Geometric Approach to the Dynamic Glass Transition

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We numerically study the potential energy landscape of a fragile glassy system and find that the dynamic crossover corresponding to the glass transition is actually the effect of an underlying geometric transition caused by the vanishing of the instability index of saddle points of the potential energy. Furthermore, we show that the potential energy barriers connecting local glassy minima increase with decreasing energy of the minima, and we relate this behavior to the fragility of the system. Finally, we analyze the real space structure of activated processes by studying the distribution of particle displacements for local minima connected by simple saddles.

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Despite a large number of investigations, there is still much to understand about the dynamic glass transition in supercooled liquids. The basic problem is that, strictly speaking, there is no dynamic transition at all. In systems known as *fragile* liquids [1], experiment finds a sharp rise of the viscosity in a very narrow interval of temperature upon cooling. The shear relaxation time increases by several orders of magnitude in a few degrees, and it becomes impossible to perform an equilibrium experiment. Nevertheless, sharp as this behavior may be, it is not a genuine dynamic singularity. At the other extreme of the experimental spectrum we find *strong* liquids [1], which experience a gentle increase of the relaxation time, often according to the Arrhenius law. Even in such systems though, when the viscosity becomes too large, equilibrium can no longer be achieved in experimental times.

The glass transition temperature T_g is conventionally defined as that where the value of the viscosity is 10^{13} P. Below T_g equilibrium experiments become really hard to perform and a sample can be considered to be in its glass phase. However, T_g is just a conventional experimental temperature, defined out of the need to mark the onset of glassy dynamics. The attempt to give a theoretical description of such an ill-defined "transition" may therefore seem pointless.

On the one hand, this conclusion is correct for the strongest liquids: here nothing peculiar happens close to T_g, and the glass transition fully displays its purely conventional nature. On the other hand, the most fragile systems resist such an objection, simply by virtue of the *extremely* steep increase of relaxation time in a small interval of temperature around T_g. This fact suggests that some kind of new physical mechanism is indeed responsible for the onset of the glassy phase in fragile supercooled liquids. We share this view, and the aim of this Letter is to shed some light on the nature of this mechanism.

The key idea is that the sharp dynamic crossover observed in fragile liquids is a consequence of an underlying topological transition, controlled by energy, rather than temperature. More precisely, the existence of an energy level where the instability index of the stationary points of the potential energy vanishes is responsible for a change in the dominant mechanism of diffusion. If energy barriers are large, this change in the mechanism of diffusion causes the fast increase of the relaxation time.

This study is part of a more general program aimed at explaining glassy dynamics in terms of properties of the potential energy landscape. Our method generalizes the ideas of Goldstein [2], and Stillinger-Weber [3], by extending to unstable stationary points the analysis formerly restricted to minima of the potential energy. The first steps in this direction have been done in [4], building on the ideas of [5,6], and more concrete results have been recently obtained in [7,8]. Further inspiration came from the approach of Keyes and co-workers [9], which related diffusion to the stability properties of instantaneous configurations. In the present work we firmly establish the connection between topological properties of the landscape and fragile glassy dynamics. Furthermore, we study the role of potential energy barriers and we analyze the real space structure of activated processes.

We consider a soft-sphere binary mixture [10], a fragile model glass former. In addition to capturing the essential features of fragile glasses [10–13], this model can be thermalized below T_g with the efficient Monte Carlo (MC) algorithm of [12]. Furthermore, previous investigations of the saddle points have focused on Lennard-Jones systems, so it is useful to look at a broader class of models. Most of our data are obtained for $N = 70$ particles, but we tested our key results for $N = 140$ as well. We impose periodic boundary conditions in $d = 3$ dimensions. Particles are of unit mass and belong to one of two species $\alpha = 1, 2$, present in equal amounts and interacting via a potential

$$\mathcal{V} = \sum_{i<j}^{N} V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) = \sum_{i<j}^{N} \left[\frac{\sigma_{\alpha(i)} + \sigma_{\alpha(j)}}{|\mathbf{r}_i - \mathbf{r}_j|}\right]^{12}. \quad (1)$$

