Isomerization-Induced Dynamic Heterogeneity in a Glass Former below and above T_g

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We report the first molecular dynamics simulations of the effect of the photoisomerization of probe molecules on the nonequilibrium dynamics of a glassy or supercooled molecular material. We show that the isomerization of the probe molecules creates a new mobile dynamic heterogeneity inside the matrix. Together with these induced cooperative motions, we find an important increase of the diffusion coefficient leading to liquidlike diffusion below the glass-transition temperature. This result could explain the massive mass transport that leads to surface relief grating formation in azobenzene containing amorphous materials. We find that the isomerization process controls the heterogeneity and the non-Gaussian parameter of the material, leading to extremely rapid variations of these quantities.

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A central question in the field of the glass transition is the relation between dynamic heterogeneities (DHs) and the relaxation dynamics of supercooled liquids and glassy materials [1–3]. In order to shed some light on this relation, we investigate various methods to modify the dynamic heterogeneities and then observe the resulting effects on the relaxation dynamics. Since confinement induces a cutoff in the correlation length of any cooperative mechanism present in the material, it has been seen as a promising direction of study. The liquid may be confined inside pores, micelles, or nanoparticles may be dispersed within it. However, in most cases, surface effects predominate in the dynamical properties of confined supercooled liquids. For example, depending on the surface properties of the confining medium, the dynamics is slowed down or accelerated [4–7]. In this Letter, we present a new straightforward method to modify the DH inside a supercooled or a glassy material. We show that the photoisomerization of probe molecules induces a new DH inside the matrix. We then study the modification of the matrix dynamics and find, in accordance with recent experimental results [8], an important increase of the diffusion. Under continuous holographic exposure of thin polymer films doped with azo dyes, Rochon *et al.* [9] and Kim *et al.* [10] observed the formation of surface relief gratings (SRGs) corresponding to a massive photoinduced mass transport [8,11–13] well below the glass-transition temperature of the material. Various theories have been proposed to explain this effect [14–18]. Recently, SRGs have also been observed in molecular glasses [19–21] suggesting universality in the mechanism of SRG formation. An increase of the local diffusion has been suggested [14,17] as a possible cause for SRG formation but it is still a matter of controversy.

We simulate the isomerization (iso) of dispersed red (DR1) molecules ($C_{16}H_{18}N_4O_3$, the probes) inside a matrix of methylmethacrylate (MMA) molecules ($C_5H_8O_2$). The simulation box contains 336 MMA molecules and one or seven DR1 molecules. We have used the Gear algorithm with the quaternion method to solve the equations of motions with the following potential functions [22] (DR1) and [23] (MMA) without Coulombic interactions. The time step is 0.5×10^{-15} s. The density is set constant at $1.19\ \mathrm{g/cm^3}$. The temperature is controlled using a Berendsen thermostat [24]. The DR1 molecules are in some simulations treated as rigid bodies in the *trans* isomer in order to study the dynamics without iso. In other simulations, in order to study the iso effect, the DR1 molecules change periodically and continuously from the *trans* to the *cis* isomer in a time $t_1 = 300$ fs. This value is typical of the iso process [25]. Then it stays in the *cis* configuration during a time t_2, changes from *cis* to *trans* in a time t_1, and stays in the *trans* configuration during a time t_2. Results presented in this Letter correspond to $t_2 = t_1$ or $t_2 = 30t_1$ that are short waiting time values [26]. The system (DR1 and MMA) is aged at the temperature of study during 1 ns before any treatment. We define the mobility of molecule i within a characteristic time t as the scalar displacement of molecule i during this time t [27–29]. The DH is characterized [27–32] by the transient aggregation of the molecules of highest mobility in the liquid. This concerns here the 6% most mobile molecules. In order to quantify the DH we define a cluster as a group of the most mobile MMA molecules that reside in the first neighbor shell of each other [29]. Then we define n as the maximum number of molecules belonging to the same cluster and 2ζ as the largest distance between two molecules inside the same cluster. n is then averaged over time cycles and ζ over all clusters and time cycles. These aggregations are the fingerprints of the cooperativity of motion inside the supercooled liquid and disappear around the melting temperature T_m [28–32]. When the iso is switched off, we observe typical DH in the MMA + DR1 material investigated here [33].

