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## An Overview on Short and Long Time Relaxations in Glass-forming Supercooled Liquids

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# An Overview on Short and Long Time Relaxations in Glass-forming Supercooled Liquids

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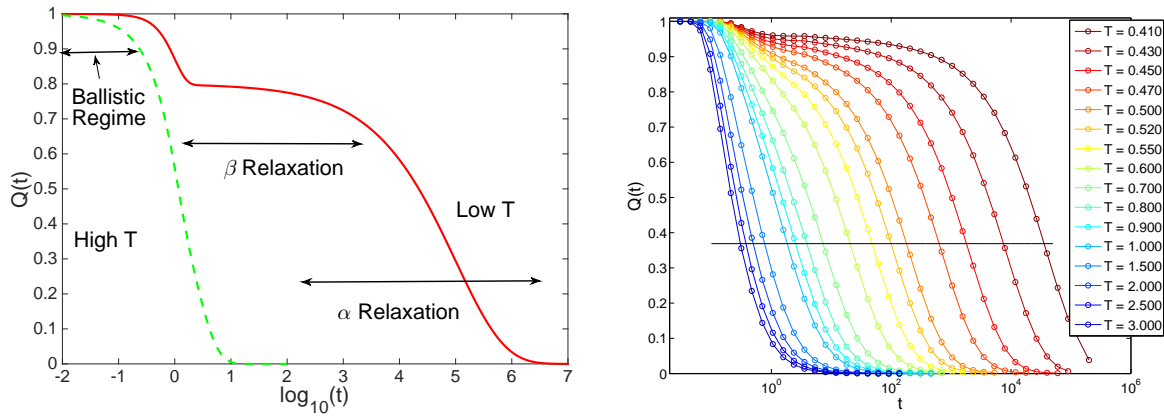
**Abstract.** Density fluctuations in supercooled liquids near the glass transition relax in multiple steps. The short time relaxation is known as  $\beta$ -relaxation and the final long time relaxation is called  $\alpha$ -relaxation. It is believed that the long time  $\alpha$ -relaxation is a cooperative phenomena associated with a growing length scales, whereas the short-time  $\beta$ -relaxation is often attributed to spatially local processes involving the rattling motion of a particle in the transient cage formed by its neighbors. Using molecular dynamics simulations of few model glass-forming liquids, we show that the  $\beta$ -relaxation is also cooperative in nature and the length scale extracted from the detailed finite-size scaling analysis of  $\beta$ -relaxation is found to be the same as that of the length scale that describes the spatial heterogeneity of local dynamics in the long-time  $\alpha$ -relaxation regime. These results provide a clear connection between short-time dynamics and long-time structural relaxation in glass-forming liquids.

## 1. Introduction

Dramatic increase in viscosity or relaxation time with decreasing temperature in glass forming liquids remain as an unsolved problem even after decades of research [1, 2, 3]. The increase in viscosity is so dramatic that with few tens of degrees of change in temperature, viscosity can change as much as 13 orders of magnitude and the temperature at which viscosity reaches  $10^{13}$  Poise is termed as calorimetric glass transition temperature,  $T_g$ . The density-density correlation functions at low temperatures for these glass forming liquids show multiple relaxation steps. The short time relaxation is termed as  $\beta$ -relaxation and the final longer time scale relaxation is called  $\alpha$ -relaxation as depicted in Fig.1. This long time  $\alpha$ -relaxation gets sluggish with decreasing temperature and it is generally believed that this process is cooperative in nature. On the other hand the short time relaxation process is often assumed to be trivially associated with motion of some part of a complex molecule in glass forming liquids, e.g. rotation of side groups, leading to short time scale relaxation. All short time relaxation mechanisms, however, need not related to such trivial intra-molecular motions and can happen even for rigid molecules. A detailed understanding of these relaxation processes is important as it is believed that the short time relaxation is the main relaxation process below calorimetric glass transition temperature and is probably one of the main relaxation processes responsible for aging and rejuvenation in glasses.

