An alternative approach to study the heterogeneous dynamics and its consequent dynamic correlation length that emerges in a glass-former.

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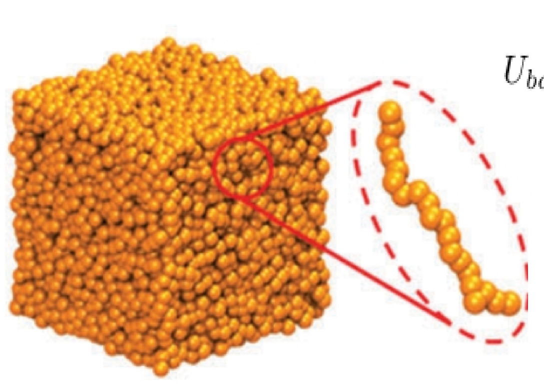
INTRODUCTION

Dynamic slowdown of glass-former liquids, leading to a breakdown of Arrhenius behavior of relaxation and Stokes-Einstein relationship (SER), as the glass transition is approached, is still not fully understood despite decades of study. These are usually associated to the emergence of *dynamic heterogeneity* (DH). Nevertheless, the physical origin of the DH, and in particular, the question whether they have a structural origin or they are a purely dynamical phenomenon, is still under debate [1].

In this work, the relationship between non-Arrhenius behavior, breakdown of SER and DH was analyzed, by means of Molecular Dynamic simulations of a supercooled polymeric glass-former. Our results reinforce the idea that both effects are associated to dynamic heterogeneity related to structural effects. Also, the structural and dynamic correlation lengths that emerge in the system were quantified. The results lead to a consensus of similar scaling of structural and dynamical length scales, reinforcing the idea of the theories of Adam-Gibbs and Random First Order Transition.

METHODS

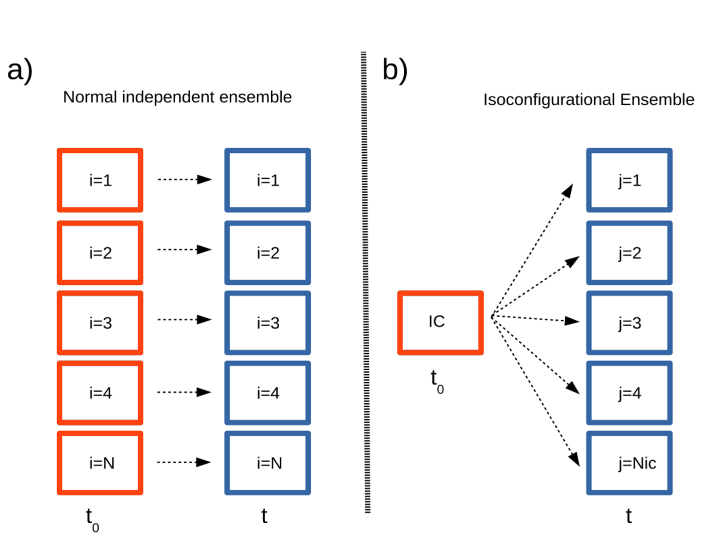
The attractive Kremer-Grest linear polymer model [2]



$$U_{bond}(r_{ij}) = -15R_0^2 \ln\left[1-(r_{ij}/R_0)^2\right]$$

$$U(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

- 30 Monomers per chain
- Periodic Boundary Conditions
- LAMMPS Software
- NVE ensemble for production runs
- Isoconfigurational Ensemble (ICE)[3]:



References & Acknowledgments

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[6] C. Balbuena and E.R. Soulé, JPCM, undereview.
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RESULTS