When the iso is switched on, the behavior of the dynamic heterogeneities changes totally. Figures 1(a) (below T_g) and 1(b) (above T_g) show the evolution of the DH for

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configurations corresponding to various time windows during and following the iso. For relatively short time scales (around 1 ps), a peak develops during the iso and then decreases when the iso is stopped. For larger time scales (between 10 and 300 ps), another peak is present. This secondary peak is not modified during the iso. Figures 1(a) and 1(b) show the large increase of the heterogeneity that takes place during the iso and the decrease when the iso is stopped. We observe in Fig. 1(b) that the induced DH is 4.7 times larger than the thermal DH at the same temperature. Thus the cooperative motions are increased for iso while it will be decreased for shear stress [30] or for a temperature increase. Figure 1(c) shows the temperature dependence of the size of the heterogeneity ($\langle n \rangle$ and $\langle \zeta \rangle$). These data are averaged on the whole set of time windows during and following the iso process. Because of the rapid decrease of the DH after the iso, these mean values are much smaller than the maximum of the DH during the iso. This figure shows a significant increase of the DH when short t_2 values are used (triangles). When large t_2 values are used, due to the average with iso off configurations, the effect is slighter.

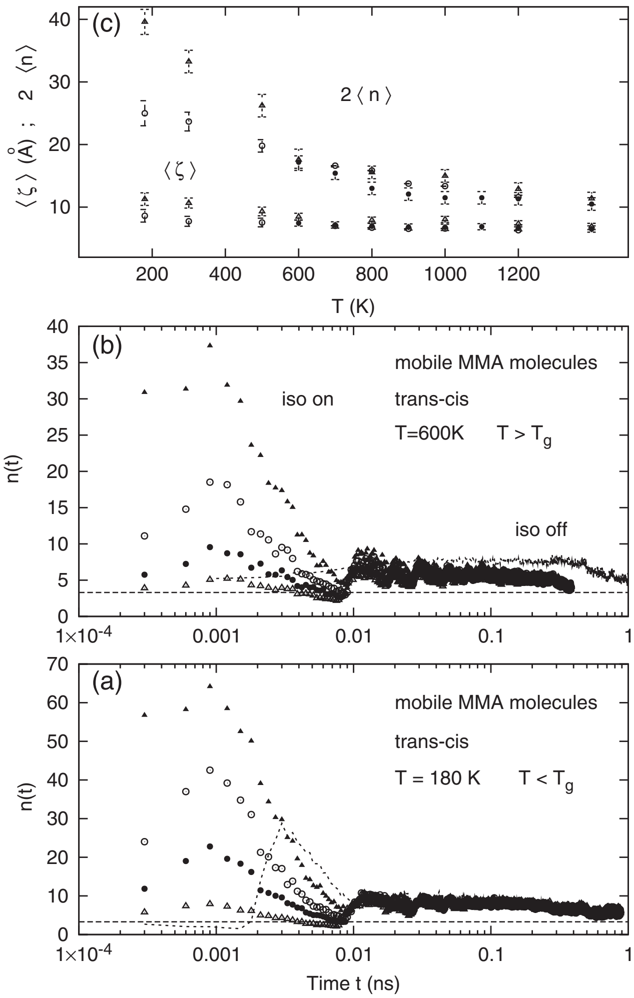

FIG. 1. (a) Number $n(t)$ of mobile MMA molecules in the largest clusters below T_g. Circles and triangles: isomerization (iso) for various time origins following the iso. Dashed line: iso off. Solid triangles, open circles, solid circles, and open triangles: during and 0.3, 0.6, or 1.5 ps after the *trans-cis* iso. We have seven DR1 and $t_2 = 30t_1$. The small dashed line corresponds to the very beginning of the creation of the induced heterogeneity, which seems to appear from a modification of the thermal heterogeneities. The straight line is the random aggregation number in the same conditions (thus the zero of the figure). (b) Same figure above T_g. (c) Half mean length $\langle \zeta \rangle$ (Å) and mean number $\langle n \rangle$ of MMA molecules of the largest clusters. Solid circles: iso off. Open circles: iso on with seven DR1 and $t_2 = 30t_1$. Open triangles: iso on with one DR1 and $t_2 = t_1$. $\langle n \rangle$ has been multiplied by a factor of 2 for figure clarity and corresponds to the upper points.

