Pinning Susceptibility : A Novel Method to Study Growth of Amorphous Order in Glass-forming Liquids – Supplementary Information

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This supplementary information is arranged as follows. In Sec. I, we describe the methods we used to obtain the static length scale ξ_s. In Sec. II, we report some aspects (*e.g.* size of the impurity particles) of the effects of the chosen impurity particles. In Sec. III, we present a new argument, based on our obtained values of the pinning susceptibility, about the possibility of an ideal glass state at some critical value of the pinning concentration. We also outline a new explanation of the scaling form of $\tau_\alpha(c,T)$ on pinning concentration c used in Refs. [1] and [2]. The arguments are based on the non-singular dependence of the peak height of the pinning susceptibility on the pinning concentration. Finally in Sec. IV, we discuss the dependence of $\chi_p(t)$ on the choice of δc.

I. METHODS OF CALCULATING THE STATIC LENGTH SCALE, ξ_s

Although there is a consensus on the existence of a static length scale in supercooled liquids that grows as the temperature is lowered, obtaining it may be quite challenging. In this work, we have used the following three methods to obtain the static length scale.

A. Point-To-Set Method:

The point-to-set (PTS) length scale was introduced by Bouchaud and Biroli in Ref. [3] and it was numerically calculated for the first time in Ref. [4] in a model binary glass former. This method is useful at somewhat high temperatures when the length scale is not too large. The main difficulty comes from the dynamical procedure involved in calculating this length scale. In the PTS method, one needs to take an equilibrated configuration at a given temperature and then define a smaller spherical region of radius, R. The particles outside this spherical cavity are pinned at their respective positions and only the particles inside the cavity are allowed to evolve according to Newtonian dynamics. The static overlap correlation is calculated for the particles inside the cavity and in order to remove boundary effects the static overlap is calculated only for those particles which are in the center of the cavity. This procedure is repeated for many different sizes of the cavity and the size dependence of the static overlap is obtained to finally extract the point-to-set length scale.

The external pinned boundary makes the dynamics of the internal particles very slow especially for small cav-

ities and one needs to employ a sophisticated sampling method (Swap Monte Carlo Method [5]) to partly overcome this difficulty. As this enhanced sampling method is not generically applicable to any model system, the sampling problems are not always easy to overcome [6] especially at lower temperature. In this study we have used PTS methods only at those temperature regime where it can be done within accessible computation time. Some of the PTS length scale reported in this work are taken from Ref. [2].

In Ref. [7], it was claimed that the PTS method fails to capture the relevant static length scale in a weakly polydisperse system where the relevant static length scale is the one associated with hexatic ordering. It raised questions about the usefulness and validity of PTS length scale in measuring the right static length scale in the problem. In Ref. [8], it was shown that if one takes in to account the fluctuations due to the polydispersity and the packing fraction in the cavities, especially for polydisperse system, then one indeed finds the PTS length scale to be the same as the hexatic length scale. We therefore believe that the PTS still captures the right static length scale and it is still order agnostic. We have also shown that for different binary model systems where there are predominant hexatic order upon supercooling, PTS length scale unambiguously picks up the relevant hexatic length scale. It is important to note that although in Ref. [8] a possible resolution to the claimed failure of PTS method for measuring the relevant static length-scale for model systems with medium range crystalline order have been suggested, a complete theoretical understanding for the same is still not available.

B. Finite Size Scaling of Minimum Eigenvalue:

The second method is the finite-size-scaling of the minimum eigenvalue of the Hessian matrix corresponding to an inherent structure of the supercooled liquid at a given temperature [9]. This method is expected to work in the low temperature regime where the supercooled liquid spends a considerable amount of time around a given minimum of its free energy landscape and a harmonic approximation works for a finite (but short) time. We will briefly describe the method here. Please refer to Ref. [9] for the details of this method.

