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ABSTRACT

We study the effect of heavy impurities on the dynamics of supercooled liquids. In a supercooled liquid, when we make a small fraction of particles heavier, they exhibit slower dynamics than the original particles and also make the overall system slower. If one looks at the overlap correlation function to quantify dynamics in the system, it has different behaviors for the heavy and the light particles. In particular, at the relaxation time of the overall system, the degree of relaxation achieved by the heavier particles is lesser, on average, than that achieved by the lighter particles. This difference in relaxation, however, goes down drastically as a crossover temperature, T_0 , is crossed. Below this crossover temperature, particles in the system have similar relaxation times irrespective of their masses. This crossover temperature depends on the fraction of the heavy particles and their masses. Next, we isolate the effect of mass heterogeneity on the dynamics of supercooled liquids and find that its effect increases monotonically with temperature. We also see that the development of dynamical heterogeneity with decreasing temperature is less dramatic for the system with impurities than for the pure system. Finally, the introduction of heavy impurities can be seen as a way of reducing the kinetic fragility of a supercooled liquid.

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I. INTRODUCTION

The role of growing length-scales in triggering the glass transition in supercooled liquids has been debated for the last few decades.^{1–6} Even though there is some consensus about the existence of a growing dynamic length-scale and the phenomenon of dynamical heterogeneity, its importance in the glass transition phenomenon is not yet clear. On the other hand, the structural signature correlated with the growing dynamic length-scale remains controversial,^{7–15} and the very existence of a universal static length-scale across all glassy systems is still questioned.^{3,4} It is, therefore, important to focus on each of these length-scales and understand what causes them to grow and how to suppress or enhance their growth. This may help in establishing whether the glass transition is indeed a result of the divergence of one or both of them. In this article, we try to control the amount of dynamical heterogeneity present in a supercooled liquid by manipulating the masses of the constituent particles. We present a situation in which we alter

the growth of the dynamic length-scale without affecting its static properties.

We take a supercooled liquid and study its dynamics with varying temperature. We then make a new system as follows. We choose a small fraction of particles in the liquid and increase their mass by a large constant factor. Even though this step is similar in spirit to the idea of random pinning, the important difference is that no disorder averaging is needed in this case to match the thermodynamic properties of the system with impurities with the pure system. All particles in the new system still enjoy the same degrees of freedom as they did in the pure system, while randomly pinning the position of a few particles changes the number of degrees of freedom in the system. The potential energy landscape of the system is also left unchanged.

The main findings of this article are as follows. First, the dynamic heterogeneities in the system with mass impurity and the pure system are found to be qualitatively different. Second, in the system with mass impurity, the difference between the relaxation

dynamics of the heavy and light particles jumps at a crossover temperature, T_0 , which is a function of the fraction of heavy particles and their masses. Third, if we factor out the effect of mass increase and isolate the effect of mass heterogeneity alone, we see that the system with the heterogeneity in masses is faster than the pure system, and this difference monotonically increases with temperature. Fourth, the presence of heavy impurities results in a slowdown of the growth of the dynamic length-scale from its high temperature value. Fifth, there is an apparent decrease in the kinetic fragility because of the presence of heavy impurities.

II. SYSTEM STUDIED

We study a polydisperse system of Lennard-Jones particles with a mean diameter $\bar{\sigma} = 1$ and a standard deviation of $\Delta = 12\%$,

$$V_{ij} = 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (1)$$

$$r_{ij} = |\vec{r}_i - \vec{r}_j|, \epsilon = 1.$$

The potential was truncated and shifted to zero at $r_{cut} = 2.5\sigma_{ij}$. The polydispersity in this system is discrete. There are $n_{poly} = 100$ types of particles in an equal proportion. The effective “diameters” take n_{poly} equally spaced values in the range $\left[\bar{\sigma} - \Delta \sqrt{\frac{3(n_{poly}-1)}{n_{poly}+1}}, \bar{\sigma} + \Delta \sqrt{\frac{3(n_{poly}-1)}{n_{poly}+1}} \right]$. For a pair of particles of different types, the effective σ parameter is taken as the average of the two particle diameters. All particles in the system have unit mass. The density of the system is chosen so that the “packing fraction” defined as in Ref. 16 is $\phi = \frac{\pi}{6V} \sum_i \sigma_{ii}^3 = 0.55$. The system with impurities is obtained by choosing a fraction c of particles in the original system and changing their mass to $m_{imp} > 1$. Most of the results presented are for a system of $N = 1000$ particles. However, to calculate the dynamic length-scale, we used a system of $N = 8000$ particles.

The temperature was measured in the unit of ϵ and time in units of $\bar{\sigma}\sqrt{m/\epsilon}$, with m being the mass of a particle in the pure system equal to unity.