DYNAMICS

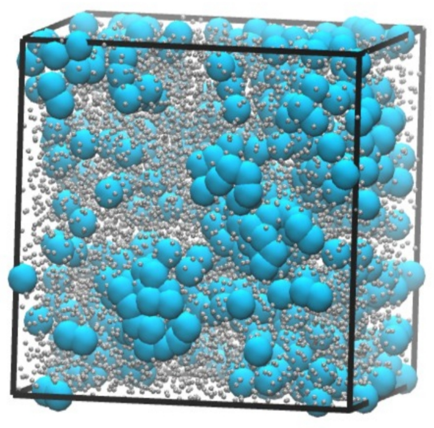
DYNAMIC HETEROGENEITY AND CORRELATION LENGTH

We employed the Person's coefficient in the ICE. It quantifies the dynamics correlation from the relative displacement of the particles [4]

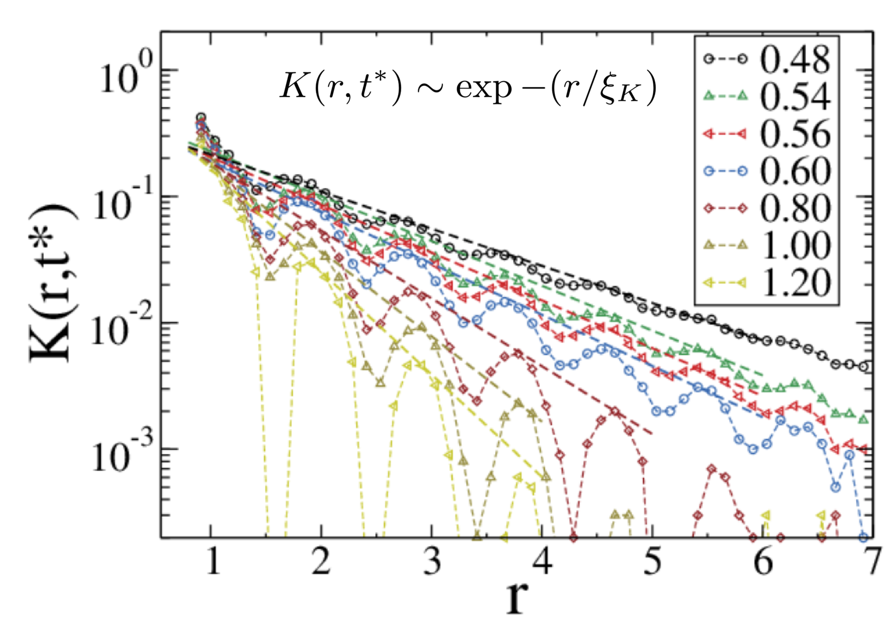
$$k^*_{ij}(r_{ij}) = \frac{1}{S_i(t^*)S_j(t^*)}\sum_{w=1}^{N_{IC}} \psi_i(w,t^*)\psi_j(w,t^*)$$

$$\psi_i(w,t^*) = |(\mathbf{r}_i(w,t^*) - \mathbf{r}_i(0)| - \langle \Delta r_i(t^*)\rangle_{IC}$$

$$K(r,t^*) = \frac{\sum_{ij}^{N} k^*_{ij}(r_{ij})\delta(r-r_{ij})}{\sum_{ij}^{N}\delta(r-r_{ij})}$$



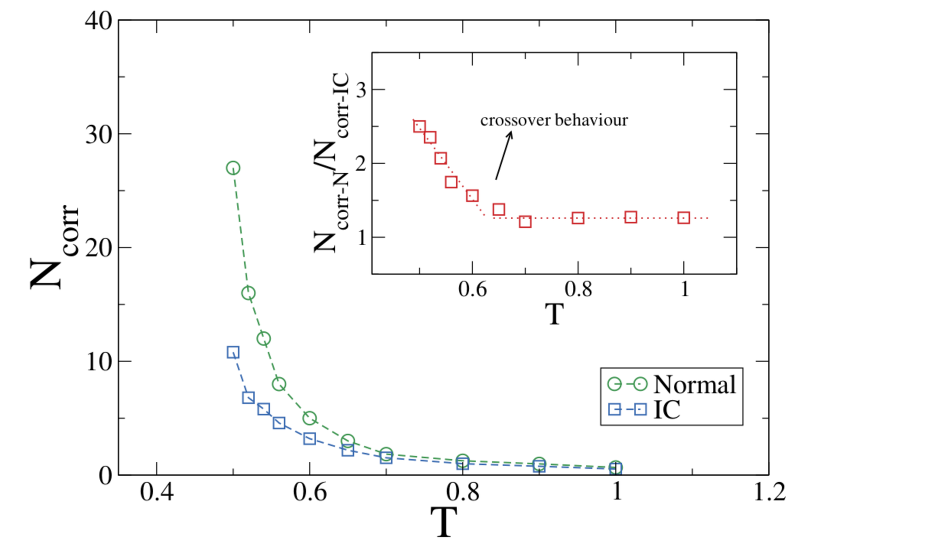
Cluster of particles with high correlation



