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Link to published version (if available):
10.1103/PhysRevLett.118.215501

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From glass formation to icosahedral ordering by curving three-dimensional space

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Geometric frustration describes the inability of a local molecular arrangement, such as icosahedra found in metallic glasses and in model atomic glass-formers, to tile space. Local icosahedral order however is strongly frustrated in Euclidean space, which obscures any causal relationship with the observed dynamical slowdown. Here we relieve frustration in a model glass-forming liquid by curving 3-dimensional space onto the surface of a 4-dimensional hypersphere. For sufficient curvature, frustration vanishes and the liquid freezes in a fully icosahedral structure via a sharp 'transition'. Frustration increases upon reducing the curvature, and the transition to the icosahedral state smoothens while glassy dynamics emerges. Decreasing the curvature leads to decoupling between dynamical and structural length scales and the decrease of kinetic fragility. This sheds light on the observed glass-forming behavior in the Euclidean space.

The very large increase in viscosity found in glass-forming liquids upon cooling or compression without significant change in structure remains a major outstanding challenge in condensed-matter physics. Among the key questions is whether vitrification is linked to an underlying thermodynamic phase transition or whether the process is predominantly dynamical [1]. The well-established phenomenon of dynamical heterogeneities, in the form of "liquid-like" fast-moving and "solid-like" slow-moving regions whose lifetime and size increase upon supercooling [2, 3], has been interpreted in favor of an underlying dynamical transition [4]. Although arguments have been put forward to tie slowdown of relaxation and growth of a static length [5], a strong piece of evidence for a structural or thermodynamic mechanism would be the identification of static length scales that grow signifcantly when approaching the glass transition, at a pace that follows that of the "dynamical" length scales [6].

In order to define a relevant static length, one needs to identify a change in the amorphous structure. Different types of static lengths have been proposed, as those related to the growth of some generic amorphous order resulting from the rarefaction of available metastable states as temperature decreases and captured by point-to-set correlations [5, 7–11]. Another suggestion for a subtle change in structure in a supercooled liquid is that the atoms or molecules organize into locally preferred structures, *i.e.*, local geometric motifs. For many 3-dimensional (3-d) systems of spherical particles, the constituents arrange into five-fold symmetric motifs, such as icosahedra [12–17]. These do not tile 3-d Euclidean space periodically and may then suppress crystallization. This idea has been further developed in the framework of geometric frustration [18–20]. For single-component systems of spheres, it has been theoretically shown [18, 21] and observed in simulations [22] that 120 particles on the surface of a 4-d hypersphere, the "3-sphere" S^3, of a specific curvature (in units of the particle radius) can realize a perfect tiling of space with every particle at the center of an icosahedron: the so-called $\{3, 3, 5\}$ polytope. Flattening space then induces frustration [23, 24]. However, at the end of the flattening process, in Euclidean space, frustration is strong and the growth of icosahedral order is strongly suppressed [16, 25–28]. In particular, at the degree of supercooling accessible to computer simulations (and colloid experiments), *i.e.*, the first 4-5 decades of increase of the structural relaxation time τ_α relative to the normal liquid, rather limited domain sizes of icosahedral regions are found and the associated length scales remain small [14, 17, 27, 28]. Furthermore, these structural lengths are significantly smaller than the dynamical lengths associated with the growingly heterogeneous character of the dynamics [16, 17, 25–27]. Despite many claims or suggestions [14, 17, 19, 29, 30], this calls into question whether such structures can be the main cause of dynamic arrest. At the very least, it is fair to state that the description of the mechanism by which frustrated icosahedral order influences slow dynamics remains an unresolved problem. To make progress on this issue, we curve 3-d space to relieve frustration and we use curvature as an additional control parameter to investigate equilibrium glass-forming liquids. This can only be achieved in computer simulations and we present here the first study of this kind for a 3-d system (for a discussion of the 2-d case [31, 32], see below).