The radii σ_α are fixed by $\sigma_2/\sigma_1 = 1.2$ and setting the effective diameter to unity; that is, $(2\sigma_1)^3 + 2(\sigma_1 + \sigma_2)^3 + (2\sigma_2)^3 = 4l_0^3$, where l_0 is the unit of length. The density is $\rho = N/V = 1$ in units of l_0^{-3}, and we set Boltzmann's constant $k_B = 1$. We obtain equilibrium configurations at several temperatures by the swap Monte Carlo algorithm of [12]. A long-range cutoff at $r_c = \sqrt{3}$ is imposed. However, to find the stationary points we need a potential with a continuous second derivative. Thus, instead of simply shifting the pair potential by a constant C_{ij} [so that $V_{ij}(r \geq r_c) = 0$], we use a smooth cutoff, setting $V_{ij}(r) = B_{ij}(a - r)^3$ for $r_c < r < a$ and $V_{ij}(r) = 0$ for $r \geq a$, fixing a, B_{ij}, and C_{ij} by imposing continuity.

We sample the stationary points of the potential energy by quenching the equilibrium MC configurations onto saddle points. This is done by numerically solving the $3N$ nonlinear equations $\partial \mathcal{V}/\partial \boldsymbol{r}_i = 0$ by means of a backtracking Newton method with finite-difference approximation to the Jacobian [14]. Once a saddle point is found, we measure its potential energy U and its instability index K, that is, the number of negative eigenvalues of the Hessian matrix at the saddle.

In Fig. 1 (top) we plot the average index density $k = K/3N$ as a function of the potential energy density $u = U/N$. As in [8], we find a well defined function $k(u)$ which vanishes at a threshold value of the energy, $u_{\rm th}$. For $N = 70$, a comparison between the linear fit of the data and the last point of the curve gives $u_{\rm th} = 1.75 \pm 0.01$. For $N = 140$, despite worse statistics, we find $u_{\rm th} = 1.73 \pm 0.01$, consistently with the result for $N = 70$. Note that the threshold energy is not the ground state of the system, and in fact we found minima down to $u_0 = 1.68$ ($N = 70$). The threshold energy marks the border between unstable saddle points, dominating the landscape above $u_{\rm th}$, and stable minima, dominant for $u_0 < u < u_{\rm th}$. Therefore, a topological transition takes place at $u_{\rm th}$, where the stability properties of the landscape change.

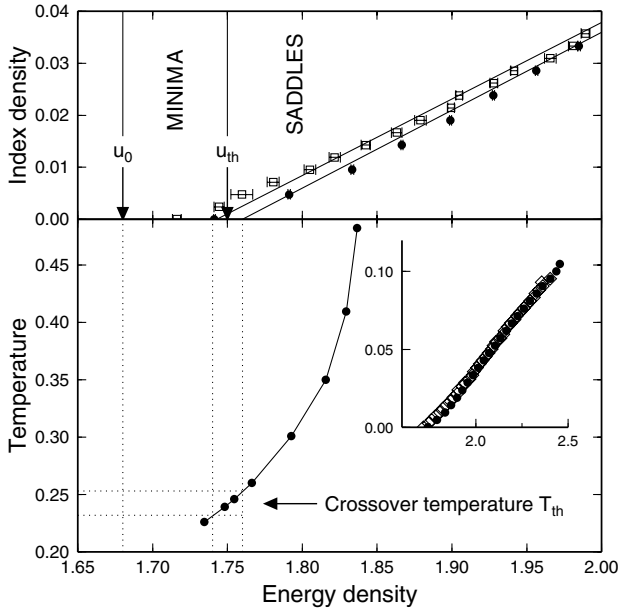

FIG. 1. Top: Average instability index density k vs potential energy density u of the stationary points. Bottom: Temperature vs equilibrium bare potential energy density, $u_b = u_{\rm eq} - 3/2k_BT$. Inset: $k(u)$ on the whole range sampled. Open symbols: $N = 140$; filled symbols: $N = 70$.

