled by the same asymmetry of the potential, with the probability of a fluctuation increasing with decreasing Δ. For smaller Δ the difference between the transition rates between the two energy levels is smaller. In other words, the system becomes less ordered with greater probability of rearrangements. But since these rearrangements are local, they are not connected to the macroscopic density of the system.

A very different means to alter the density of a polymer is by chemically cross-linking the chains to form a network. Cross-linking was carried out on the PVE at atmospheric pressure well above T_g, with the material subsequently cooled isobarically to the glassy state. The formation of a network yields density increases of as much as 5% and also systematically increases the glass transition temperature (by about 15 K for the highest cross-link density).[41] As shown in Fig. 3(b), the PVE network with the highest degree of cross-linking exhibits a JG relaxation significantly faster than for the linear PVE (sample A) but has a similar activation energy ($E_{\mathrm{JG}}^D = 42 \pm 2$ kJ mole^{-1}, $\log_{10}(\tau_{\mathrm{JG}}^D) = -13.9 \pm 0.3$). Thus, higher macroscopic density via cross-linking yields the same anomalous effect on the microscopic motion—denser PVE exhibits faster JG dynamics. (A comparison of the dielectric strength was not feasible because of experimental uncertainties associated with comparing the permittivity of different polymer films. These uncertainties are on the order of 1% and therefore larger than the changes observed; for example, the change in Fig. 2 is ~0.4%.) Note also that since T_g increases with cross-linking, making this comparison at the same $T - T_g$ would result in an even larger difference in the τ_{JG}.

Since E_{JG} remains almost unaltered, in the framework of the mADWP model the difference between the τ_{JG} of the linear and the cross-linked samples is due to either larger Δ or/and smaller U for the latter. An increase in Δ is attributable to the limited mobility of the segments in proximity to the cross-linking. Although no x-ray data are available, it can be argued that network formation should hinder the small scale density fluctuations. Thus, there is again consistency with the experimentally observed correlation of density fluctuation and τ_{JG}; i.e., smaller density fluctuations are correlated with smaller τ_{JG}.

Similar to its effect on the JG process, cross-linking affects the mechanical properties of the PVE in similar fashion to that observed for physical aging, reduced extensibility leading to a brittle material. Measuring the JG relaxation for different degrees of cross-linking, we find that while the macroscopic density increases with cross-linking, as long as the material retains its property of high elasticity (distance between crosslinks > Kuhn length), τ_{JG} is unaffected. However, for higher degrees of cross-linking (crosslink distance < Kuhn length), τ_{JG} begins to decrease. Thus, again the properties of the microscopic JG motion relate directly to the macroscopic mechanical properties. The anomaly of shorter τ_{JG} for greater mass density in the networks is associated with their reduced ductility (extensibility), implying a concomitant decrease in the local density fluctuations.

IV. CONCLUSIONS

The changes observed in the JG dynamics for different methods of vitrification yield interesting revelations about the nature of the JG process. It is clear that the JG properties are not governed by the macroscopic density (nor the entropy), but can be explained qualitatively in terms of change in the local energy potential using the mADWP model. We find that the JG motion follows the local (<1 nm) density fluctuations and therefore can be used to probe them on the nanometer scale. This is important since, as we have seen, the nanometer-scale density fluctuations have a direct bearing on macroscopic mechanical properties in the glassy state such as ductility. The mADWP provides a qualitative understanding of the correlation between local density fluctuation and JG relaxation. A better understanding of this connection is technologically desirable in view of the widespread use of polymers in their glassy state and the recent advances in manipulating materials at the nanometer level. We believe these results are likely applicable to other classes of materials such as metallic glasses. The results by Ichitsubo *et al.*[42] for metallic glasses showed that the β (secondary) process is faster in lower density areas of metallic glasses. Our results herein indicate that the JG relaxation can potentially track the local (nanometer) structure of the glass, so that the properties of the JG process reveal structural and conformational information that is otherwise not easy to obtain. However, further studies and comparison with other techniques (e.g., x-ray) are necessary to gain a more quantitative understanding.

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[1] T. Hecksher, A. I. Nielsen, N. B. Olsen, and J. C. Dyre, Nat. Phys. **4**, 737 (2008).
[2] G. B. McKenna, Nat. Phys. **4**, 673 (2008).
[3] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).

