

# 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 [1] 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 [2] and simulations [3, 4] 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 [5] 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 [6]. Studies by several groups [7] 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 super-

cooled 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 [8]. 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  $m_i = \bar{m}(\frac{\sigma_i}{\bar{\sigma}})^3$ . 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  $\frac{\epsilon}{k_B}$  and time in units of  $\tau = (\frac{\bar{m}\sigma^2}{\epsilon})^{\frac{1}{2}}$ ). 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 [9, 10, 11]. Fig 1(a) and (b) show the variation of the average inherent structure energy ( $\langle e_{IS} \rangle$ ) with temperature ( $T$ ) at both the volume fractions studied. The value of  $\langle e_{IS} \rangle$  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 [9, 12] that *the start of fall in  $\langle e_{IS} \rangle$  coincides with the onset of non-exponential relaxation in the time correlation*

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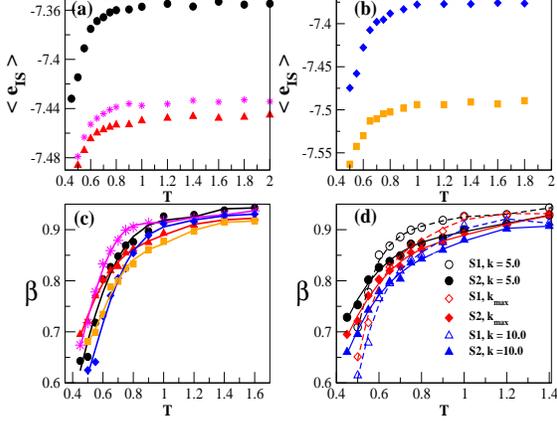


FIG. 1: (a) and (b) Temperature dependence of the average inherent structure energy,  $\langle e_{IS} \rangle$ . For Fig 1 (a), (b) & (c), filled circles, stars and triangles are for  $S = 0.10$ ,  $S = 0.15$  &  $S = 0.20$  at  $\phi = 0.52$  and filled diamonds and squares are for  $S = 0.10$  &  $S = 0.20$  at  $\phi = 0.54$ , respectively. (c) The stretched exponent  $\beta$  vs.  $T$  obtained by fitting KWW equation to self-intermediate scattering function,  $F_s(k_{max}, t)$  where  $k_{max} \sim 7.0$ . The lines are guide to the eye. Comparison between (a)/(b) and (c) shows that the fall of  $\langle e_{IS} \rangle$  corresponds to the onset of non-exponential relaxation in  $F_s(k_{max}, t)$ . (d)  $\beta$  vs.  $T$  from  $F_s(k, t)$  for different  $k$  values. Data shown for  $S = 0.1(S1)$  &  $S = 0.2(S2)$  at  $\phi = 0.52$ .  $S = 0.15$  omitted for clarity.

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 [13, 14], which speeds up the dynamics of the whole system. A

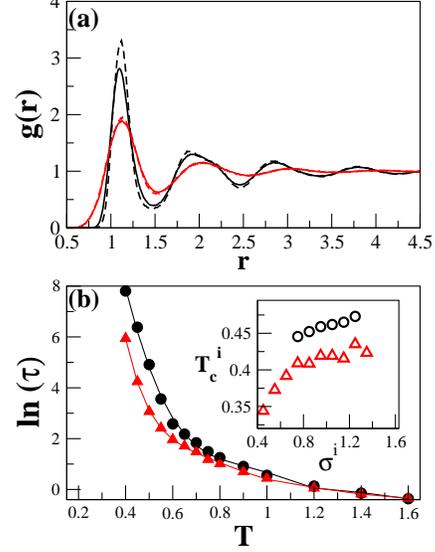


FIG. 2: (a) Average radial distribution functions (rdf) for the parent liquid (solid line) and the inherent structure (dashed line) for  $S = 0.10$  (black) and  $S = 0.20$  (red) systems at  $T = 0.50$  and  $\phi = 0.52$ . (b) Relaxation time  $\tau$  from KWW fit to  $F_s(k_{max}, t)$  for  $S = 0.10$  (filled circles) and  $S = 0.20$  (filled triangles) at  $\phi = 0.52$ . [Inset: Critical temperature  $T_c^i$  for particles of different sizes  $\sigma^i$  obtained from the MCT equation,  $D^i \sim (T - T_c^i)^\gamma$  for  $S = 0.10$  (open circles) and  $S = 0.20$  (open triangles) at  $\phi = 0.52$ .]