Karmakar *et. al.* in [9] argued that the minimum eigenvalue $\lambda_{min}(T)$ of the Hessian matrix obtained at the inherent structure closest to the configuration of a supercooled liquid at given temperature T takes the scaling
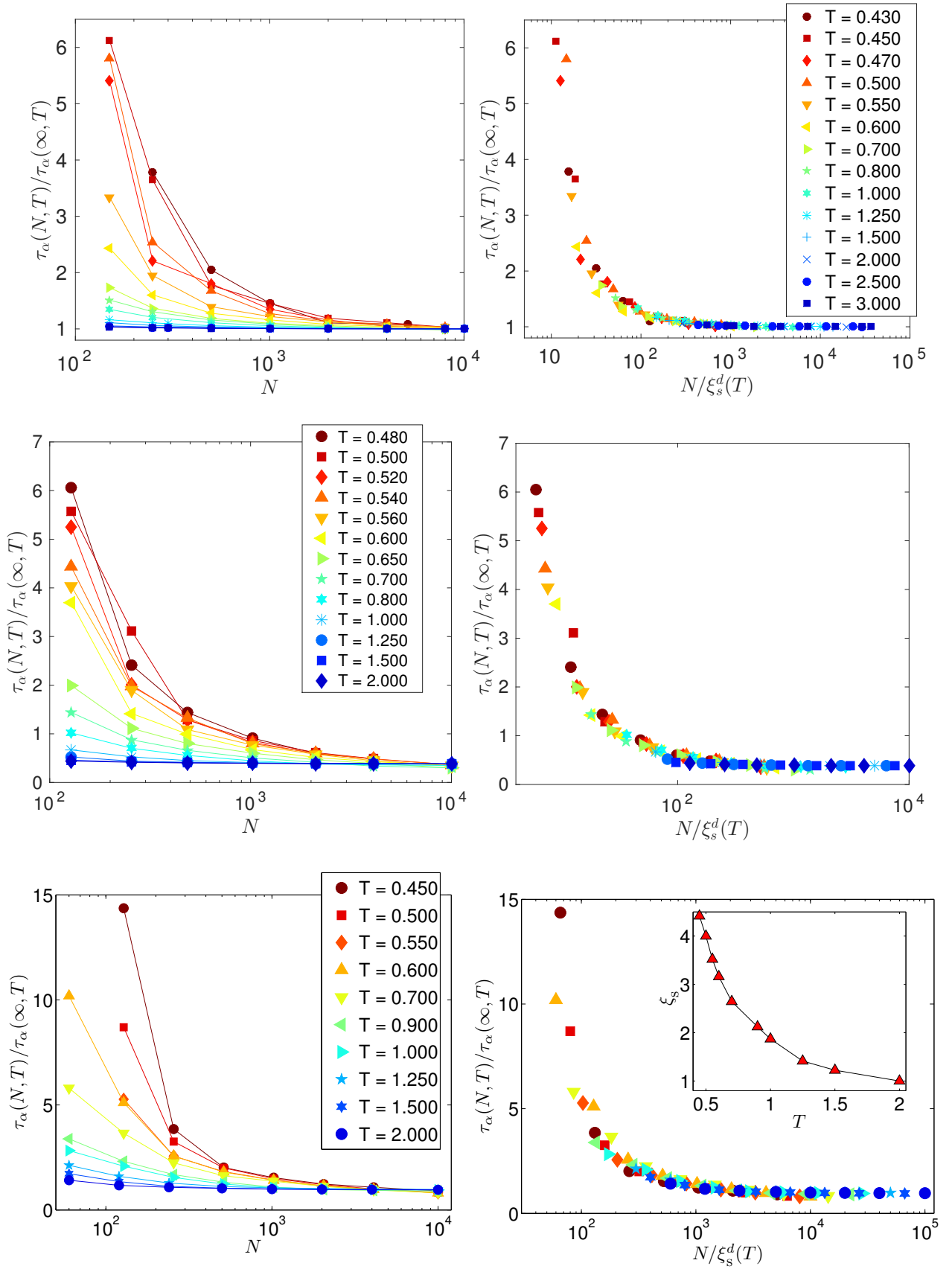
FIG. 1: Top Panel: Finite size effects of τ_α for the 3dKA model and the corresponding data collapse to obtain static length scale ξ_s shown in the next panel. Similar analysis done for 2dR10 model (middle panel) and 2dmKA model (bottom panel) are also shown. In all these case scaling collapse observed to be very good.