Many different approaches to understand the slowing down of long time  $\alpha$ -relaxation invoke the existence of correlation lengths that grow [1, 2, 4, 5, 6, 7, 8, 9, 10, 11] as the temperature is decreased. It is already established that there are at least two different length scales in the system : a dynamic length scale associated with the heterogeneity in local dynamics and a static length scale associated subtle amorphous order. Recent theoretical and experimental studies on dynamic heterogeneity in supercooled glass forming liquids [12, 13, 14, 15] provided clear





**Figure 1.** Left panel: Sketch of two point density-density correlation function  $Q(t)$ . Right panel: Calculated  $Q(t)$  using molecular dynamics simulations for a binary glass forming liquids for different temperatures as indicated in the legend. Notice the appearance of two step relaxation with decreasing temperature.

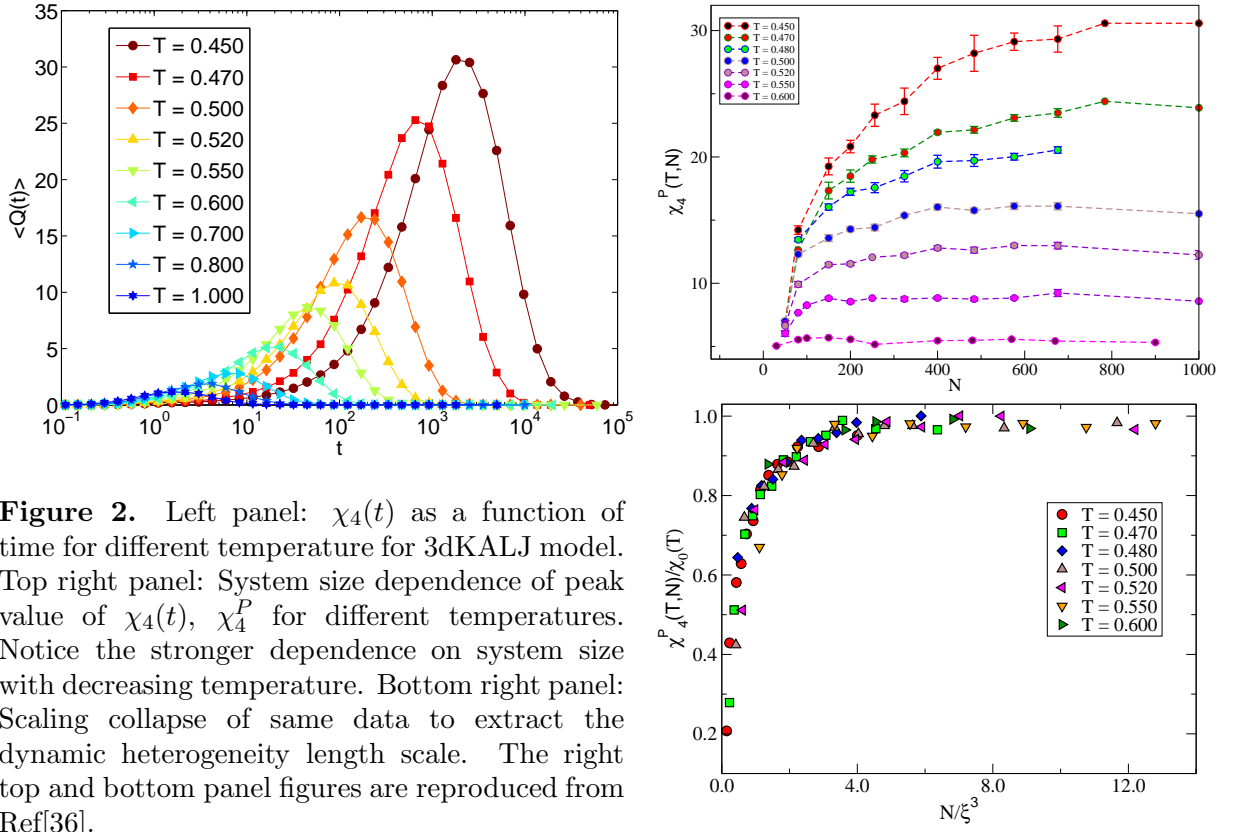
evidence for the existence of this dynamical length scale [16, 17, 18, 19, 20, 10, 25]. These spatial correlations have been studied through a four-point susceptibility [21, 22, 23, 24] defined as

$$\chi_4(t) = \frac{1}{N} [\langle Q^2(t) \rangle - \langle Q(t) \rangle^2], \quad \text{where} \quad Q(t) = \sum_{i=1}^N w(|\mathbf{r}_i(0) - \mathbf{r}_i(t)|), \quad (1)$$