We consider a model glass-forming liquid, the Wahnström model, which is a Lennard-Jones binary mixture with size ratio $\sigma_A/\sigma_B = 6/5$ and which is known to dis-
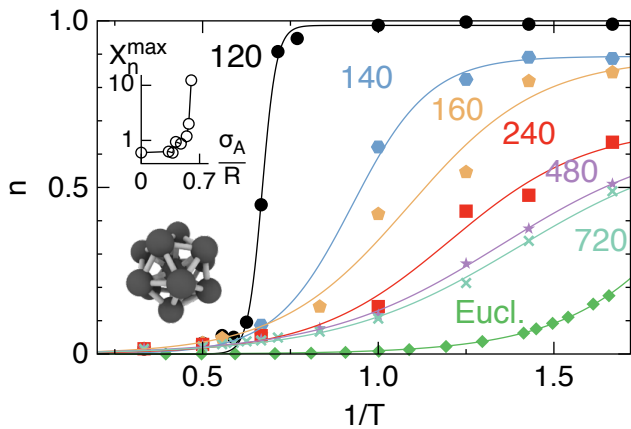
FIG. 1. Concentration n of particles found in domains of icosahedra (see ball-and-stick model) as a function of the inverse of the reduced temperature T for several curvatures characterized by the system size N (see Eq.1). The lines are hyperbolic-tangent fits, from which the maximum of the derivative $\chi_n = dn/dT$ can be estimated: see the case $N = 120$ in the inset.

play a significant correlation between slow dynamics and the formation of local icosahedral motifs in Euclidean space [14, 17, 33–36].

We perform Monte Carlo (MC) simulations of $N \in [120, 720]$ particles on the 3-sphere S^3, with a modified Marsaglia method [37, 38] in order to isotropically sample the surface of the 4-d hypersphere. The results in curved space are complemented with molecular dynamics (MD) results in Euclidean space [39]. We fix the reduced density

$$\tilde{\rho} = \frac{N}{V(R)} \frac{V_{\text{cap}}(R, \sigma_A) + V_{\text{cap}}(R, \sigma_B)}{E(\sigma_A) + E(\sigma_B)} = 1.296 \sigma_A^{-3}, \quad (1)$$

where N is the total number of particles, V(R) the (hyper)area of the 3-sphere, $V_{\text{cap}}(R, \sigma)$ is the (hyper)area of a spherical cap of height $h = R(1 - \cos \sigma/2R)$ and $E(\sigma)$ the Euclidean volume of a particle of diameter σ. At fixed density the number of particles N and the radius of curvature R are therefore coupled: the range $N = 120 - 720$ corresponds to $R \approx 1.666 - 3.037 \sigma_A$. In the limit $R \to \infty$, one recovers the usual expression $\tilde{\rho} \to N/V$ (see the Supplementary Material (SM) for more details [40]).

We first investigate the effect of the curvature on the structure of the system. To do so, we compute the pair correlation function $g(r)$ with r the geodesic distance on the 3-sphere. Its first minimum provides a suitable cutoff length which is used, together with the Delaunay triangulation obtained from the convex hull of the particle coordinates, to get the network of nearest neighbors (see SM for more details). This then allows for the detection of icosahedral order throughout the system via a modified topological cluster classification [41].

We find that for $N = 120$ the bidisperse Wahnström

model abruptly freezes in an ordered icosahedral structure (the $\{3, 3, 5\}$ polytope [21]) as the temperature T is lowered, just like a monodisperse system of spherical particles [18, 22]. This is illustrated in Fig. 1 where we plot the concentration n of particles detected in icosahedral domains as a function of $1/T$ for various curvatures characterized by the total number of particles N. For $N = 120$ a sharp crossover, which is the finite-size version of a first-order transition, from an icosahedra-poor liquid to an icosahedral structure is observed (see also the inset of Fig. 1). Frustration is thus relieved by curvature and the concentration fluctuations due to the bidispersity have no significant influence at this curvature.

As curvature decreases (and N and R increase), the crossover smoothens: the growth of icosahedral order becomes more gradual while the maximum concentration of icosahedra saturates at lower values, which is a sign of increasing frustration. The temperature range over which the change takes place broadens and shifts to lower temperatures. The Euclidean case is the end point of this continuous variation with curvature.