form,

$$\frac{\langle \lambda_{min}(T) \rangle}{\langle \lambda_D(T) \rangle} = \mathcal{F} \left[\xi_s^d(T) \left(\frac{1}{N} - \frac{Ad}{2} \left(\frac{\langle \lambda_{min}(T) \rangle}{\langle \lambda_D(T) \rangle} \right)^{d/2} \right) \right] . (1)$$

$\lambda_D(T)$ is the square of the Debye frequency, d is the dimensionality of space, A is an adjustable constant chosen to get the best scaling collapse and $\mathcal{F}$ is an unknown scaling function. In Ref. [9], the validity of this method was demonstrated for a few model glass forming liquids and later in Ref. [10] it was shown that the temperature dependences of the PTS and minimum eigenvalue length scales are the same for various generic glass forming liquids. Recently in Ref. [11], this method was used to obtain the static length scale for a glass forming liquids for which equilibrium state can be relatively easily sampled using the Swap Monte Carlo technique. A large change in length scale was reported in that work.

C. Finite Size Scaling of α-relaxation time

The third method we use is the finite-size-scaling of the α-relaxation time, τ_α. The α-relaxation time of supercooled liquids shows a strong system size dependence. It decreases monotonically with increasing system size before attaining its asymptotic value at the thermodynamic limit. In Ref. [12], it is shown that the finite size effect observed in relaxation time can be rationalized from the finite size effect of configurational entropy via Adam-Gibbs relation. It is also shown that the finite size dependence of four-point dynamic susceptibility and relaxation time are controlled by two different length-scales. As configurational entropy is a static quantity, one expects that the length-scale that controls the finite size effects of it will be a static length-scale. Thus it is natural to expect that the length-scale obtained from the finite size scaling analysis of α-relaxation time will also be a static length-scale. The following scaling form is used to obtain it.

$$\frac{\tau_\alpha(N, T)}{\tau_\alpha(\infty, T)} = \mathcal{G} \left(\frac{N}{\xi_s^d(T)} \right). \quad (2)$$

$\mathcal{G}(x)$ is an unknown scaling function. The infinite system size relaxation time $\tau_\alpha(\infty, T)$ and the static length scale $\xi_s(T)$ are chosen so as to get a good data collapse when $\tau_\alpha(N, T)/\tau_\alpha(\infty, T)$ is plotted against $N/\xi_s^d(T)$ for all temperatures on the same graph. In Fig. 1, we have shown such data collapse to obtain the static length scale for some of the studied systems. In Ref. [13], it is demonstrated that the length scale obtained from the FSS analysis of τ_α is indeed the same as the length scale obtained using PTS and FSS of minimum eigenvalue method. For an in-depth discussion on the importance of various length scales in the dynamics of supercooled liquids see, *e.g.*, Refs. [13] and [14].
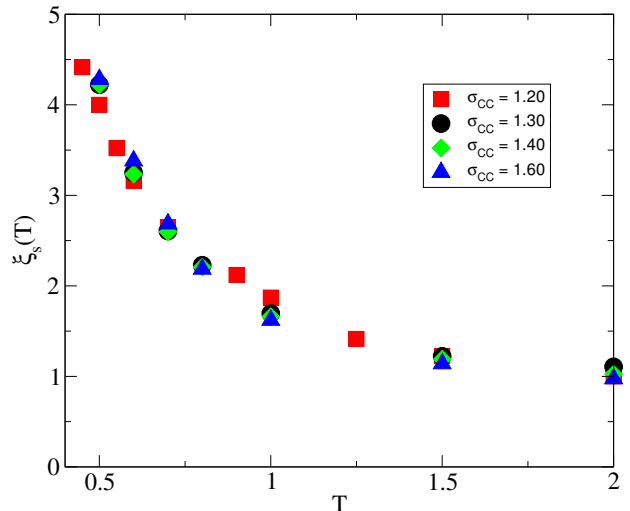
II. CHOICE OF THE SOLUTE PARTICLES

FIG. 2: Effect of the size σ_{CC} of added solute particle (C Ttype) for the 2dmKA model. $\sigma_{CC} = 1.20$ is used in the main article. Here we report data for $\sigma_{CC} = 1.3, 1.4, 1.6$. The temperature dependence of χ_p is independent of the size of C type particles within this studied range.