where  $\mathbf{r}_i(t)$  is the position of particle  $i$  at time  $t$ ,  $N$  is the total number of particles,  $w(r) = 1$  if  $r \leq a_0$  and zero otherwise, and  $a_0$  is a short-distance cutoff chosen to be close to the distance at which the root-mean-square displacement (RMSD) of the particles as a function of time exhibits a plateau. The window function  $w(r)$  is used to coarse grain the small-amplitude vibrational motion of a particle in the “cage” formed by its neighboring particles. The peak value of  $\chi_4(t)$  is defined as  $\chi_4^P \equiv \chi_4(t = \tau_4)$ , where  $\tau_4$  is the time at which  $\chi_4(t)$  attains its maximum value (see left panel of Fig.2) and  $\tau_4 \simeq \tau_\alpha$  at all temperatures. Typical time-temperature dependence of two point correlation function  $Q(t)$  is shown in the right panel of Fig.1. The  $\alpha$ -relaxation time,  $\tau_\alpha$  is defined at the time where this correlation function decays to  $1/e$  to its initial value as  $Q(t = \tau_\alpha) = 1/e$ .

Predictions obtained from inhomogeneous mode coupling theory (IMCT) [5, 16, 17] suggest an initial power-law growth of the cooperativity length scale in time up to the  $\beta$ -relaxation time followed by a saturation region that continues up to a time scale comparable to the  $\alpha$ -relaxation time. However, it is still not understood how the dynamics cross over from its short-time behaviour to that at long times. There are many ideas and observations that seem to suggest a close relation between dynamical features observed at short and long time scales [26, 27, 28, 29, 30, 31, 32, 33]. Thus, a proper understanding of relaxation processes in both  $\beta$  and  $\alpha$  regimes and their underlying relation (if any) is extremely important in the overall understanding of glassy dynamics and its rich phenomenology.

In Ref.[36] the method of finite size scaling (FSS) [34] is used to extract the growing dynamic correlation length in a model glass forming liquid. This method has been used extensively in past for obtaining accurate numerical results for critical properties of a system near a conventional continuous phase transition [34]. Ref.[36] clearly demonstrated that the method of FSS is very useful [21, 35, 36] to study glass transition and also showed the importance of FSS compared to other conventional methods. In the left panel of Fig.2 we have plotted  $\chi_4(t)$  as a function of time for different temperatures.  $\chi_4(t)$  shows a peak at time close to the  $\alpha$ -relaxation time and both the peak height and peak position increase with decreasing temperature. The peak height measures the typical size of the cooperatively rearranging region (CRR) in the system. This peak value of  $\chi_4(t)$ ,  $\chi_4^P$  has been found to show finite size effect and the effect becomes



**Figure 2.** Left panel:  $\chi_4(t)$  as a function of time for different temperature for 3dKALJ model. Top right panel: System size dependence of peak value of  $\chi_4(t)$ ,  $\chi_4^P$  for different temperatures. Notice the stronger dependence on system size with decreasing temperature. Bottom right panel: Scaling collapse of same data to extract the dynamic heterogeneity length scale. The right top and bottom panel figures are reproduced from Ref[36].

much more stronger as one decreases temperature. In the right top panel we have shown the system size dependence of  $\chi_4^P$  for different temperatures for Kob-Andersen model in three dimensions (referred here as 3dKALJ) [45] and one can clearly see that at higher temperature, the dependence is weak and it grows with decreasing temperature. In the right bottom panel, we have shown the finite size scaling done to extract the length scale associated with this cooperativity. It was subsequently shown that the heterogeneity length obtained in this way is in good agreement with that obtained by analyzing the four-point structure factor [37, 38].

In this article, we describe the results of FSS studies of a short time scale  $\tau_\beta$  and long time scale  $\tau_\alpha$  for two generic model glass-formers. The simulation details are provided in Sec.[2]. We compare the estimated length scales with those obtained from FSS analysis of  $\chi_4^P$ , which quantifies dynamic heterogeneity at the  $\alpha$  relaxation time scale, and find that the two length scales agree well for all the model systems we studied whereas the length scale associated with the long time scale are completely different. We also find a universal relationship between  $\beta$  time scale and  $\alpha$  relaxation time over the whole range of timescale accessible in simulations. These results are described in Sec.[3]. Sec.[4] contains a discussion of our results and a summary.