[4] K. L. Ngai, J. Phys.: Condens. Matter **15**, S1107 (2003); Comments Solid State Phys. **9**, 121 (1979).
[5] J. P. Dyre and N. B. Olsen, Phys. Rev. Lett. **91**, 155703 (2003).
[6] G. Diezemann, U. Mohanty, and I. Oppenheim, Phys. Rev. E **59**, 2067 (1999).
[7] R. Casalini and C. M. Roland, Phys. Rev. Lett. **91**, 015702 (2003).
[8] C. M. Roland, R. Casalini, and M. Paluch, Chem. Phys. Lett. **367**, 259 (2003).
[9] R. Böhmer, G. Diezemann, B. Geil, G. Hinze, A. Nowaczyk, and M. Winterlich, Phys. Rev. Lett. **97**, 135701 (2006); A. Nowaczyk, B. Geil, G. Hinze, and R. Böhmer, Phys. Rev. E **74**, 041505 (2006).
[10] C. M. Roland, D. F. Roland, J. Wang, and R. Casalini, J. Chem. Phys. **123**, 204905 (2005).
[11] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).
[12] A. Hofmann, A. Alegría, J. Colmenero, L. Willner, E. Buscaglia, and N. Hadjichristidis, Macromolecules **29**, 129 (1996).
[13] R. Casalini, K. L. Ngai, C. G. Robertson, and C. M. Roland, J. Polym. Sci., Polym. Phys. Ed. **38**, 1841 (2000).
[14] C. M. Roland, Macromolecules **27**, 4242 (1994).
[15] G. P. Johari, J. Chem. Phys. **77**, 4619 (1982).
[16] P. Lunkenheimer, R. Wehn, U. Schneider, and A. Loidl, Phys. Rev. Lett. **95**, 055702 (2005).
[17] D. Prevosto, S. Capaccioli, M. Lucchesi, P. A. Rolla, and K. L. Ngai, J. Chem. Phys. **120**, 4808 (2004).
[18] H. Yardimci and R. L. Leheny, J. Chem. Phys. **124**, 214503 (2006).
[19] N. B. Olsen, T. Christensen, and J. C. Dyre, Phys. Rev. E **62**, 4435 (2000).
[20] N. B. Olsen, J. Non-Cryst. Solids **235–237**, 399 (1998).
[21] G. Power, J. K. Vij, and G. P. Johari, J. Chem. Phys. **124**, 074509 (2006).
[22] R. Casalini and C. M. Roland, Phys. Rev. Lett. **102**, 035701 (2009).
[23] J. M. O'Reilly, J. Polym. Sci. **57**, 429 (1962).
[24] J. E. McKinney and R. Simha, Macromolecules **7**, 894 (1974).
[25] R. E. Robertson, R. Simha, and J. G. Curro, Macromolecules **18**, 2239 (1985).
[26] K. Grzybowska, A. Grzybowski, J. Zioło, and M. Paluch, J. Chem. Phys. **125**, 044904 (2006).
[27] S. Sharifi, D. Prevosto, S. Capaccioli, M. Lucchesi, and M. Paluch, J. Non-Cryst. Solids **353**, 4313 (2007).
[28] A. K. Doolittle and D. B. Doolittle, J. Appl. Phys. **28**, 901 (1957).
[29] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[30] J. B. Yourtee and S. L. Cooper, J. Appl. Polym. Sci. **18**, 897 (1974).
[31] I. M. Hodge, Science **267**, 1945 (1995).
[32] L. C. E. Struik, *Physical Aging in Amorphous Polymers and Other Materials* (Elsevier, New York, 1978).
[33] G. B. McKenna, J. Phys.: Condens. Matter **15**, S737 (2003).
[34] H. H. Song and R. J. Roe, Macromolecules **20**, 2723 (1987).
[35] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1977), Vol. 5.
[36] K. S. Gilroy and W. A. Phillips, Philos. Mag. B **43**, 735 (1981).
[37] M. Pollak and G. E. Pike, Phys. Rev. Lett. **28**, 1449 (1972).
[38] U. Buchenau, Phys. Rev. B **63**, 104203 (2001).
[39] U. Bucheau, J. Chem. Phys. **131**, 074501 (2009).
[40] The version of the ADWP model introduced by Dyre and Olsen is a "minimal model" since it uses a single asymmetry and energy barrier, while the ADWP of Gilroy and Phillips (Ref. 36) assumes a distribution of asymmetries and energy barriers.
[41] The absolute values of the specific volume in Fig. 2 of Ref. 10 are incorrect. An erratum has appeared in J. Chem. Phys. **128**, 179902 (2008).
[42] T. Ichitsubo, E. Matsubara, H. S. Chen, J. Saida, T. Yamamoto, and N. Nishiyama, J. Chem. Phys. **125**, 154502 (2006).