To describe the slowing down of the dynamics while avoiding the complexity brought by curvature and the parallel transport along geodesics we consider a simple time-dependent correlation function derived from the definition of the neighborhood:

$$C(t) = \left\langle \frac{1}{N} \sum_{i=1}^{N} \frac{\vec{v}_i(t_0 + t) \cdot \vec{v}_i(t_0)}{\vec{v}_i^2(t_0)} \right\rangle_{t_0}, \quad (2)$$

where $\vec{v}_i(t)$ is the indicator vector of length N identifying the nearest neighbors of particle i at time t. The function $C(t)$ corresponds to the average fraction of neighbors that has not changed between time t_0 and time t. While being independent of the local curvature of the space, it provides a measure of the slow (α) relaxation. Through a stretched-exponential fit to $C(t) - C(\infty)$ (see SM) we obtain an estimate of the structural relaxation time τ. In the case of the two larger curvatures, $N = 120$ and 140, the crossover is so sharp that the relaxation time jumps from a finite value to an exceedingly large one in the icosahedral state, which then behaves as a solid for our purposes. This is much like the dynamical behavior at a first-order transition, albeit here in a finite-size system: the relaxation time does not truly diverge but is too large to be accessible in a computer simulation. In contrast for $N = 160$ and furthermore, the crossover is smooth enough that we can access the relaxation time even when the growth of icosahedral order has saturated and we then see no sign of divergence.

The results for the relaxation time are shown in Fig. 2 (a). For $T \gtrsim 2$ curvature has little or no influence on the relaxation (see also the SM). But this is no longer true at lower temperature. While the two largest curvatures exhibit an abrupt freezing to a solid icosahedral phase, the transition appears to be avoided for weaker curvatures
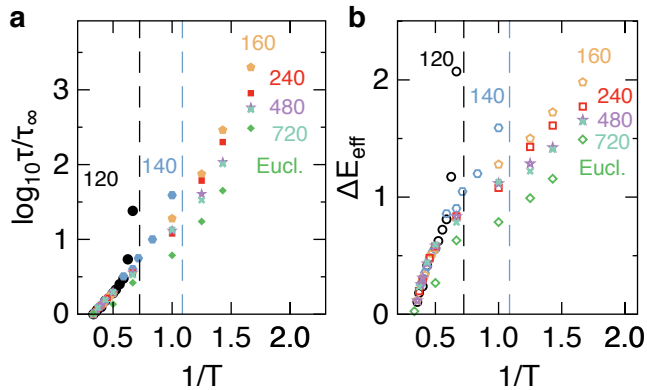
FIG. 2. (a) Logarithm of the relaxation time (a) and Effective activation energy $\Delta E_{\text{eff}} = T \log \tau/\tau_\infty$ (b) versus $1/T$ for several curvatures. The vertical dashed lines approximately indicate the temperatures at which the $N = 120$ and $N = 140$ systems freeze into a solid icosahedral phase.
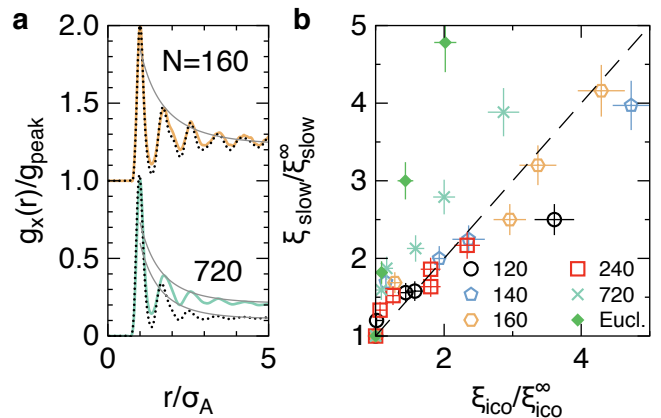

FIG. 3. (a) Radial distribution functions $g_{\text{slow}}(r; \tau)$ (continuous) and $g_{\text{icos}}(r)$ (dotted) for $N = 160, 720$ and $T = 0.8$. (b) Rescaled dynamic length versus the rescaled structural length for different curvatures, down to the Euclidean limit.

and a continuous increase of the relaxation time is found over the accessible range, as in the Euclidean space.