In Fig. 2 we establish that in the limit of dilute impurities, the size of the impurity particles does not affect the value of the length scale calculated (via χ_p). In Fig. 3, we establish that the solute particles indeed diffuse slower than the rest of the liquid particles showing that they can be thought of as a milder version of pinned particles. At lower temperatures diffusion constants of the solute particles are more than an order of magnitude smaller than the solvent particles.

III. A NOTE ON THE POSSIBLE IDEAL GLASS TRANSITION WITH RANDOM PINNING

If there is an ideal glass transition as a function of the pinning strength, the pinning susceptibility must diverge for all times larger than some finite time for that value of the pinning strength. This can be proven as follows. Suppose, the ideal glass transition takes place at $c = c_0(T)$ at temperature T. In that case, at temperature T and pinning fraction $c_0(T)$, the overlap correlation function must not decay to zero at any finite time. Thus, $Q[c_0(T), T, t] > 0$ for all t. However, for a slightly lower pinning fraction, the overlap correlation function must decay to zero at some finite time. Therefore, there must exist a time-scale $t_0(\delta c)$ such that $Q[c_0(T) - \delta c, T, t] = 0$ for all $t > t_0$. Thus, the pinning susceptibility χ_p must be infinite for all $t > t_0$. It must be noted that the time-scale at which χ_p diverges must be shorter than the α-relaxation time of the system for any finite $\delta c > 0$ with $t_0(0) \gtrsim \tau_\alpha \rightarrow \infty$. From top panel of Fig.4, it is clear that
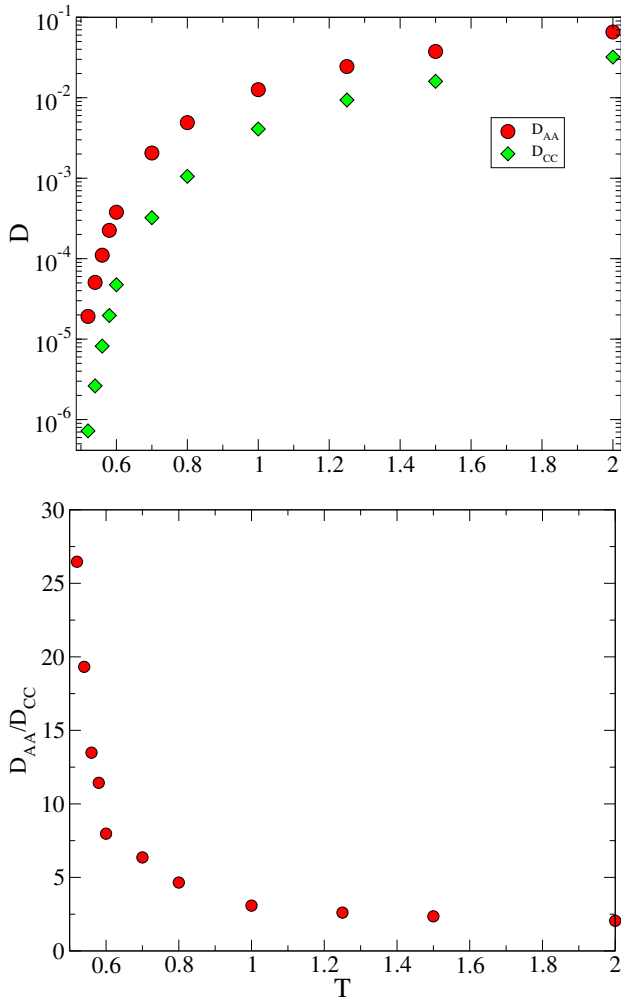
FIG. 3: Top panel: Comparison of diffusion constants of solvent particles (A or B type) with that of solute particles (C type) that are added to mimic the pinning effect. The results are for 3dR10 model. One can clearly see that diffusion constant of C type particles are more than an order of magnitude smaller than the solvent particles. Bottom panel: Ratio of the two diffusion constants.