The systems were evolved in an NVT ensemble, with temperature being held fixed using the Nose-Hoover thermostat. The LAMMPS package was used for performing the simulations.^{17,18} The dynamics was studied using the ensemble averaged overlap correlation function, $Q(t)$, which is the fraction of particles in the system that have moved by $w = 0.3\bar{\sigma}$ or less in time t . When comparing the overlap correlation functions of the pure system and the system with impurities, we use $Q(t)$ to denote the overlap function for the pure system and $Q(c, m_{imp}, t)$ to denote the overlap function for a system in which a fraction c of the particles have been made heavier by a factor m_{imp} , i.e., $Q(c, m_{imp}, t)$ is the fraction of particles (heavy or light) that have moved by less than w in time t in the system with impurities. In addition, in the system with impurities, we use $Q^{(m)}$ to denote the overlap function for particles of mass m , i.e., the fraction of particles of mass m that have moved by less than w in time t . Thus, $Q(c, m_{imp}, t) = cQ^{(m_{imp})}(t) - (1-c)Q^{(1)}(t)$.

III. THE CROSSOVER IN RELAXATIONAL DYNAMICS AND THE CROSSOVER TEMPERATURE

We calculate the overlap correlation functions for the heavy and light particles separately in a system with a fraction c of heavy impurities with mass m_{imp} . Their difference, $\Delta Q(t)$, measures the difference in the relaxation of the heavy and light particles,

$$\Delta Q(t) = Q^{(m_{imp})}(t) - Q^{(1)}(t), \quad (2)$$

where $Q^{(m_{imp})}$ and $Q^{(1)}$ are the overlap correlation functions for heavy and light particles, respectively. We focus on the value of this quantity at the relaxation time, τ_α , of the overall system [$Q(c, m_{imp}, \tau_\alpha) \equiv 1/e$]. This quantity, $\Delta Q(\tau_\alpha)$, shows a jump at some crossover temperature T_0 , which depends on c and m_{imp} , as shown in Fig. 1. The temperature, T_0 , can be thought of as a temperature below which the overall dynamics of the liquid is governed by collective phenomena and the masses of the individual particles have a little role to play.¹⁹ For a fixed fraction of heavy particles, this temperature decreases with an increase in the mass of the heavy particles. For a fixed mass of the heavy particles, it increases with the fraction of them present. The asymptotic high temperature value of $\Delta Q(\tau_\alpha)$ can be calculated analytically. In the high temperature limit, it is expected that most of the light particles move by a distance more than w before any of the heavy particles move by w . Thus, we get

$$Q^{(m_{imp})}(\tau_\alpha) = 1, \quad Q^{(1)}(\tau_\alpha) = \frac{e^{-1-c}}{1-c}, \quad \text{if } c \leq 1/e, \text{ and}$$

$$Q^{(m_{imp})}(\tau_\alpha) = \frac{1}{ec}, \quad Q^{(1)}(\tau_\alpha) = 0, \quad \text{if } c > 1/e,$$

$$\Rightarrow \Delta Q_\infty(\tau_\alpha) = \begin{cases} \frac{1-e^{-1}}{1-c} & \text{if } c \leq 1/e, \\ \frac{1}{ec} & \text{if } c > 1/e. \end{cases} \quad (3)$$

FIG. 1. $\Delta Q(\tau_\alpha)$ plotted against inverse temperature. The infinite temperature point is obtained analytically. The value of $\Delta Q(\tau_\alpha)$ shows a significant drop across some temperature T_0 that is dependent on the mass of the heavy particles and the fraction of them present. In the top inset, we see that T_0 decreases with m_{imp} , and in the bottom one, we see that it increases with the fraction of heavy impurities [the curves in the insets are fits to the form shown in Eq. (A1)].

IV. EFFECT OF HEAVY IMPURITIES AND THE EFFECT OF MASS HETEROGENEITY

A. Susceptibility to heavy impurities

The susceptibility $\chi_m(c, m_{imp}, t)$ to heavy impurities can be defined as follows:

$$\chi_m(c, m_{imp}, t) = \frac{Q(c, m_{imp}, t) - Q(t)}{c}. \quad (4)$$

The arguments c and m_{imp} have been suppressed in the following discussion, and their values have been held fixed at 12.5% and 4096, respectively. This can be related to the pinning susceptibility, $\chi_p(t)$,²⁰ via the following relation:

$$\chi_p(t) = \lim_{c \rightarrow 0} \left[\lim_{m_{imp} \rightarrow \infty} \chi_m(c, m_{imp}, t) \right]. \quad (5)$$

We plot $\chi_m(t)$ vs t for varying temperature in Fig. 2. Unlike the pinning susceptibility χ_p , which keeps growing with decreasing temperature, the susceptibility to heavy impurities χ_m stops growing below a temperature T^* , which depends on c and m_{imp} . This temperature can be thought of as the temperature at which the system responds most to the imposed perturbation. It is interesting that the temperature T_0 , below which the heavy and light particles achieve similar levels of relaxation at τ_α , and the temperature T^* , at which the dynamics of the system with impurities is the most different from the pure system, are close to each other.