## 2. Method and Simulation Details

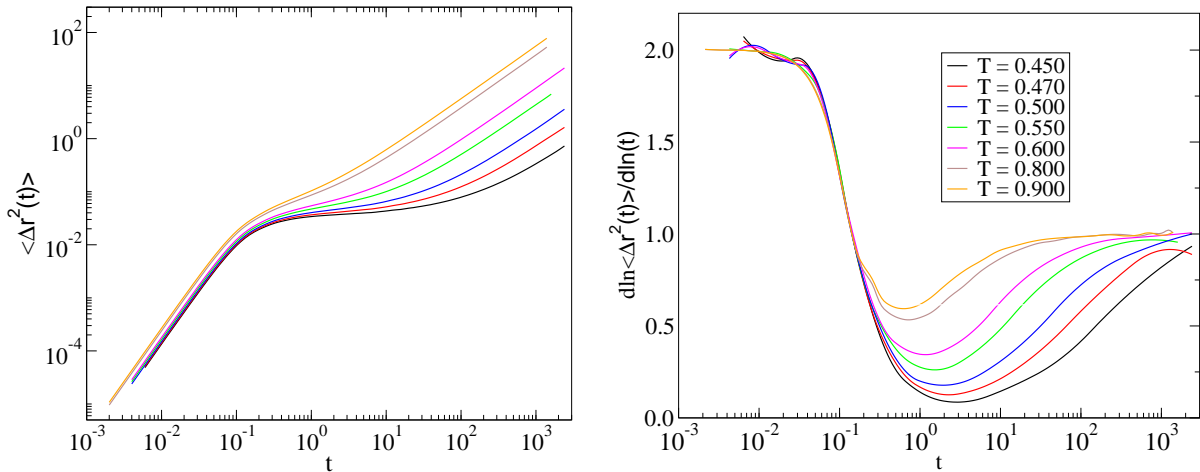
We report studies done on two model liquids in this work. They are: (i) the three-dimensional Kob-Andersen binary Lennard-Jones mixture (referred here as 3dKALJ) [45], (ii) a three-dimensional system characterized by a repulsive inverse power-law potential (3dR10) [47] whose range of interaction is smaller compared to that in the first model. For the first model system the interaction range covers the second neighbouring shell whereas for the second case it is truncated within the first shell. These models have been studied extensively and found to be very good glass formers. The interaction potential of 3dKALJ is given by

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\frac{\sigma_{\alpha\beta}}{r})^{12} - (\frac{\sigma_{\alpha\beta}}{r})^6] \quad (2)$$

where  $\alpha, \beta \in \{A, B\}$  and  $\epsilon_{AA} = 1.0$ ,  $\epsilon_{AB} = 1.5$ ,  $\epsilon_{BB} = 0.5$ ,  $\sigma_{AA} = 1.0$ ,  $\sigma_{AB} = 0.80$ ,  $\sigma_{BB} = 0.88$ . The interaction potential was cut off at  $2.50\sigma_{\alpha\beta}$  and the number density of particle is  $\rho = 1.20$ . We have done simulations in 3D in a cubic simulation box with periodic boundary conditions. Simulation was done in canonical ensemble (NVT) with Newtonian dynamics. We have used modified leap-frog algorithm to do the constant temperature simulation with Berendsen thermostat. Length, energy and time scales are measured in units of  $\sigma_{AA}$ ,  $\epsilon_{AA}$  and  $\sqrt{\sigma_{AA}^2/\epsilon_{AA}}$ . We have done simulation in the temperature range  $T \in [0.90, 0.45]$ . We have equilibrated the system for  $\sim 10^8 - 10^9$  MD steps depending on the system size and the production runs are at least 5 – 6 times bigger than the equilibration runs. We have used integration time steps  $dt = 0.005$ . The system sizes studied are in the range  $N \in [150, 28160]$ . The second model is purely repulsive and the potential is given by [47]