$\chi_p^{max}(T)$ shows no tendency to diverge even when higher and higher pinning fraction data are considered. This gives us a compelling evidence against the possibility of achieving an ideal glass state by just increasing the number of pinned particles in a system. In the bottom panel of Fig. 4, we have shown the variations of peak heights with increasing concentrations of larger third particles for the ternary 2dR10 model to demonstrate the similarity with the pinning susceptibility for random pinning. This clearly shows that peak value of pinning susceptibility does not depend on the pinning concentrations or amount of third particles in the case of ternary models. Similar results are obtained for other model systems also.

At pinning concentrations which are significantly higher than those considered in this work and other stud-

ies on random pinning present in the literature, the system goes in to a phase known as the Lorentz gas which is nothing but diffusive motion of particles in a medium with a high concentration of random obstacles or in porous media. Such systems have been studied in Refs. [15, 16]. In this regime of pinning concentration all our analysis breaks down.

IV. DEPENDENCE OF $\chi_p^{max}(T)$ ON δc

In this section, we check the dependence of χ_p^{max} for various temperatures on the choice of δc used while cal-
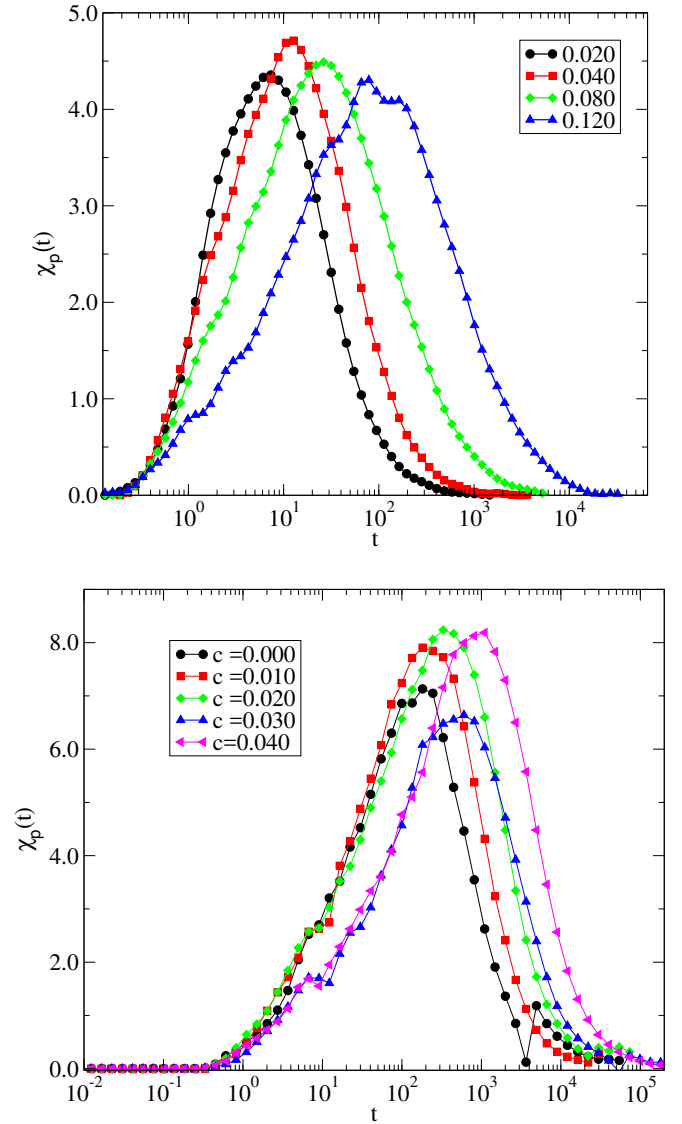

