Energy Landscape, Anti-Plasticization and Polydispersity Induced Crossover of Heterogeneity in Supercooled Polydisperse Liquids

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Polydispersity is found to have a significant effect on the potential energy landscape; the average inherent structure energy decreases with polydispersity. Increasing polydispersity at fixed volume fraction decreases the glass transition temperature and the fragility of glass formation analogous to the antiplasticization seen in some polymeric melts. An interesting temperature dependent crossover of heterogeneity with polydispersity is observed at low temperature due to the faster build-up of dynamic heterogeneity at lower polydispersity.

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Polydispersity is ubiquitous in nature. It is present in clays, minerals, paint pigments, metal and ceramic powders, food preservatives and in simple homogeneous liquids. It is common in synthetic colloids, which frequently exhibit considerable size polydispersity and is also found in industrially produced polymers, which contain macromolecules with a range of chain length. Polydispersity has significant effects on both the structure and dynamics of the system. Experiments and simulations on colloidal systems show that increasing polydispersity, at a constant volume fraction, lowers structural correlations, pressure, energy and viscosity. Polydisperse colloidal systems are known to be excellent glass formers. William et al \cite{1} suggest that colloidal glass formation results from a small degree of particle polydispersity. Crystal nucleation in a polydisperse colloid is suppressed due to the increase of the surface free energy. Studies by several groups \cite{2} have shown that the glass becomes the equilibrium phase beyond a terminal value of polydispersity.

Despite being natural glass formers, relationships between polydispersity, fragility, energy landscape and heterogeneous dynamics have not been adequately explored in these systems. Because these systems exist in the glassy phase over a wide range of polydispersity, they offer opportunity to test many of the theories and ideas developed in this area in recent years. We find that polydispersity introduces several unique features to the dynamics of these systems not present in the binary systems usually employed to study dynamical features in supercooled liquids and glasses.

In this work we particularly investigate how polydispersity influences the potential energy landscape, fragility and heterogeneous dynamics of polydisperse Lennard-Jones (LJ) systems in supercooled regime near the glass transition. The polydispersity in size is introduced by random sampling from a Gaussian distribution of particle diameters, \( \sigma \). The standard deviation \( \delta \) of the distribution divided by its mean \( \bar{\sigma} \) gives a dimensionless parameter, the polydispersity index \( S = \frac{\delta}{\bar{\sigma}} \). The mass \( m_i \) of particle \( i \) is scaled by its diameter as \( m_i = \frac{m}{\bar{\sigma}} \left( \frac{\sigma}{\bar{\sigma}} \right)^3 \). Micro canonical (NVE) ensemble MD simulations are carried out at a fixed volume fraction, \( \phi \) on a system of \( N = 864 \) particles of mean diameter \( \sigma = 1.0 \) and mean mass \( m = 1.0 \) for \( S = 0.10, 0.15 \) and \( 0.20 \) at \( \phi = 0.52 \) and \( S = 0.10 \) and \( 0.20 \) at \( \phi = 0.54 \). All quantities in this study are given in reduced units (length in units of \( \sigma \), temperature in units of \( k_B \) and time in units of \( \tau = \frac{\sigma^2}{m} \)). The LJ interaction parameter \( \epsilon \) is assumed to have the same value for all particle pairs.

At large supercooling the system settles into glassy phase. We first analyze the system from the perspective of potential energy landscape (PEL), which has emerged as an important tool in the study of glass forming liquids \cite{3,10,11}. Fig.1(a) and (b) show the variation of the average inherent structure energy \( \langle \epsilon_{IS} \rangle \) with temperature \( T \) at both the volume fractions studied. The value of \( \langle \epsilon_{IS} \rangle \) remains fairly insensitive to the variation in \( T \) at high \( T \) before it starts to fall with \( T \) (around \( T \sim 1.0 \)). It has been established earlier in the context of the binary mixtures \cite{3,12} that the start of fall in \( \langle \epsilon_{IS} \rangle \) coincides with the onset of non-exponential relaxation in the time correlation...

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functions of the system. We show in Fig. 1(c) that this correlation continues to hold in polydisperse systems. The fall of \( \langle e_{IS} \rangle \) with \( T \) is consistent with the Gaussian landscape model.