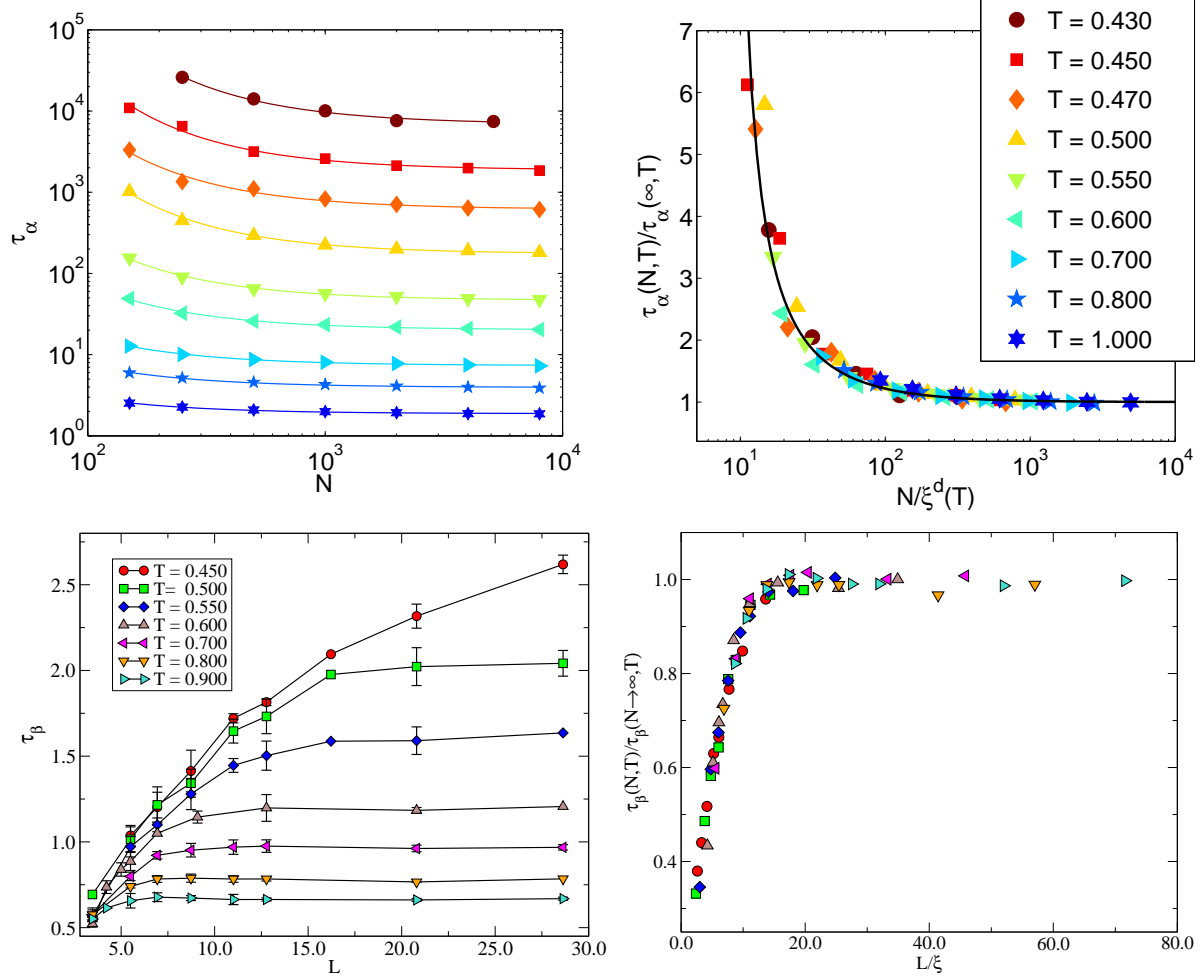
$$V_{\alpha\beta}(r) = \epsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{r} \right)^n \quad (3)$$

where  $\alpha, \beta \in \{A, B\}$  and  $\epsilon_{\alpha\beta} = 1.0$ , for all  $\alpha$  and  $\beta$ .  $\sigma_{AA} = 1.0$ ,  $\sigma_{AB} = 1.18$ ,  $\sigma_{BB} = 1.40$ ,  $n = 10$ . The interaction potential was cut off at  $1.38\sigma_{\alpha\beta}$ . For this model, system sizes studied are in range  $N \in [64, 4000]$  at number density  $\rho = 0.81$  for 9 temperatures in the range  $T \in [0.50, 1.000]$ . All other simulations details are same as the previous model. Results for another model system (3dIPL model) [46] are not reported here and details of the model and some of the results can be found in [48].