FIG. 4: Top panel: The variation of pinning susceptibility with time for various pinning fractions for the 3dKA model with 2000 particles at $T = 0.80$. Bottom panel: The variation of pinning susceptibility with time for various concentrations of third particles for the ternary version of 2dR10 model with 1000 particles at $T = 0.60$ with $\delta c = 0.01$.
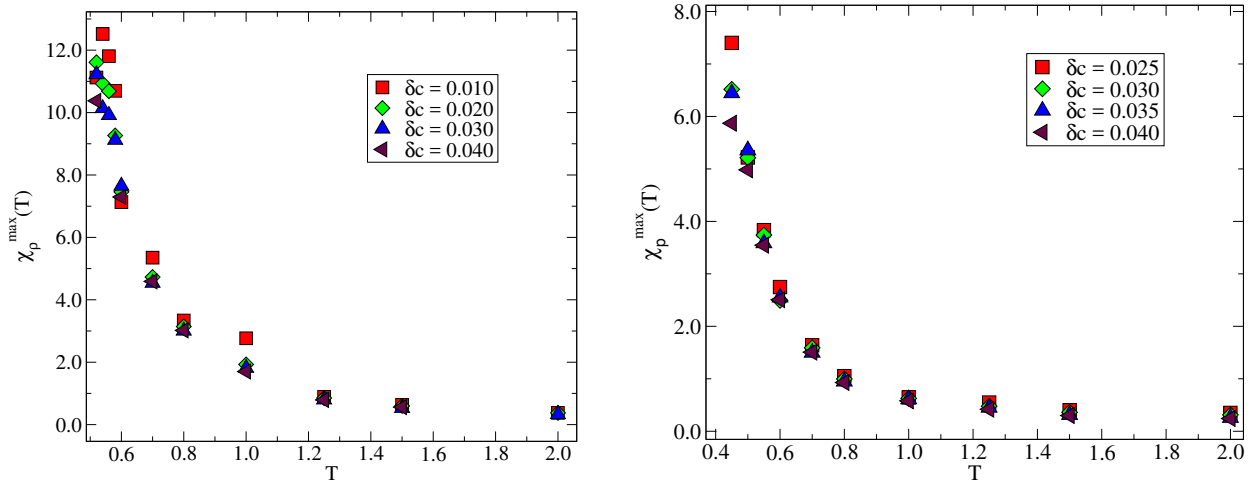
FIG. 5: Left panel: χ_p^{max} for different choices of δc for 2dR10 Ternary model. Notice that up to $\delta c = 0.04$, there is not much dependence of χ_p on δc. Right Panel: Similar plot for 3dKA Ternary model. One can clearly see that the peak value of the χ_p^{max} does not depend on the choice of the δc for the studied models.
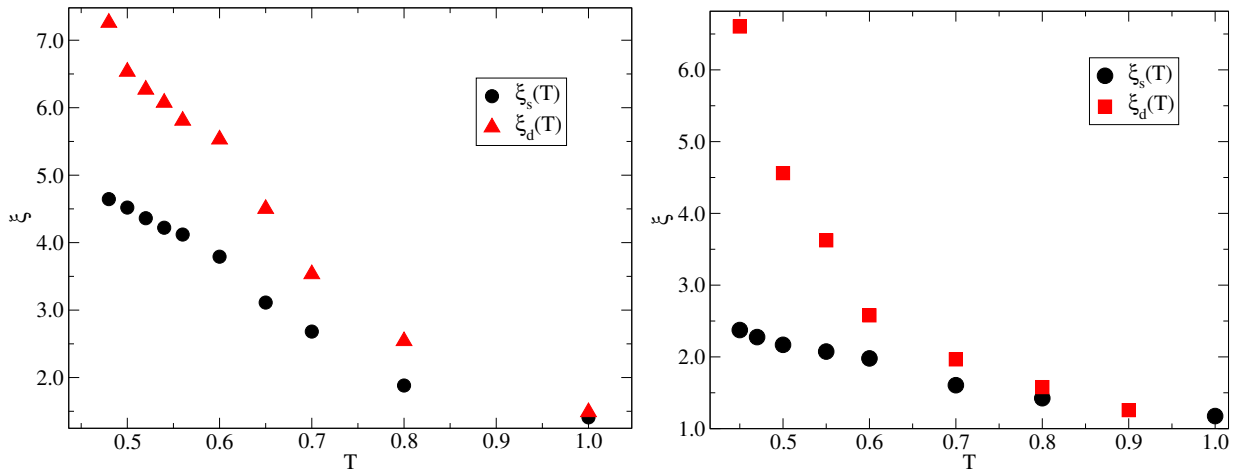