The average inherent structure energy decreases with polydispersity (Fig. 1(a) and (b)), which indicates that the packing is more efficient at higher S. In Fig. 2 we plot the inherent structure (IS) and the parent liquid radial distribution functions (rdf). At \( S = 0.20 \) there is hardly any difference between the rdf of the parent liquid and the IS. The coordination number, \( N_c \) at \( S = 0.10 \) and \( S = 0.20 \) obtained from the IS rdf are 13.1 and 14.6, respectively. This shows that packing is more efficient at higher S and one would expect a slowing down of dynamics at higher S. Instead, we find that similar to colloidal hard spheres polydisperse LJ systems also show a speed up of relaxation with S. The presence of smaller particles at higher S provides some sort of lubrication \(^{12, 14}\), which speeds up the dynamics of the whole system. A plot of the Mode Coupling Theory (MCT) \(^{15}\) critical temperature \( T_c^\circ \) for particles of different sizes \( \sigma \) \(^{1}\) (inset of Fig. 2(b)) shows that the \( T_c^\circ \) for the largest-sized particles in \( S=0.20 \) system is smaller than the smallest-sized particles in \( S=0.10 \) system. This tells us that not only the smaller particles in \( S = 0.20 \) system but the whole system has a faster relaxation. The rate of growth of relaxation time upon lowering of T decreases with S (Fig. 2(b)). Hence as the system is cooled, vitrification is expected to occur at a lower T for the system at higher S. This should lead to a lowering of the glass transition temperature with S.

Fragility is a term being used to characterize and quantify the non-Arrhenius transport behavior in glass-forming liquids as they approach glass transition \(^{24}\). To study the effect of polydispersity on fragility, we plot the diffusion coefficients in an Angell-like fragility plot in Fig. 3. The plot clearly shows that \textit{increasing polydispersity} at fixed volume fraction \textit{reduces the fragility} of the liquid so that the system is a stronger glass former at higher polydispersity.
This effect is analogous to the antiplasticization that has been observed in polymer melts. PEL analysis shows that the antiplasticized system has smaller barriers to overcome in order to explore the configuration space in high T. In the rest of the paper we explore the correlations between fragility and non-exponential relaxation/heterogeneous dynamics.

Fragility is usually correlated to the stretch exponent $\beta$ which is found to be valid for many materials. From PEL perspective, fragile liquids display a proliferation of well-separated basins which result in a broad spectrum of relaxation times leading to stretched exponential dynamics. The correlation is also consistent within the framework of coupling model (CM) according to which the strength of the intermolecular coupling is given by $(1 - \beta)$. The rate of growth of intermolecular coupling with decrease in T is a measure of fragility which according to CM would depend on the rate of fall of $\beta$ with T. We indeed find that as S increases (fragility decreases) the rate of fall of $\beta$ with T decreases (Fig 1c). However, if we look only at the $\beta$ values and not its T-dependence we find that at high T, stretching is anti-correlated with fragility whereas at low T, we get the reverse scenario where the stretching is correlated with fragility. This leads to a cross-over of the $\beta$ values for different S at intermediate T as shown in Fig 1c. The $\beta$ values in Fig 1c are obtained by KWW fit to $F_s(k_{max},t)$. However, these crossovers are independent of k values as shown in Fig 1d. The interplay between the T-independent intrinsic heterogeneity (due to the particle size and mass distribution) and the dynamic heterogeneity which builds up at low T seems to be the microscopic origin of the anti-correlation between fragility and stretching at high T and the observed crossover at intermediate T.

To investigate this point in further details, we study the non-Gaussian parameter, $\alpha_2(t)$ which also shows a correlation with fragility for most materials. The non-zero values of $\alpha_2(t)$ in a monodisperse system is purely due to the presence of dynamic heterogeneity whereas in polydisperse system, in addition to dynamic heterogeneity, there is an intrinsic heterogeneity due to particle size and mass distribution which is present at all T. Thus for the latter, $\alpha_2(t)$ reflects a coupled effect of both these heterogeneities. As seen in Fig 4 for a polydisperse system $\alpha_2(t)$ is nonzero both in the short time limit (due to the mass distribution) and in the long time limit (due to the spread in diffusion coefficients with particle size and...
mass). At high $T$, the non-zero value of $\alpha_2(t)$ is predominantly due to the intrinsic heterogeneity and thus increases with $S$ (Fig. 4(d)). As $T$ is lowered, the effects of dynamic heterogeneity starts to dominate, as was shown by the onset of connected clusters of fast moving particles [1, 21] whose size increases as one approaches glass transition. Since the relaxation time increases with decrease of $S$ (Fig. 2(b)), there is a faster build-up of dynamic heterogeneity at lower $S$ which leads to the observed crossovers (Fig. 4(c)&(b)) in the values of $\alpha_2(t)$ between different $S$ (similar to that observed for $\beta$ in Fig. 4(c)). Hence at low $T$, one gets the scenario where $\alpha_2(t)$ decreases with polydispersity (Fig. 4(d)). Since fragility decreases with $S$, these crossovers in $\beta$ and $\alpha_2(t)$ would mean that fragility is correlated only to the dynamic heterogeneity and not to the intrinsic heterogeneity in the system.