A system confined to the minima-dominated region of the landscape, $u < u_{\rm th}$, must resort to barrier hopping to diffuse in phase space. It is therefore essential to find the temperature $T_{\rm th}$ below which this confinement takes place. To this end we must realize that a system trapped in a single potential well has a potential energy density equal to the bare energy of the bottom of the well, plus a vibrational contribution proportional to k_BT. Therefore, it is the *bare* potential energy of the system which we must compare with the threshold energy [8]. We can write the bare energy as $u_b(T) = u_{\rm eq}(T) - 3/2k_BT$. When the bare energy $u_b(T)$ drops below the threshold $u_{\rm th}$, the system is effectively confined to the minima dominated region of the landscape. For $N = 70$ this happens at $T_{\rm th} = 0.242 \pm 0.012$ (Fig. 1, bottom). Note that, unlike previous investigations [7,8], for $N = 70$ we thermalize the system *below* the threshold, giving an accurate determination of $T_{\rm th}$ [15]. Hence, the dynamic effect of the topological transition at $u_{\rm th}$ must be a qualitative change in the mechanism of diffusion at $T_{\rm th}$.

The fact that barrier crossing becomes the main mechanism of diffusion below $T_{\rm th}$ does not necessarily imply a slowing down of the dynamics: large energy barriers among threshold minima are also needed, i.e., $\Delta U(u_{\rm th})$ substantially larger than $k_BT_{\rm th}$. The value of $\Delta U(u_{\rm th})$ can be estimated as the average difference in energy between simple saddles ($K = 1$) and threshold minima ($K = 0$). This difference can be extracted from the slope of $k(u)$, as $\Delta U(u_{\rm th}) \approx 1/[3k'(u_{\rm th})]$ [4,5]. Note that the slope of $k(u)$ for $N = 70$ and $N = 140$ is the same. This is consistent with the fact that activated processes are local in space (as we discuss later), and therefore barriers do not depend on the size of the system. We find $\Delta U(u_{\rm th}) \approx 2.2 \approx 10k_BT_{\rm th}$. This is an important result: at the temperature $T_{\rm th}$ where activation becomes dominant, potential energy barriers are already very large compared to the available thermal energy. Activation is therefore highly inefficient at the temperature where for the first time it is actually needed. This, we believe, is the most striking feature of very fragile liquids and it confirms the conjecture of [4] that the fragility of a system is higher the larger the potential energy barriers at $T_{\rm th}$. We thus predict that a sharp slowing down of the dynamics must occur at $T_{\rm th}$. Note that the change in the mechanism of diffusion at $T_{\rm th}$ *would not* be accompanied by a dynamic slowing down if barriers at $T_{\rm th}$ were small. In this case there would rather be a fragile-to-strong crossover at $T_{\rm th}$, as discussed in [4].

To test our prediction about the slowing down we must find the temperature marking the onset of glassiness. For

soft spheres, this is generally accepted to be $T_c \approx 0.226$ [11]. This value is affected by the same arbitrariness as the experimental T_g, since an arbitrary time scale (set by the simulation times) is involved [11]. However, as stressed in the introduction, the slowing down of fragile glasses is so sharp that it makes sense to define a T_c, as long as one keeps the above proviso in mind.

Given that we use a nonstandard cutoff for the potential, we perform an independent determination of T_c for $N = 70$. To this end we compute the Van Hove self-correlation function $G_s^\alpha(r,t)$ from configurations sampled in a molecular dynamics (MD) run which uses equilibrium MC configurations as starting points. Of course, the MD simulation falls out of equilibrium at higher temperatures than the MC swap dynamics. G_s^α is defined as

$$G_s^{(\alpha)}(\mathbf{r},t) = \frac{1}{N_\alpha}\sum_{i=1}^{N_\alpha}\langle\delta[\mathbf{r}_i(t) - \mathbf{r}_i(0) - \mathbf{r}]\rangle. \qquad (2)$$

The probability that a particle of type α has moved a distance r in a time t is proportional to $r^2 G_s^{(\alpha)}(r,t)$, which is plotted in Fig. 2 for several times and temperatures.

A reliable dynamic diagnostic for T_c is to look at the evolution of the first peak of $r^2 G_s^{(\alpha)}(r,t)$ [11]. In the liquid phase, the peak moves to the right and rapidly becomes Gaussian (top panel in Fig. 2). On the other hand, in the glassy phase it takes a huge amount of time to reach the hydrodynamic limit, and the simulations show an unmoving peak whose area very slowly decreases as a secondary peak grows (bottom panel). The middle panel shows an intermediate situation. On this basis, we estimate $T_c \approx 0.24$, not far from the standard T_c. This value is consistent with the topological transition temperature $T_{\rm th} \approx 0.242$ we found above, a result which strongly supports our scenario. Let us stress the difference between T_c and $T_{\rm th}$: The first depends on the time scale of the experiment and it can be sensibly defined only if the dynamic crossover is sharp. The latter marks the point where activation starts ruling the dynamics, and it is uniquely defined. In fact, $T_{\rm th}$ has the same nature as the critical temperature of mode coupling theory [17].