B. Susceptibility to mass heterogeneity

So far in this work, we have focused on the effect of the heavy impurities. In this section, we isolate the effect of the heterogeneity in mass from the overall change in mass. We compare dynamics of two systems with the same average mass of the particles, equal to unity.

FIG. 2. $\chi_m(t)$ vs time for various temperatures in a system with $c = 12.5\%$ and $m_{imp} = 4096$.

FIG. 3. $\tilde{\chi}_m(t)$ vs time for various temperatures in a system with $c = 12.5\%$ and $m_{imp} = 4096$. Inset: $\frac{\tau_\alpha}{\sqrt{\langle m \rangle}}$ plotted against $1/T$.

1. In the first system, all particles have unit mass, i.e., this is the same as the pure system studied in earlier sections.
2. In the other system, a fraction c of particles are heavier by a factor m_{imp} , i.e., the lighter particles are of mass $\frac{1}{cm_{imp}+1-c}$ and the heavier ones are of mass $\frac{m_{imp}}{cm_{imp}+1-c}$. The dynamics of this system can be obtained trivially from the system with heavy impurities described in earlier sections, just by dividing the timescales by the square root of the average mass of particles, $\langle m \rangle = cm_{imp} + 1 - c$.

With this rescaling of time, we find that the system with the heterogeneity in mass relaxes faster than the one with particles of identical mass. This is shown in the inset of Fig. 3. Similar to the susceptibility to heavy impurities defined in Eq. (4), we can define the susceptibility to mass heterogeneity quantifying the speedup in relaxation imparted by the mass heterogeneity,

$$\tilde{\chi}_m(c, m_{imp}, t) = \frac{Q(t) - Q(c, m_{imp}, t\sqrt{cm_{imp} + 1 - c})}{c}. \quad (6)$$

This quantity is plotted in Fig. 3. It is clear that the presence of mass heterogeneity is felt the most at high temperatures, and its effect diminishes with decreasing temperature.

V. THE DYNAMIC LENGTH-SCALE

The growing spatial heterogeneity in dynamics with decreasing temperature in a supercooled liquid can be quantified using the dynamic length-scale $\xi_d(T)$. This length-scale can be calculated by first calculating the dynamic susceptibility,

$$\chi_4(t) = N \langle [Q(t) - \langle Q(t) \rangle]^2 \rangle, \quad (7)$$

FIG. 4. Top left: $\chi_4^{\max}$ plotted against a block size for various temperatures for the pure system. Top right: data collapse using $\chi_4^{\max}$ on the vertical axis and $\xi_d(T)$ on the horizontal axis. The corresponding plots for the system with impurities look qualitatively similar and have, therefore, not been put here. Bottom left: $\xi_d(T)$ vs $1/T$. Bottom right: $\chi_4^{\max}(\infty, T)$ vs $1/T$.

and then looking at the system size dependence of its peak value, $\chi_4^{\max}(T)$ [note that in Eq. (7), to get the dynamic susceptibility of the system with impurities, one must plug in $Q(c, m_{\text{imp}}, t)$ instead of $Q(t)$]. In this work, we calculated the dynamic length-scale using the block analysis technique applied to $\chi_4^{\max}(T)$.²¹ In Fig. 4, we show the calculation of $\xi_d(T)$ via $\chi_4^{\max}(T)$. The top left plot shows the block size dependence of $\chi_4^{\max}(T)$ for various temperatures for the pure system. These data are collapsed in the top right plot by rescaling the vertical and horizontal axes by the thermodynamic limit of $\chi_4^{\max}(T)$ and the dynamic length-scale, respectively. Similar plots for the system with impurities have not been included here as they do not appear qualitatively different. The bottom left and right plots of Fig. 4 show, respectively, the variation of the dynamic length-scale and $\chi_4^{\max}(\infty, T)$ with inverse temperature. We find that the system with impurities has a slower growth of the dynamic length-scale with a decrease in temperature. Surprisingly, however, the peak value of the dynamic susceptibility in the thermodynamic limit is not significantly different in the pure system and the one with impurities.