plot of the Mode Coupling Theory (MCT)[15] critical temperature  $T_c^i$  for particles of different sizes  $\sigma^i$  (inset of Fig 2(b)) shows that the  $T_c^i$  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 *increasing polydispersity* at fixed volume fraction *reduces the fragility* of the liquid so that the system is a stronger glass former at higher polydispersity.

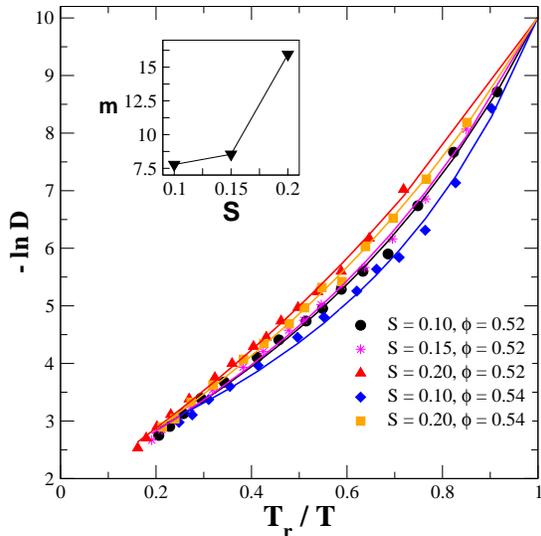


FIG. 3: Angell-like fragility plot at different  $S$  for the two  $\phi$  studied. The thick lines are VFT fit to the diffusivity data,  $D = D_0 \exp(\frac{E_D}{T-T_0})$ . The reference temperature  $T_r$  is chosen such that  $D(T_r) = 4.5 \times 10^{-5}$ . The VFT extrapolation is used to locate  $T_r$ . The plot shows that fragility decreases with  $S$  and that for a given  $S$  fragility increases with increase in  $\phi$ . [Inset: Strength parameter  $m$  (where  $m = \frac{E_D}{T_0}$  [24]) obtained from VFT fit as a function of  $S$  at  $\phi = 0.52$ .]

This effect is analogous to the *antiplastification* that has been observed in polymer melts [16]. PEL analysis shows that the antiplastified system has smaller barriers to overcome in order to explore the configuration space [17]. 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 [18]. 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 [10]. The correlation is also consistent within the framework of coupling model (CM) [19] 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 1(c)). However,

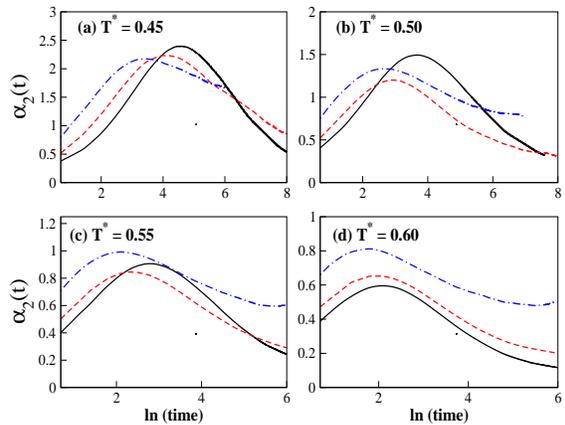


FIG. 4: The non-Gaussian parameter,  $\alpha_2(t)$  for  $S = 0.10$  (solid line),  $S = 0.15$  (dashed line) and  $S = 0.20$  (dot-dashed line) at four different  $T$  depicting the crossovers between different  $S$ . Data is shown for  $\phi = 0.52$ .

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 1(c). The  $\beta$  values in Fig 1(c) are obtained by KWW fit to  $F_s(k_{max}, t)$ . However, these cross-overs are independent of  $k$  values as shown in Fig 1(d). 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 [22]. 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 [20]) 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 [4, 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 1(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 as polydispersity 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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