We now turn to consider the effect on the matrix dynamics. The non-Gaussian parameter $\alpha_2(t)$ is an important characteristic of the non-Markov dynamics in supercooled liquids. $\alpha_2(t)$ is widely believed to reflect the heterogeneity. Figure 2(a) shows $\alpha_2(t)$ with and without iso at the same temperature above T_g. $\alpha_2(t)$ increases when the iso is on, and near the probe $\alpha_2(t)$ is much larger. We also observe a secondary peak on the mean $\alpha_2(t)$ with iso. The time position of this peak corresponds to $\alpha_2(t)$ without iso. This result suggests that the thermal DHs are still present inside the material at some distance from the probe. However, near the probe several secondary peaks occur at the *cis-trans* cycles periods. These peaks are induced by the isomerization process and also contribute to the mean $\alpha_2(t)$. In Fig. 2(b), we show $\alpha_2(t)$ below T_g and $\alpha_2(t)$ without iso above T_g. We define t^*_{thermal} as the time corresponding to the maximum of $\alpha_2(t)$ when the iso is off. When the iso is on, we observe peaks and dips and an envelope curve. Thus, we define two time scales: t^*_{short} and t^*_{mean} corresponding, respectively, to the peaks' oscillation and to the maximum of the envelope curve. The oscillations correspond to the *trans* and *cis* periods used in our simulation for the iso. The envelope curve has an usual shape for $\alpha_2(t)$, but the time scale $t^*_{\mathrm{mean}} = 8$ ps is typical of a viscous liquid at a much higher temperature. At the same temperature, the characteristic time t^*_{thermal} of $\alpha_2(t)$ is higher than 1 ns when the iso is switched off. When the iso is off, Fig. 2(c) shows that t^*_{thermal} is proportional to the diffusion time scale, leading to a linear dependence with $1/D$. This is an usual relation showing the connection between the diffusion process and the heterogeneous dynamics. When the iso is on, however, t^*_{mean} is roughly constant. Different iso conditions lead to a different value of this constant. This result suggests that t^*_{mean} is controlled by the iso process while t^*_{thermal} is controlled by the diffusion process. This is, to our knowledge, the first observation of a mechanism that increases the cooperativity while decreasing the relaxation times.

Figure 3 shows the mean square displacement $\langle r^2(t) \rangle$ of the matrix molecules below T_g. At this temperature, when there is no iso, the motion is stopped on the time scale of the simulation. This is shown on the lower curve of Fig. 3.