In order to assess the change with curvature of the kinetic fragility, *i.e.*, the degree of super-Arrhenius temperature dependence of the relaxation time, we consider the effective activation energy $\Delta E_{\text{eff}} = T \log(\tau/\tau_\infty)$ where τ_∞ is the relaxation time at high T_*: it is shown in Fig. 2 (b). The two curvatures where freezing takes place behave very differently from the others. For $N \geq 160$ to the Euclidean limit, ΔE_{eff} is found to increase continuously with increasing $1/T$, which is the signature of a super-Arrhenius, fragile, behavior. The differences between the curvatures are not dramatic but there is a clear trend toward a monotonic decrease of fragility as curvature decreases. Since the high-T behavior is independent of curvature, this can be seen unambiguously and without data-fitting by comparing the effective activation energies (or the relaxation times) at low T (see Fig. Fig. 2): The kinetic fragility decreases as the curvature decreases (and at the same time frustration increases, consistently with previous work [42, 43]).

As mentioned above, the emergence of slow dynamics in glass-forming systems is often attributed to the growth of spatial correlations in the dynamics and the statics [6]. The former manifest themselves as dynamical heterogeneities [2]; the latter are found through investigations of point-to-set correlations or through some characterization of the growth of the local order [6, 28]. As also already stressed, for most glass-formers studied by computer simulations, including the Wahnström mixture, one finds a rapid increase for the dynamical lengths but a modest increase of the static lengths [17, 25, 44]. One is of course limited by the range accessible to computer simulations, so that it is hard to attain the deeply supercooled regime near the glass transition. In addition, it is hard to conclude on the origin of the observed de-

coupling. We cannot improve the accessible range but by adding a new control parameter, the curvature, we can shed more light on this decoupling.

In order to explore dynamic correlations, we focus on low-mobility (slow) particles, following [45]. To do so, we define a neighbor-dependent mobility and use a thresholded persistence function of the indicator neighbor vectors v_i in order to identify the slow particles. The number of slow particles is then defined as

$$N_{\text{slow}}(t) = \left\langle \sum_{i=1}^{N} \Theta[\vec{v}_i(t_0 + t) \cdot \vec{v}_i(t_0) - \tilde{N}] \right\rangle_{t_0} \quad (3)$$

where $\Theta(x)$ is the Heaviside function and $\tilde{N}$ the minimum number of neighbors of a particle that must not change for this particle to be taken as slow: we chose $\tilde{N} = 8$ but we checked that the results are not very sensitive to the choice of this particular threshold ($5 \leq \tilde{N} \leq 10$). We can then study the average of the number of slow particles during time t and the fluctuations, characterized by the susceptibility $\chi(t) = (1/N)(\langle N_{\text{slow}}^2(t) \rangle - \langle N_{\text{slow}}(t) \rangle^2)$.

To extract a dynamic length, we work in real space [46]: we compute the radial distribution function restricted to the particles that are slow at $t = \tau$, $g_{\text{slow}}(r; \tau)$. From it we estimate a typical correlation length via an exponential fit, $g_{\text{slow}}(r; \tau) \sim \exp[-r/\xi_{\text{slow}}(\tau)]/r + c$, where c is a long-range normalization constant depending on the finite-size limitations of our systems: see Fig.3 (a) and the SM. The resulting length, after a rescaling by its high-temperature value, is shown in Fig. 3 (b) for several curvatures. It grows as T decreases, which indicates increasing spatial correlations in the dynamics and bigger dynamical heterogeneities, and does so more slowly as curvature is reduced, down to the Euclidean case (with again a markedly different behavior for $N = 120, 140$).

We find a qualitatively similar behavior for the peak value χ^{max} of the dynamic susceptibility $\chi(t)$, which occurs for $t \approx \tau$ as generically found in glass-formers and can loosely be taken as a relative measure of the number of dynamically correlated particles [47]: see the SM.