VI. HOW CAN AN INCREASE IN MASS HETEROGENEITY NOT RESULT IN AN INCREASE IN DYNAMICAL HETEROGENEITY?

In this section, we try to explain how a system made out of particles of varying mass does not always have more dynamical heterogeneity than a system without any heterogeneity in particle masses. Dynamical heterogeneity is the dynamic spatial segregation of particles on the basis of their mobilities. When all particles in the liquid have the same mass, the system can arbitrarily choose which particles become the fast particles and which ones become slow at a given instant of time. A close proximity of fast and slow particles is avoided because of viscosity, and since the viscosity grows with the decrease in temperature, a growing dynamic length-scale is observed. The presence of heavier impurity particles imposes additional constraints. Because of their inherent inertia, the heavier particles cannot change their speeds as spontaneously as the light particles and, therefore, have a smaller fluctuation in their dynamics. It is plausible that starting from a high temperature at which the

dynamics of the pure system is almost homogeneous, as one lowers the temperature, the growth of the dynamic clusters are obstructed by the heavy particles, resulting in a slower growth of the dynamic length-scale.

VII. EFFECT ON FRAGILITY

The introduction of heavy impurities can prolong (in terms of temperature range) the regime of the Arrhenius relationship between the relaxation time or the viscosity and the temperature. In other words, the kinetic fragility of the system with heavy impurities is smaller than that of the pure system. This is clearly seen in the Arrhenius plots shown in Fig. 5. The calculation of the viscosity was performed using the Green-Kubo relation using the autocorrelation of the off-diagonal components of the stress tensor,

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{xz}(0) P_{xz}(t) \rangle dt, \quad (8)$$

where P_{xz} is an off-diagonal component of the stress tensor, $\mathcal{P}$, given by

$$\mathcal{P} = \frac{1}{V} \sum_i \left(\frac{\vec{p}_i \vec{p}_i}{m_i} + \sum_{j>i} \vec{r}_{ij} \vec{F}_{ij} \right), \quad (9)$$

where the vector products are outer products. A similar result is also present in the context of random pinning.²² However, making a system with heavy impurities can be much easier in experiments than randomly pinning particles. In experiments, both the process of pinning and keeping the pinning random can be quite challenging. Putting in heavy impurities can be quite straightforward both in colloidal mixtures consisting of solid and hollow particles and also in many atomic systems where heavier isotopes could be used as the impurity particles. The thermodynamic fragility at low temperatures, however, becomes indifferent to the presence of the heavy particles since at sufficiently low temperatures, the ratio of the relaxation time of the pure system and the one with impurities veers toward a constant value. Also included in Fig. 5 are the Arrhenius plots for the diffusion constant, which also shows a qualitatively similar result.

VIII. CONCLUSIONS

In conclusion, we have reported that the presence of heavy impurities is a method of altering the dynamics of a supercooled liquid without affecting its static properties. Our main finding is the existence of a crossover temperature below which the heavy and light particles contribute equally to the relaxation of the system and above which the dominant contribution to relaxation comes from the lighter particles. In addition, we have shown suppression of the growth of dynamical heterogeneity and a decrease in the kinetic fragility as a result of the introduction of heavy particles in the system, which suggest a way of using a mixture of heavy and light particles for designing new materials with desired properties.

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APPENDIX: DEPENDENCE OF THE CROSSOVER TEMPERATURE ON c AND m_{imp}

In this appendix, we investigate the possible existence of a relationship of the crossover temperature with c and m_{imp} . Even though it is unlikely that a simple relationship $T_0(c, m_{imp})$ can be obtained from first principles, the trend near points in the $c - m_{imp}$ plane where we have data can be looked at. We look for such a relationship using a simple form for $T_0(c, m_{imp})$ chosen to be of the type $f(c)g(m_{imp})$, where f and g are simple functions. We know that as $m_{imp} \rightarrow 1$, the dynamics of the particles would become indistinguishable for any temperature. Thus, $T_0 \rightarrow \infty$ as $m_{imp} \rightarrow 1$. We find that our data fit well to the following form:

FIG. 5. Top: The Arrhenius plot for the viscosity. Bottom: The Arrhenius plot for the diffusion constant. The constants $\{\eta_\infty, D_\infty, E_a\}$ are fitting parameters for the Arrhenius fit (dashed lines) to the high temperature data.

FIG. 6. T_0 (in color) as a function of c and m_{imp} . The white dashed lines correspond to $c = 12.5\%$ and $m_{imp} = 4096$, which were used in the insets of Fig. 1 of the manuscript.

$$T_0(c, m_{imp}) = 0.734 \left(1 + 8.82c^{3/2} \right) \left(1 + \frac{7.40}{\sqrt{m_{imp} - 1}} \right). \quad (\text{A1})$$

The exponents $3/2$ and $1/2$ were chosen to be rational numbers close to numbers obtained from initial fits and should not be taken seriously. The variation of T_0 with c and m_{imp} is shown in Fig. 6 using Eq. (A1). We alert the reader that such relationships should only be used for interpolations or small extrapolations to understand the trend near the parameter values at which the study has been carried out (the white dashed lines).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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