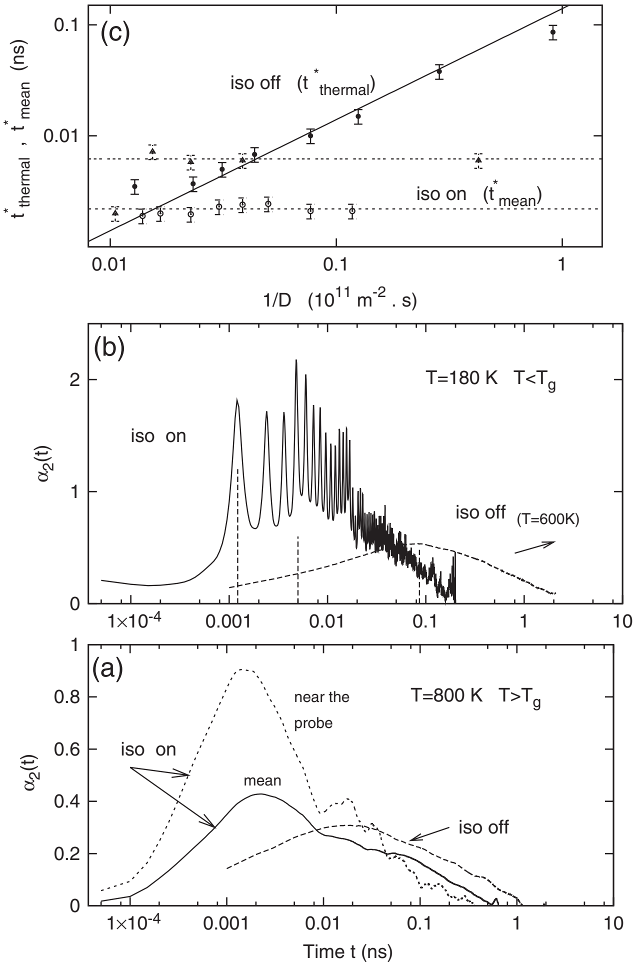

FIG. 2. (a) Continuous line: $\alpha_2(t)$ of the center of masses of the MMA molecules when the iso is switched on. We have seven DR1 and $t_2 = 30t_1$. Dotted line: same conditions but restricted to MMA molecules at a distance $R < 6$ Å from a DR1 molecule. Dashed line: $\alpha_2(t)$ without iso in the same conditions. (b) Continuous line: $\alpha_2(t)$ when the iso is switched on. We have one DR1 and $t_2 = t_1$. The plot has been restricted to MMA molecules at a distance $R < 6$ Å from the DR1 molecule. Dashed lines: $\alpha_2(t)$ with the iso off ($T = 600$ K) is also shown for comparison. For a lower temperature $\alpha_2(t)$ will be increased and shifted in the direction of the arrow. The vertical lines correspond, respectively, from the left- to the right-hand side, to the characteristic times: $t^*_{\rm short}$ ($T = 180$ K), $t^*_{\rm mean}$ ($T = 180$ K), and $t^*_{\rm thermal}$ ($T = 600$ K). (c) Characteristic time t^* of $\alpha_2(t)$ versus $1/D$. Solid circles: iso off ($t^*_{\rm thermal}$), open circles: iso on ($t^*_{\rm mean}$) with seven DR1 and $t_2 = 30t_1$, and open triangles: iso on ($t^*_{\rm mean}$) with one DR1 and $t_2 = t_1$.

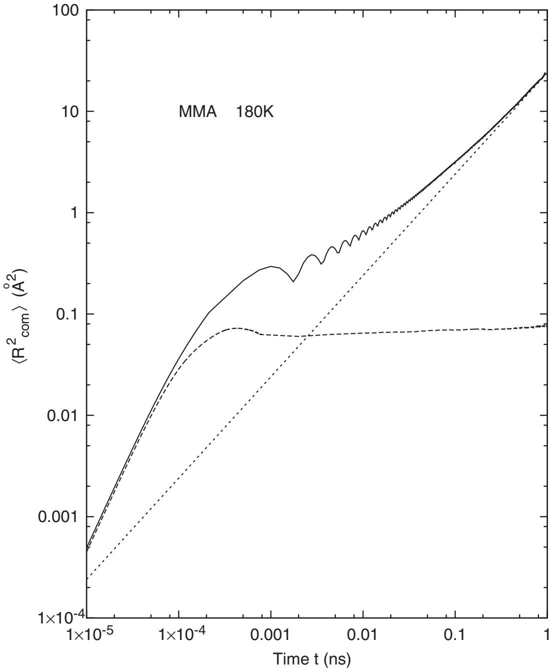

FIG. 3. Mean square displacement $\langle r^2(t) \rangle$ versus time below T_g, when the isomerization is switched on (upper curve) or off (lower curve). We have seven DR1 and $t_2 = t_1$.

The plateau of $\langle r^2(t) \rangle$ begins around 0.5 ps and continues up to the larger times of the simulation. However, when the iso is switched on, the plateau disappears and is replaced by oscillations. The disparition of the plateau suggests induced cage breaking process as the cause for the accelerated dynamics. For each iso, the energy impulse makes the matrix molecules move slightly, leading to diffusive motion for large times. Figure 3 shows that for large times $\langle r^2(t) \rangle$ follows the Einstein law for Brownian motion (dashed line). For large times, we then observe a liquidlike diffusion law. The diffusion coefficients D calculated from this law are displayed in Fig. 4. The oscillations in $\langle r^2(t) \rangle$ correspond to the *cis-trans* iso process. It is maximum for the *cis* isomer and minimum for the *trans* isomer.