Our estimate of the barriers can be criticized, since the *average* distance in energy between threshold minima and simple saddles neglects the requirement that they must be connected to each other. To test our estimate we perform for $N = 70$ a direct sampling of the potential energy barriers. Starting from a simple saddle we follow the gradient in the two opposite directions along the unstable eigenvector, obtaining two connected minima.

In Fig. 3 we plot the average barrier size ΔU as a function of the energy density u of the adjacent minimum. On the same plot we report the value of $u_{\rm th}$ ($N = 70$), and the estimate of $\Delta U(u_{\rm th})$ obtained from the slope of $k(u)$: this estimate agrees with the value that can be read off from the plot. We conclude that the function $k(u)$ provides the threshold energy *and* the potential energy barriers among threshold minima.

A second important piece of information is contained in Fig. 3: the typical barriers grow with decreasing energy. The consequence is that below $T_{\rm th}$ the dynamic slowing down is enhanced not only by the decrease of the thermal energy available for activation, but also by the increase of the typical barriers. Thus, below $T_{\rm th}$, we expect super-Arrhenius behavior of the relaxation time [18].

A brief comment on barrier crossing is in order here. Thermal activation must be introduced within a canonical description, since in the microcanonical ensemble the total

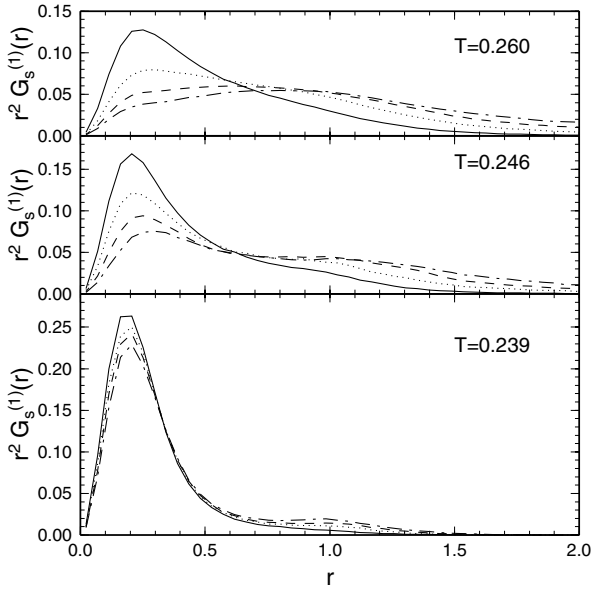

FIG. 2. Van Hove self-correlation functions for particle type 1, at times $t = 88$ (full line), 177 (dotted line), 265 (dashed line), and 353 (dash-dotted line). $N = 70$.

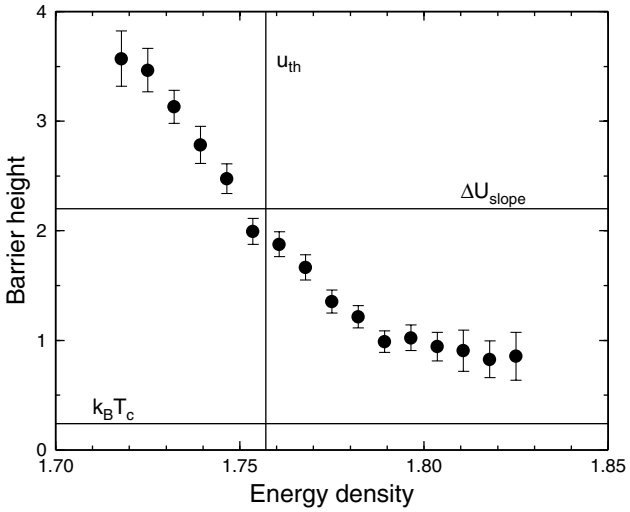

FIG. 3. Average potential energy barriers as a function of the potential energy density of the adjacent minimum. Points are an average over 1652 barriers. $N = 70$.

