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Strong geometric frustration in model glassformers

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ABSTRACT

We consider three popular model glassformers, the Kob–Andersen and Wahnström binary Lennard–Jones models and weakly polydisperse hard spheres. Although these systems exhibit a range of fragilities, all feature a rather similar behaviour in their local structure approaching dynamic arrest. In particular we use the dynamic topological cluster classification to extract a locally favoured structure which is particular to each system. These structures form percolating networks, however in all cases there is a strong decoupling between structural and dynamic lengthscales. We suggest that the lack of growth of the structural lengthscale may be related to strong geometric frustration.

1. Introduction

Among the challenges of the glass transition is how solidity emerges with little apparent change in structure [1,2]. However, using computer simulation and with the advent of particle-resolved studies in colloid experiments [3], it has become possible to construct and use higher-order correlation functions [4–7]. These can directly identify local geometric motifs in supercooled liquids, long-since thought to suppress crystalisation in glassforming systems [8]. Other indirect approaches include the use of reverse Monte Carlo techniques to extract higher-order information from two-point correlation functions [9] which is used in metallic glassformers for example [10].

Such measurements have correlated the occurrence of geometric motifs and slow dynamics in a number of glassformers in both particle-resolved experiments on colloids [11–13] and simulation [14–18]. Identification of these motifs has led to the tantalising prospect of finding a structural mechanism for dynamic arrest. It has been demonstrated that at sufficient supercooling, there should be a coincidence in structural and dynamic lengths, associated with regions undergoing relaxation for fragile glassformers [19]. Thus recent years have seen a considerable effort devoted to identifying dynamic and structural lengthscales in a range of glassformers. The jury remains out concerning the coincidence of structural and dynamic lengthscales, with some investigations finding agreement between dynamic and structural lengthscales in experiment [20] and simulation [21–28], while others find that while the dynamic lengthscale increases quite strongly, structural correlation lengths grow weakly [29–37]. Other interpretations include decomposing the system into geometric motifs and considering the motif system. One such effective system exhibits no glass transition at finite temperature [38].

Here we consider the approach of geometric frustration [39]. Geometric frustration posits that upon cooling, a liquid will exhibit an increasing number of locally favoured structures (LFS), which minimise the local free energy. In some unfrustrated curved space, these LFS tessellate, and there is a phase transition to an LFS-phase. In Euclidean space, frustration limits the growth of the LFS domains. As detailed in Section 2, the free energy associated with the growth of these LFS domains may be related to an addition term to classical nucleation theory (CNT), as illustrated schematically in Fig. 1.

Now in 2d monodisperse hard discs, the locally favoured structure (hexagonal order) is commensurate with the crystal. The transition is weakly first order to a hexatic phase which exhibits a continuous transition with the 2d crystal [40,41]. Thus in 2d one must curve space to introduce geometric frustration. This has been carried out by Sausset et al. [42], curving in hyperbolic space, where the degree of curvature can be continuously varied. Weakly curved systems have a strong tendency to hexagonal ordering, which was controllably frustrated by the curvature. However, the upper bound on all correlation lengths was dictated by the curvature in this system. In other words, frustration is encoded into the system through the curved space, suppressing any divergent structural lengthscales. However structural lengthscales were observed to grow up to the limit set by the curved space [25,43].

In 3d, 600 perfect (strain-free) tetrahedra formed from 120 particles can be embedded on the surface of a four-dimensional sphere [44,45]. Each particle in this 4d Platonic solid or "polytope" is at the centre of a 12-particle icosahedrally coordinated shell, and indeed simulations indicate a continuous transition in this system [46–48]. However, a 120 particle system is clearly inappropriate to any investigation of increasing lengthscales.

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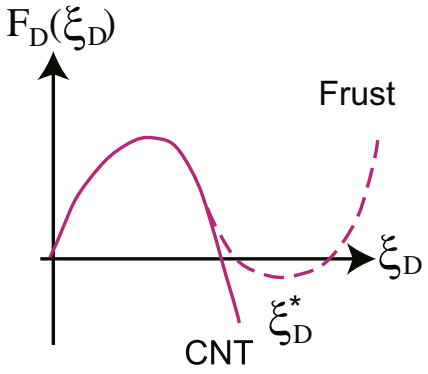

Fig. 1. Schematic of geometric frustration limiting the growth of domains of locally favoured structures. Solid line is conventional CNT with the first two terms in Eq. (1) which would occur in the non-frustrated case. Dashed line denotes the effect of the third term which incorporates frustration, leading to a preferred lengthscale for the LFD domain ξ_D^*.

Here we focus on geometric frustration in 3d Euclidean space. We carry out simulations on a number of well-known glassformers of varying degrees of fragility: polydisperse hard spheres, and the Kob–Andersen [49] and Wahnström binary Lennard–Jones mixtures [50]. In each system we identify a system-specific locally favoured structure [7], which becomes more prevalent as the glass transition is approached. We measure the dynamic correlation length ξ_4 and identify a structural correlation length $\xi_{\rm LFS}$ [36,37]. We show that the dynamic correlation length grows much more than the structural correlation length associated with the LFS in each system. The LFS do not tile 3d space, but instead form system spanning networks. We conclude that the growth of LFS in all these cases is strongly frustrated. Given the system specific nature of the LFS, we speculate that an LFS-phase might not in principle require curved space and we suggest that geometric frustration might be considered not as a function of curvature but as composition.