NUMBER OF CORRELATED PARTICLES

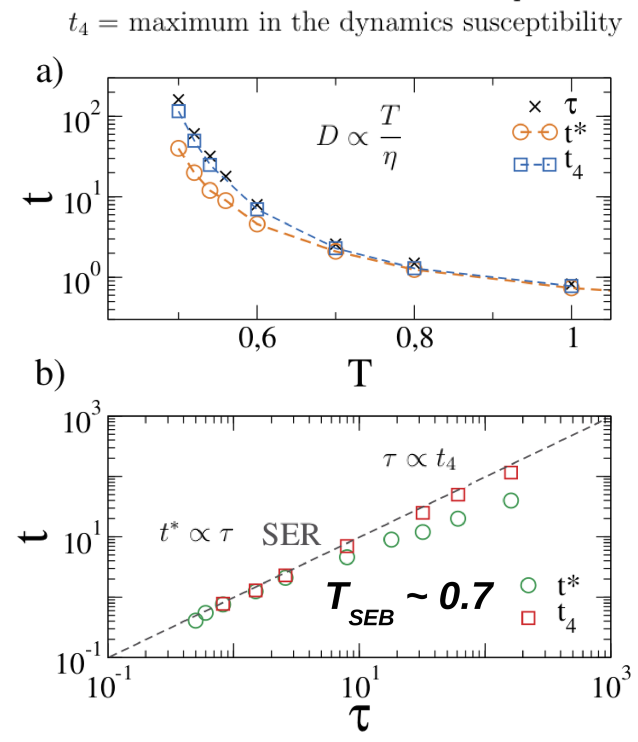
The N_{corr} from the behavior of dynamics susceptibility was calculated.

$$\chi_4 = \frac{\beta V}{N^2}[< Q(t)^2 > - < Q(t) >^2] \longrightarrow N_{corr} = \max_t\{\chi_4(t)\} = \chi_4(t_4)$$

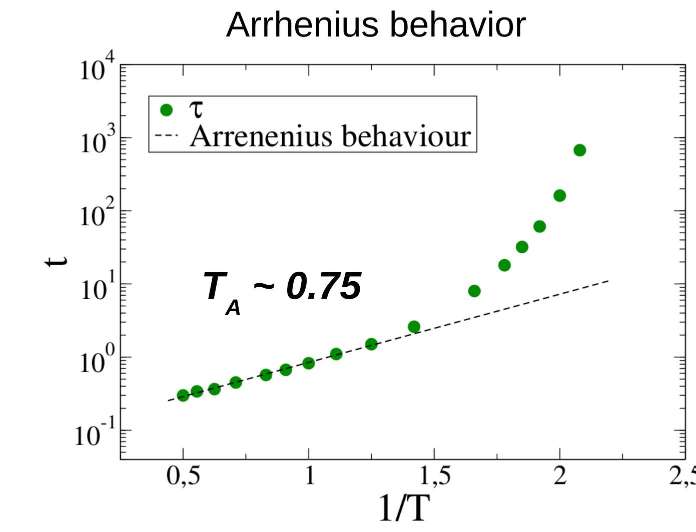


BREAKDOWN OF STOKES-EINSTEIN RELATIONSHIP

t^* = maximum in the non-Gaussian parameter
t_4 = maximum in the dynamics susceptibility