Figure 4 shows the diffusion coefficient of the matrix molecules versus temperature. When the iso is switched off, we observe an Arrhenius evolution $D = D_1 \exp(-E_{a1}/T)$ with $E_{a1} = 4000$ K. The diffusion coefficients in Fig. 4 may also be fitted with a MCT law: $D = D_0(T - Tc)^\gamma$ with $Tc = 447.2$ K and $\gamma = 2.3$. From this result and the typical temperature difference between T_c and T_g, we tentatively estimate T_g to be at this density around 400 K. When the iso mechanism is switched on, the diffusion coefficient increases. For low temperature, these diffusion coefficients are typical of viscous liquids and not of glassy materials. We thus observe in Fig. 4 a liquidlike diffusion mechanism at a temperature much below T_g. This comportment is validated by recent experimental data [8]. The diffusion evolution is the sum of two Arrhenius laws: $D = D_1 \exp(-E_{a1}/T) + D_2 \exp(-E_{a2}/T)$ with $E_{a2} = 250$ K. This result suggests that the iso adds a new Arrhenius process to the original dynamics of the matrix. The inverse of the alpha relaxation times ($1/\tau_\alpha$) shows a similar behavior. τ_α is here calculated as the time where the normalized intermediate scattering function decays to a value $1/e$, evaluated for a wave number of 1.38 Å^{-1}, which corresponds to the location of the first peak in the static structure factor. The inset shows the breakdown of the Stokes-Einstein (SE) relation at low temperature with

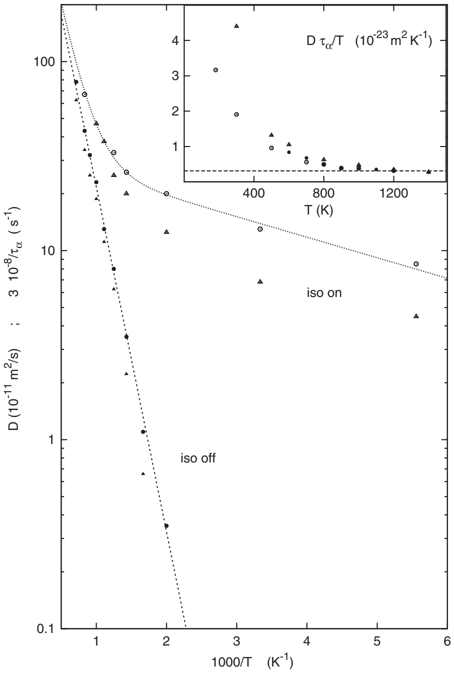

FIG. 4. Diffusion coefficient and $1/\tau_\alpha$ of the matrix versus $1/T$. Iso on (seven DR1 and $t_2 = 30t_1$): open circles (D) and open triangles ($1/\tau_\alpha$). Iso off: filled circles (D) and filled triangles ($1/\tau_\alpha$). The dashed line fit (iso off) corresponds to $D = D_1 \exp(-E_{a1}/T)$ with $E_{a1} = 4000$ K. When the iso is switched on, the diffusion coefficient increases. The dotted line fit (iso on) follows the law: $D = D_1 \exp(-E_{a1}/T) + D_2 \exp(-E_{a2}/T)$ with $E_{a2} = 250$ K. This result suggests that the iso adds a new Arrhenius process to the original dynamics of the matrix. We estimate [26] that D must be multiplied by a rough factor 10^{-7} if compared with typical SRG experimental conditions. Inset: breakdown of the Stokes-Einstein relation at low T. Filled circles: iso off, open circles: iso on with seven DR1 and $t_2 = 30t_1$, and open triangles: iso on with one DR1 and $t_2 = t_1$.

and without iso. A commonly proposed explanation for the breakdown of the SE relation [34] is the presence of dynamical heterogeneity. Because of the heterogeneity, diffusion is enhanced relative to viscosity. The figure shows that the breakdown is larger when the iso is on in the $t_2 = t_1$ condition and roughly equal to the iso off breakdown in the $t_2 = 30t_1$ condition. This result is consistent with the mean sizes of the heterogeneity displayed in Fig. 1's inset.

In conclusion, our study shows that the isomerization of probe molecules in glassy materials creates a new mobile heterogeneity inside of the material. The characteristic times t^*_{short} and t^*_{mean} of this DH are directly controlled by the isomerization process, and its size is also dependent on the isomerization conditions. This result suggests a new method to study the effect of the heterogeneity on the material dynamics, using the photoisomerization of probe molecules to control the heterogeneity. Finally, these results suggest a possible control of the dynamical properties of amorphous materials and of the glass-transition mechanism via the creation of heterogeneity which may lead to a new route for cryopreservation of biomaterials.

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