**Figure 3.** Mean square displacement (MSD) (left panel) and the derivative (right panel) of the logarithm of MSD with respect to the logarithm of time  $t$ , shown as a function of  $t$ . The minimum of the derivative defines  $\tau_\beta$ . (see text for details). The figure is reproduced from Ref[48].

In [41],  $\tau_\beta$  was defined as the time at which an inflection occurs in a log-log plot of the mean squared displacement *vs.* time. We use the same definition to evaluate  $\tau_\beta$  as a function of system sizes and temperature. In left panel of Fig. 3, we show the mean squared displacement (MSD) as a function of time in a log-log plot for different temperatures. Notice the appearance of plateau in the intermediate time regime with decreasing temperature. The derivative is plotted in the right panel of Fig. 3. Note that as expected the slope at small time is 2, indicating the ballistic motion of particles and then a dip appears at intermediate time and the slope tends to 1 at long time. Thus the observed clear dip in the derivative and its variation with temperature indicate that this estimation of  $\tau_\beta$  can be done unambiguously and without much uncertainty. We use this definition of  $\tau_\beta$  in the present work.



**Figure 4.** Top left panel:  $\tau_\alpha$  for the 3dKALJ model, shown as a function of system size for different temperatures in the interval  $T \in [0.45, 0.90]$ .  $\tau_\alpha$  decreases with increasing system size and saturates at a value which increases with decreasing temperature and the right panel shows the scaling collapse of the same data. Bottom panel:  $\tau_\beta$  increases with increasing system size in stark contrast with the behaviour seen for  $\tau_\alpha$ . The right panel shows the data collapse. The collapse in both top and bottom panels are observed to be very good. Top panel is reproduced from Ref[3] and bottom panel from Ref[48].

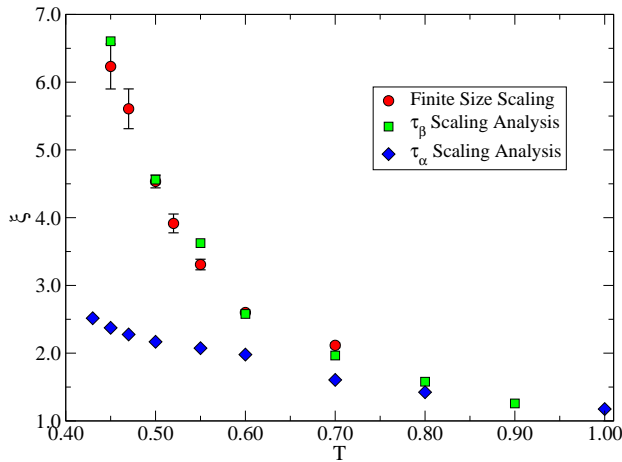
### 3. Results

In Fig. 4, we show the system-size dependence of  $\tau_\alpha$  (top panel) and  $\tau_\beta$  (bottom panel) for different temperatures for the 3dKALJ model. Notice the dramatic difference in the system size dependence of these two time scales.  $\tau_\alpha$  decreases with increasing system size [36] whereas  $\tau_\beta$  shows a completely opposite behaviour [48]. This was interpreted as indicating a mixing of activated and non-activated mechanisms of structural relaxation (see also [42, 43]). It has been suggested [43] that behaviour described by IMCT, without the influence of activated dynamics, should be expected instead in the short-time dynamics, in a temperature window above the mode coupling transition temperature. Indeed the system size dependence of  $\tau_\beta$  is observed to be what one would expect for normal time scale determined by an underlying length scale in the system. For high temperatures the dependence is weak and the asymptotic value is reached for small system sizes, but this characteristic size becomes increasingly large with decreasing temperature. We note that the range over which  $\tau_\beta$  varies with system size and temperature is modest, unlike the behaviour observed for  $\tau_\alpha$ .