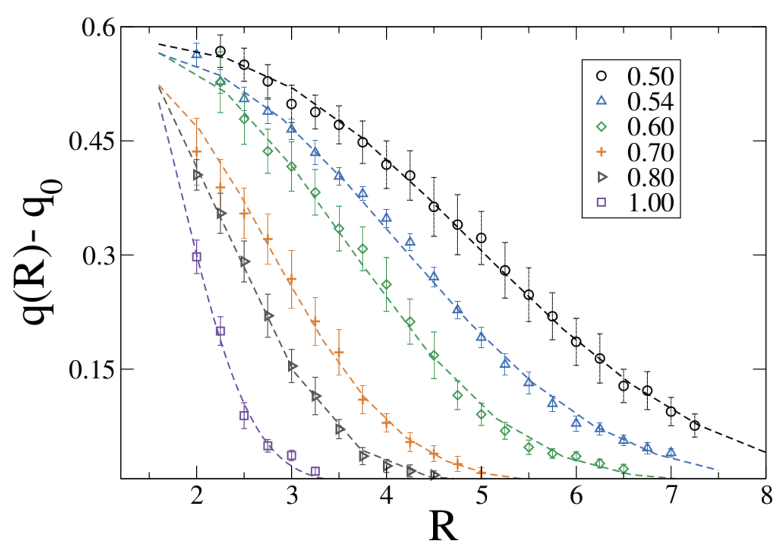
T_A ~ change from Arrhenius to super-Arrhenius behavior



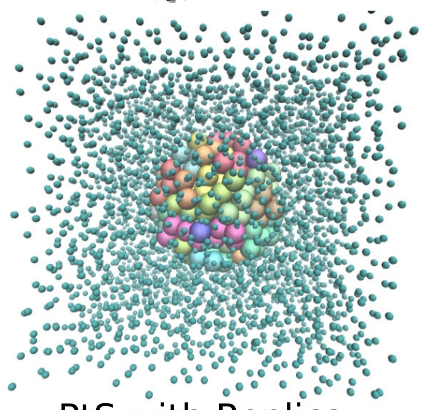
STRUCTURE

POINT-TO-SET CORRELATIONS LENGTHS

$$q_c(r) - q_0 = \Omega \exp[-((R-a)/\xi_{PtS})^{\zeta}]$$



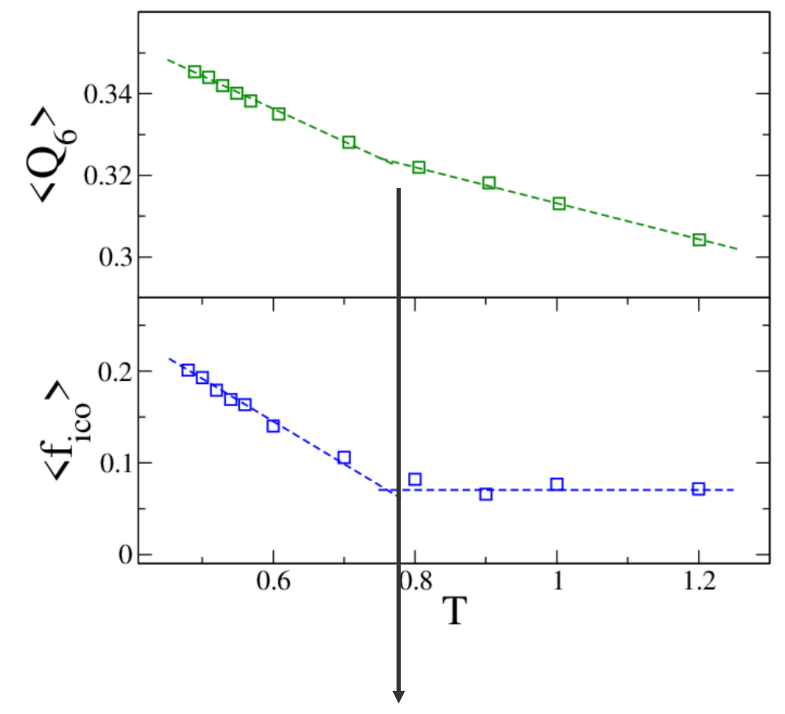
$$q_c(R) = \frac{1}{l^3 N_b}\sum_{i\in v}\langle n_i(t_0)n_i(t_0+\infty)\rangle$$