To obtain a structural length scale, we use a similar approach to that for the dynamic one, except that we consider only particles in icosahedra: we compute the corresponding restricted radial distribution function $g_{\mathrm{icos}}(r)$ and extract ξ_{icos} through an exponential fit (see Fig. 3 (a) and the SM). The same comment as before is in order for $N = 120, 140$ and one finds a reduction of both the extent and the rate (with decreasing temperature) of the growth of icosahedral correlations as curvature decreases and frustration increases. This is in line with the results shown in Fig. 1.

The dynamic and structural lengths are compared in Fig. 3 (c), once rescaled to their high-temperature value. One observes a clear trend with increasing curvature (*i.e.*, decreasing N): while a significant decoupling is found in the Euclidean space, this decoupling decreases and appears to vanish for $N = 240$ and less. When the icosahedral order becomes less frustrated, dynamical and structural lengths go hand in hand as the relaxation slows down. The growth of the local order then seems to fully determine the properties of the dynamics. On the other hand, as frustration increases, this one-to-one correspondence is blurred and other mechanisms, possibly related to the mean-field description of glass-forming liquids [48, 49], must be considered in addition. Note that we do not expect the decoupling to be a mere effect of the finite size of the curved systems. It has indeed been shown (in Euclidean space) that in the range accessible to dynamical simulations the dynamics of 3-d glass-formers is not very sensitive to size effects [50, 51], quite contrary to 2-d systems [52, 53].

To summarize: We have studied the structure and the dynamics of a supercooled liquid in curved 3-d space, using curvature as a way to tune the degree of frustration of the local order. Through this additional control parameter we shed light on the otherwise limited information one has on the role of local order in glass formation, more specifically on the role of icosahedral order in 3-d systems such as the Wahnström model. Evidence for some correlation between the slowing down of relaxation and the growth of icosahedral order in this model has been reported [14, 17, 36], but it is hard to get an in-depth picture considering the limited range that is accessible to simulations and the strong frustration. Starting from The Euclidean limit and curving space, we find a continuous evolution with an increase of the extent and of the influence of the local icosahedral order on the physics of the liquid under cooling, including an increase of the kinetic fragility, until one encounters a low enough frustration that allows freezing in an ordered icosahedral structure and thereby prevents glass formation.

Interestingly, the increase of frustration with decreasing curvature is accompanied by the decoupling of the temperature evolution of the dynamical and structural lengths. This suggests that while the collective behavior of the system is controlled by the growth of the icosahedral order and the proximity to an underlying (avoided) ordering transition for sufficiently weak frustration, the slowing down is no longer uniquely dominated by the local order when frustration increases: the observed decoupling appears as a signal that other mechanisms come into play. The behavior found in the Euclidean space is the end point of this process with only remnants of the role of icosahedral ordering.

Finally, we contrast the situations in $d = 2$ and $d = 3$. The change of behavior with curvature observed in the present study is profoundly different from that found in 2-d systems of spherical particles, where 6-fold local bond-orientational order is prevalent. In the latter case, the ordering transition in the absence of frustration (which in 2-d means in the Euclidean plane) is continuous or weakly first-order [54, 55]. In 3-d, the transition appears strongly first-order and is accordingly characterized not by the continuous divergence of the relaxation time or the correlation length but by jumps from finite to infinite values in these quantities. (These jumps are moreover rounded by the intrinsic finite size of the systems.) By curving 2-d space [31, 32, 43, 56] one then encounters an *avoided continuous transition* near which the correlation length can be very large. Here instead, by flattening 3-d space, we see the effect of an *avoided first-order transition*, with a broadened crossover and limited correlation lengths. The collective behavior generated by the proximity of an avoided ordering transition is more prominent in 2-d than in 3-d, which may explain why the decoupling phenomenon between the dynamical and the static lengths appears to be absent in many 2-d liquids [42, 56, 57] and why finite-size effects are more dramatic in 2-d than in 3-d glass-formers [52]. On top of this, the influence of growing structural correlations on the relaxation slowdown may also be different: in 2-d, the defects in the local 6-fold order are point-like while in 3-d icosahedral order one expects defect lines, whose dynamics may then be strongly constrained [24]. This deserves further investigation.

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