When the polydispersity is increased at constant volume, we get results that are opposite to that obtained from constant volume fraction studies. We find that the dynamics slows down with increase in polydispersity [20]. This is because at constant volume fraction increases, the packing fraction increases [23] and hence we find a coupled effect of polydispersity and density.

Our results show that at constant volume fraction, although the increase of polydispersity leads to a more efficient packing, the dynamics become faster due to the lubrication effect. Fragility decreases with polydispersity and is found to be correlated only to the rate of growth of dynamic heterogeneity and not to the intrinsic molecular heterogeneity in the system. These results reveal that the rich dynamics of the polydisperse system can lead to new relaxations mechanisms that deserve further study.

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[1] P. N. Pusey and W. van Megen, Nature 320, 340 (1986); P. N. Pusey and W. van Megen, Phys. Rev. Lett. 59, 2083 (1987).
[2] S. Phan et al, Phys. Rev. E. 54, 6633 (1996); C. G. de Kruijff et al, J. Chem. Phys 83, 4717 (1986); J. Mewis et al, AIChE J. 35, 415 (1989); D. S. Pearson and T. Shikata, J. Rheol. 38, 601 (1994); P. N. Segre et al, Phys. Rev. Lett. 75, 958 (1995).
[3] S. R. Rastogi, N. J. Wagner and S. R. Lustig, J. Chem. Phys. 104, 9249 (1996).
[4] R. P. Sear, J. Chem. Phys. 113, 4732 (2000).
[5] S. R. Williams, I. K. Snook and W. van Megen, Phys. Rev. E. 64, 21506 (2001).
[6] S. Auer and D. Frenkel, Nature 413, 711 (2001).
[7] P. Chaudhuri et al, Phys. Rev. Lett. 95, 248301 (2005); D. A. Kohke and P. G. Bolhuis, Phys. Rev. E 59, 618 (1999); D. J. Lack and J. R. Wienthoff, J. Chem. Phys. 111, 398 (1999).
[8] R. K. Murarka and B. Bagchi, Phys. Rev. E. 67, 051504 (2003).
[9] S. Sastry, P. B. Debenedetti and F. H. Stillinger, Nature 393, 554 (1998)
[10] F. H. Stillinger, Science 267, 1935 (1995); P. B. Debenedetti and F. H. Stillinger, Nature 410, 259 (2001)
[11] D. J. Wales, Energy Landscapes (Cambridge University Press, Cambridge, England, 2003).
[12] D. Chakrabarti and B. Bagchi, Phys. Rev. Lett. 96, 187801 (2006).
[13] R. A. Lionberger, Phys. Rev. E. 65, 61408 (2002).
[14] S. R. Williams and W. van Megen, Phys. Rev. E. 64, 041502 (2001); G. Foffi et al, Phys. Rev. Lett. 91, 085701-1 (2003).
[15] B. Bagchi and S. Bhattacharyya, Adv. Chem. Phys. 116, 67 (2001).
[16] R. A. Riggleman et al, Phys. Rev. Lett. 97, 045502 (2006); A. Anopchenko et al, Phys. Rev. E 74, 031501 (2006).
[17] R. A. Riggleman, J. F. Douglas and J. J. de Pablo, Phys. Rev. E. 76, 011504 (2007).
[18] C. M. Roland and K. L. Ngai, Macromolecules 24, 5315 (1991); R. Bohmer et al, J. Chem. Phys. 99, 4201 (1993); K. Nias et al, J. Phys: Cond. Matt. 19, 76102 (2007).
[19] K. L. Ngai. Comments Solids State Phys. 9, 121 (1979); K. L. Ngai, IEEE Trans. Dielectric. Electr. Insul. 8, 329 (2001).
[20] N. Kiriyushcheva and P. H. Poole, Phys. Rev. E. 65, 011402 (2001).
[21] E. R. Weeks et al, Science 287, 627 (2000); W. K. Kegel and A. van Blaaderen, Science 287, 290 (2000).
[22] V. N. Novikov, Y. Ding and A. P. Sokolov, Phys. Rev. E. 71, 61501 (2005).
[23] D. He, N. N. Ekere and L. Cai, Phys. Rev. E. 60, 7098 (1999).
[24] C. A. Angell, J. Phys. Chem. Solids 49, 863 (1988); C. A. Angell, Science 267, 1926 (1995).