FIG. 6: Left panel: Comparison of Static and Dynamic length-scale for 2dR10 model in the studied temperature range. Right Panel: Same comparison for 3dKA model. One can clearly see that temperature dependence of static and dynamic length-scales are very different for these models in which there is no prominent medium range crystalline order. The scales are known up to a scale factor, so the data for both the length-scales are matched at the highest studied temperature.

culating χ_p^{max} via numerical differentiation. In Fig. 5, we have plotted χ_p^{max} using different values δc for our model systems. One can clearly see that the peak height does not depend explicitly on the choice of δc as long as it is small. This also directly establishes the robustness of our results based on the proposed susceptibility.

V. DECOUPLING OF STATIC AND DYNAMIC LENGTH-SCALES

In some recent works [7, 17, 18], it is suggested that the static and dynamic length-scale are same or proportional to each other. In Ref. [8], it is shown that this conclu-

sions are true only for system with predominant medium range crystalline order (MRCO) and static and dynamic length-scales decouple from each other for other generic glass forming liquids with not prominent crystalline order. In Fig.6, we have shown the temperature dependence of static and dynamic length-scales for two models systems **2dR10** and **3dKA** in the studied temperature ranges. These two models do not show detectable growth of medium range crystalline order with decreasing temperature. It is clear that the dynamic length-scale grows much faster than the static length-scale at least in the studied temperature range and their temperature dependence is completely decoupled from each other. Please see Ref.[8], for further details.

[1] S. Chakrabarty, S. Karmakar, and C. Dasgupta, Sci. Rep. **5** (2015).

[2] S. Chakrabarty, R. Das, S. Karmakar, and C. Dasgupta, J. Chem. Phys. **145**, 034507 (2016).

[3] J.-P. Bouchaud and G. Biroli, J. Chem. Phys. **121**, 7347 (2004).

[4] G. Biroli, J.-P. Bouchaud, A. Cavagna, T. S. Grigera, and P. Verrocchio, Nat. Phys. **4**, 771 (2008).

[5] T. S. Grigera and G. Parisi, Phys. Rev. E **63**, 045102 (2001).

[6] G. M. Hocky, T. E. Markland, and D. R. Reichman, Phys. Rev. Lett. **108**, 225506 (2012).

[7] J. Russo and H. Tanaka, Proc. Nat'l Acad. Sci. USA **112**, 6920 (2015).

[8] I. Tah, S. Sengupta, S. Sastry, C. Dasgupta, and S. Karmakar, arXiv:1705.09532 (2017).

[9] S. Karmakar, E. Lerner, and I. Procaccia, Physica A: Statistical Mechanics and its Applications **391**, 1001 (2012).

[10] G. Biroli, S. Karmakar, and I. Procaccia, Phys. Rev. Lett. **111**, 165701 (2013).

[11] R. Gutiérrez, S. Karmakar, Y. Pollack, and I. Procaccia, Europhys. Lett. **111**, 56009 (2015).

[12] S. Karmakar, C. Dasgupta, and S. Sastry, Proc. Natl. Acad. Sci (USA). **106**, 3675 (2009).

[13] S. Karmakar, C. Dasgupta, and S. Sastry, Rep. Prog. Phys. **79**, 016601 (2016).

[14] S. Karmakar, C. Dasgupta, and S. Sastry, Annu. Rev. Condens. Matter Phys. **5**, 255 (2014).

[15] K. Kim, S. Saito, K. Miyazaki, G. Biroli, and D. R. Reichman, J. Phys. Chem. B **117**, 13259 (2013).

[16] C. P. Dettmann, Commun. Theor. Phys. **62**, 521 (2014).

[17] H. Tanaka, Eur. Phys. J. E. **35**, 113 (2012).

[18] H. Tanaka, T. Kawasaki, H. Shintani, and K. Watanabe, Nature Mater. **9**, 324 (2010).