This paper is organised as follows. In Section 2 we briefly consider some pertinent aspects of geometric frustration theory, followed by a description of our simulations in Section 3. The results consist of a connection between the fragility of the systems studied placed in the context of some molecular glassformers in Section 4.1. In Section 4.2 we detail how the locally favoured structures are identified and discuss the increase in LFS in Section 4.3. In Section 4.4 we show structural and dynamic correlation lengths, before discussing our findings in Section 5 and concluding in Section 5.

2. Geometric frustration

For a review of geometric frustration, the reader is directed to Tarjus et al. [39]. The effects of frustration upon a growing domain of locally favoured structures may be considered as defects, which typically interact in a Coulombic fashion. Under the assumption that frustration is *weak*, this argument leads to scaling relations for the growth of domains of LFS, whose (linear) size we denote as ξ_D. Weak frustration requires that its effects only become apparent on lengthscales larger than the constituent particle size such that $\sigma << \xi_D$. Geometric frustration imagines an avoided critical point, at T_x^c, which corresponds to the phase transition to an LFS state in the unfrustrated system. At temperatures below this point, growth of domains of the LFS in the frustrated system may follow a classical nucleation theory (CNT) like behaviour, with an additional term to account for the frustration. In $d = 3$ the free energy of formation of a domain size ξ_D of locally favoured structures thus reads

$$F_D(\xi_D, T) = \gamma(T)\xi_D^\theta - \delta\mu(T)\xi_D^3 + s_{\rm frust}(T)\xi_D^5 \quad (1)$$

where the first two terms express the tendency of growing locally preferred order and they represent, respectively, the energy cost of having an interface between two phases and a bulk free-energy gain inside the domain. Eq. (1) is shown schematically in Fig. 1. The value of θ may be related to the Adam–Gibbs theory [51] or Random First Order Transition theory (RFOT) [52]. Without the third term, long-range order sets in $T = T_x^c$, in the unfrustrated system. Geometric frustration is encoded in the third term which represents the strain free energy resulting from the frustration. This last term is responsible for the fact that the transition is avoided and vanishes in the limit of non-zero frustration [39]. While actually evaluating the coefficients in Eq. (1) is a very challenging undertaking, one can at least make the following qualitative observation. In the case of weak frustration, one expects extended domains of LFS. However, in the case of strong frustration, one imagines rather smaller domains of LFS, as the third term in Eq. (1) will tend to dominate.

3. Simulation details

Our hard sphere simulations use the DynamO package [53]. This performs event-driven MD simulations, which we equilibrate for 300 τ_α, in the NVT ensemble, before sampling in the NVE ensemble. We use two system sizes of $N = 1372$ and $N = 10976$ particles, in a five-component equimolar mixture whose diameters are $[0.888\sigma, 0.95733\sigma, \sigma, 1.04267\sigma, 1.112\sigma]$, which corresponds to a polydispersity of 8%. Here σ is a diameter which we take as the unit of length. We have never observed crystallisation in this system. Given the moderate polydispersity, we do not distinguish between the different species. We use smaller systems of $N = 1372$ to determine the structural relaxation time and the fraction of particles in locally favoured structures. Static and dynamic lengths are calculated for larger systems of $N = 10976$. Further details may be found in Ref. [54].

We also consider the Wahnström [50] and Kob–Andersen [49] models in which the two species of Lennard–Jones particles interact with a pair-wise potential,

$$u_{\rm LJ}(r) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{6}\right] \quad (2)$$

where α and β denote the atom types A and B, and r_{ij} is the separation. In the equimolar Wahnström mixture, the energy, length and mass values are $\varepsilon_{AA} = \epsilon_{AB} = \varepsilon_{BB}$, $\sigma_{BB}/a_{AA} = 5/6$, $\sigma_{AB}/\sigma_{AA} = 11/12$ and $m_A = 2m_B$ respectively. The simulations are carried out at a number density of $\rho = 1.296$. The Kob–Andersen binary mixture is composed of 80% large (A) and 20% small (B) particles possessing the same mass m [49]. The nonadditive Lennard–Jones interactions between each species, and the cross interaction, are given by $\sigma_{\rm AA} = \sigma$, $\sigma_{\rm AB} = 0.8\sigma$, $\sigma_{\rm BB} = 0.88\sigma$, $\epsilon_{\rm AA} = \epsilon$, $\epsilon_{\rm AB} = 1.5\epsilon$, and $\epsilon_{\rm BB} = 0.5\epsilon$ and is simulated at $\rho = 1.2$. For both Lennard–Jones mixtures, we simulate a system of $N = 10976$ particles for an equilibration period of $300\tau_\alpha^A$ in the NVT ensemble and sample for a further $300\tau_\alpha^A$ in the NVE ensemble. The results are quoted in reduced units with respect to the A particles, *i.e.* we measure length in units of σ, energy in units of ϵ, time in units of $\sqrt{m\sigma^2/\epsilon}$, and set Boltzmann's constant $k_{\rm B}$ to unity. Further details of the simulation of the Wahnström and Kob-Andersen models may be found in [36,37] respectively.

The α-relaxation time τ_α^A for each state point is defined by fitting the Kohlrausch–Williams–Watts stretched exponential to the alpha-regime of the intermediate scattering function (ISF) of the A-type particles in the case of the Lennard–Jones mixtures and of all particles in the case of the hard spheres.

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