We next scale the system size  $N$  at each temperature by an empirically determined correlation volume  $\xi^d(T)$  such that the values of  $\tau_\alpha(N, T)/\tau_\alpha(N \rightarrow \infty, T)$  for all  $N$  and



$T$  [ $\tau_\alpha(N \rightarrow \infty, T)$  is the large- $N$  asymptotic value of  $\tau_\alpha(N, T)$ ] collapse onto a master curve when plotted versus  $N/\xi^d(T)$ .  $d$  is the dimensionality of the system ( $d = 3$  here).

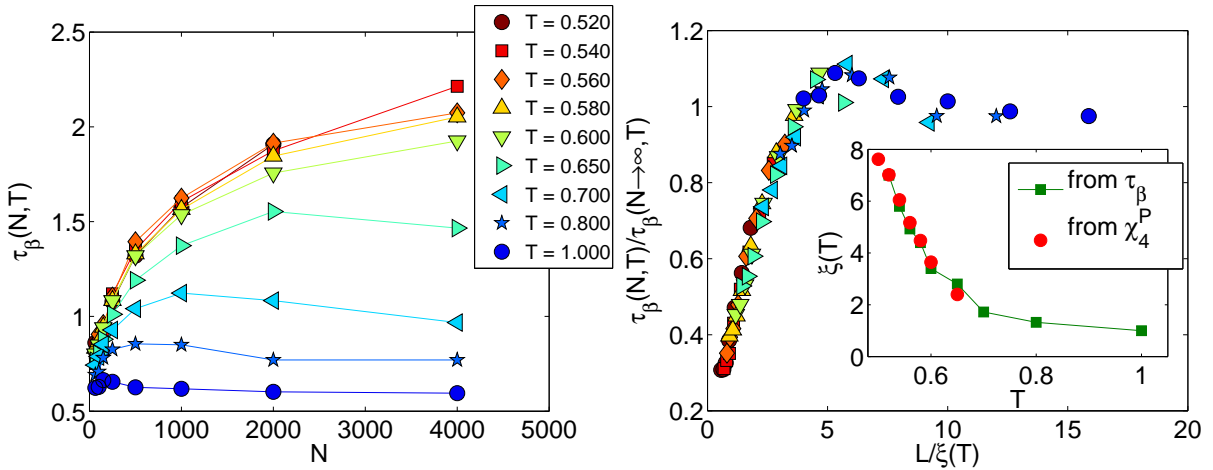


**Figure 5.** Different length scales are plotted as a function of temperature. Notice that dynamic length scale and length scale obtained from the short time relaxation is same and the length scale obtained from long time relaxation is completely different.

very well. IMCT predicts that  $\xi$  grows as a power law in time up to  $\tau_\beta$  and stays at the value  $\tau_\beta$  up to  $\tau_\alpha$ . Our results therefore confirm this expectation. Independently of IMCT predictions, the agreement is remarkable in pointing to an intimate connection between dynamics at short times ( $\beta$  regime) and long times ( $\alpha$  regime). This result suggests that the

The data collapse obtained this way, shown in top right panel of Fig. 4, is very good. This allows one to determine the length scale at the  $\alpha$ -regime. Similar analysis for  $\tau_\beta$  is shown in bottom right panel of Fig.4. Again the data collapse is found to be very good. This gives us the confidence on the reliability of the extracted length scales.

We then compare the length scale estimated in this way with the heterogeneity length estimated from system size dependence of  $\chi_4^P$  [36]. This comparison is shown in the Fig. 5. In order to make the comparison, we scale the present estimate so that the two length scales match at  $T = 0.6$ . Length scales obtained by FSS are known only up to a multiplicative factor, and hence this procedure does not introduce any additional arbitrariness. We find that the temperature dependence of the two length scales agrees

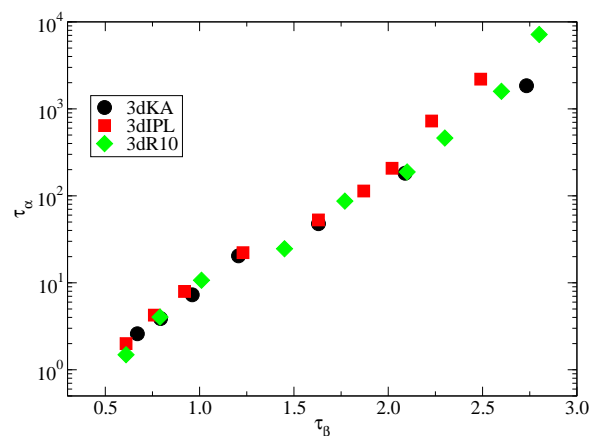


**Figure 6.** Left Panel: System size dependence of  $\tau_\beta$  for different temperature for 3dR10 model. Right panel: Data collapse of  $\tau_\beta$  to obtain the length scale associated with the cooperativity in  $\beta$ - relaxation. Inset: Comparison of the correlation length extracted from the system-size dependence of  $\tau_\beta$  with the dynamical length scale. The two length scales agree with each other to a good accuracy. Taken from Ref.[48].