PtS with Replica Exchange method [5]

SPECIFIC STRUCTURAL PARAMETERS

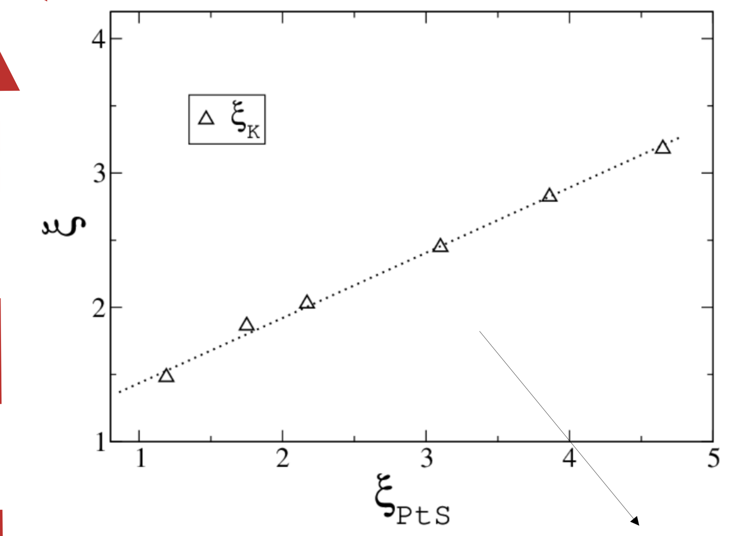
Bond Orientational Order (Q_6) and Icosahedral fraction (f_{ico}) for the Inherent configurations [7]



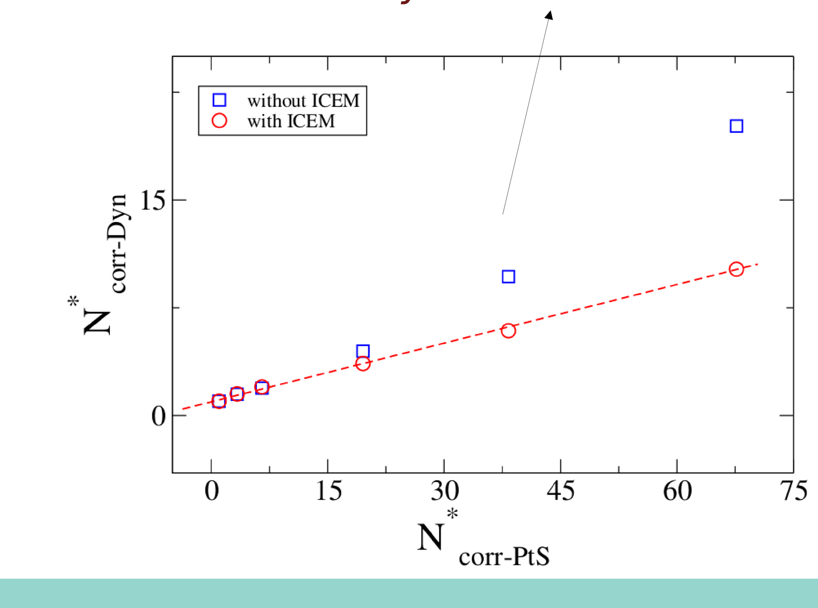
Crossover temperature in the region where the SEB and the non-Arrhenius behavior are observed

STRUCTURE

DYNAMICS



When the IC is considered in the dynamic properties, a linear relationship is obtained for the structure and the dynamic behavior!!



CONCLUSION

We show that the dynamic behavior in this glass-former can be interpreted through structural behavior. We also highlight that the alternative way of defining dynamic lengths through the ICE, can be useful to shed light in the apparent discrepancies between structural and dynamical length scales in supercooled liquids.