heterogeneity present in the dynamics in the  $\alpha$  regime has been built up already in the  $\beta$  regime, and therefore in principle, essential information about the  $\alpha$  relaxation can be obtained by studying short-time dynamics. Our result therefore lends support to many investiga-

tions and ideas that aim to relate dynamical behaviour at short times to long-time structural relaxation [26, 27, 28, 29, 30, 31, 32, 33]. It is important to note here that the length scale obtained from the finite size scaling analysis of  $\alpha$ -relaxation time is very different from these two other length scales. The growth of this length scale is much milder with temperature and many studies suggests that this length scale is same as the static length scale (see Refs. [2, 3] for in-depth discussion on the inter relation between different length scales in glassy systems). Thus although the current results suggest a strong connection between dynamics at short and long time scales, some puzzles still remain to be answered to understand the intricate connection between relaxation processes at short and long time scales.

To see whether the results obtained for the 3dKALJ model are generic, we have done similar analysis for the 3dR10 model. In Fig.6, we have shown, in the left panel we show the system-size dependence of the short time scale  $\tau_\beta$  for different temperatures and in the right panel the corresponding finite size scaling analysis done to obtain the length scale. The scaling collapse observed in this case again is very good.



**Figure 7.** Long time  $\alpha$ -relaxation timescale is plotted as a function of the short time relaxation timescale  $\tau_\beta$  for different model systems studied. It seems to suggest a possible universal relationship between these two time scales.

Over four orders of magnitude in  $\alpha$ -relaxation timescale, it seems to follow a universal relationship. Although without a proper microscopic understanding, the existence of such a universal relationship can not be established with certainty from the limited range of the data presented here, but the current results do suggest a possible interesting connection worth further investigation.

#### 4. Discussion

In this work, we have studied the system-size dependence of the  $\beta$  and  $\alpha$  relaxation time for two model liquids in three dimensions. For  $\beta$  relaxation, we find that the time scale initially increases with increasing system size and saturates for large values of the system size, exhibiting behaviour expected for the size dependence of a quantity that depends on a length scale. This is unlike the system-size dependence of the  $\alpha$  relaxation time that is found to decrease with increasing system size [36]. The length scale extracted from FSS of  $\beta$  relaxation time scale matches very well with the length scale extracted from the FSS of the four-point susceptibility  $\chi_4^P(T)$  measured at the  $\alpha$ -relaxation time scale, whereas the  $\alpha$  relaxation time itself seems to be controlled by a completely different length scale. The behaviour observed in  $\beta$ -relaxation is in qualitative agreement with the predictions of inhomogeneous mode coupling theory and suggests a possible deep connection between short and long time dynamics in glass forming liquids [29, 30, 31, 32, 33, 48] with the caveat that the  $\alpha$ -relaxation time itself seems to be

We find that the temperature dependence of the length scale obtained from the FSS of  $\tau_\beta$  matches quite well with the dynamic heterogeneity length scale, as shown in the inset of the right panel of Fig.6. The results obtained for the 3dIPL model are similar and are not reported here (see Ref.[48] for details).

As long time dynamics seem to be connected to short time dynamics, as suggested by the development of dynamic heterogeneity within the  $\beta$ -relaxation time scale and maintaining that at least up to  $\alpha$ -relaxation timescale, one might wonder whether short timescale and long time scale in these systems are related to each other by an universal relationship. In Fig. 7 we have plotted logarithm of the long time  $\alpha$ -relaxation timescale,  $\tau_\alpha$  as a function of  $\tau_\beta$  for different model system studied.



controlled by a completely different length scale. Finally the observed universal relationship between short and long time relaxation timescales is worth future investigation.

## 5. Acknowledgements

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