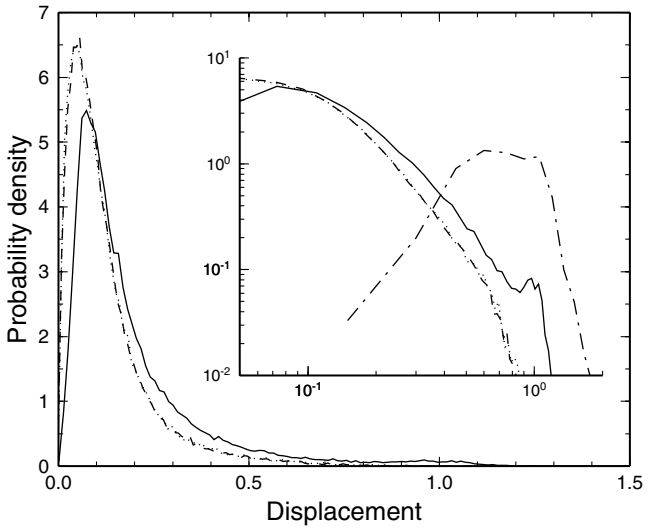

FIG. 4. Distribution of particle displacements. Full line: Distance between the two minima. Dashed (dotted) line: Distance between the saddle and the right (left) minimum. Inset: Same plot in a log-log scale. Dashed-dotted line: Distribution of largest displacement. $N = 70$.

energy is conserved. In other words, an activated transition is performed by a subsystem, with the rest acting as a thermal bath. The subsystem must be much smaller than the total system, and indeed activated processes involve a finite number of particles. For this reason, potential energy barriers associated with such processes are finite in the thermodynamic limit, implying that simple saddles and minima have the same potential energy density for $N \to \infty$. Yet, the equilibrium potential energy density is of order $k_B T$ above minima. This fact does *not* imply that barriers are easy to overcome, *nor* that thermal activation is irrelevant, but simply that activated processes involve a finite number of particles.

As we have shown, activated processes are crucial below $T_{\rm th}$ and therefore a real-space description of barrier crossing is very important. To this end we computed the distribution of the *displacement,* that is, the distance between the position of a particle in a minimum and its position in the crossing-connected minimum (Fig. 4) [19]. To interpret this result we need first to fix a reference distance: Fig. 2 shows that, even in the glassy phase, particles can easily travel a distance $r_m \approx 0.5$. The primary peak in the displacement distribution indicates that the large majority of particles moves less than r_m, while a small secondary peak can be seen at $r \approx 1$, involving only $\approx$2 particles [20]. From the radial distribution function (not shown) we know that $r \approx 1$ is the nearest-neighbor distance for type 1 particles. These facts thus suggest that in this system activated processes involve a small number of nearest-neighbor particles exchanging positions, while many particles move a small amount to make way for them. We also measure the *largest* displacement for each pair of minima and find that its distribution has no secondary peak at short distances, confirming the above interpretation. Finally, the distribution of the displacements between minimum and intermediate saddle shows no secondary peak at large distances, consistent with the fact that on the saddle the exchanging particles have not completed their transition yet.

In this Letter we argued that glassy slowing down in fragile liquids is caused by the presence of a topological transition. Potential energy barriers are much larger than the available thermal energy at the transition, and they increase with decreasing energy. Activated processes involve small numbers of particles, each moving a distance of the order of the nearest-neighbor separation.

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[1] C. A. Angell, J. Phys. Chem. Solids **49**, 863 (1988).
[2] M. Goldstein, J. Chem. Phys. **51**, 3728 (1969).
[3] F. H. Stillinger and T. A. Weber, Phys. Rev. A **25**, 978 (1982).
[4] A. Cavagna, Europhys. Lett. **53**, 490 (2001).
[5] J. Kurchan and L. Laloux, J. Phys. A **29**, 1929 (1996).
[6] A. Cavagna *et al.,* Phys. Rev. B **57**, 11 251 (1998); A. Cavagna *et al.,* Phys. Rev. B **61**, 3960 (2000).
[7] L. Angelani *et al.,* Phys. Rev. Lett. **85**, 5356 (2000).
[8] K. Broderix *et al.,* Phys. Rev. Lett. **85**, 5360 (2000).
[9] G. Seeley and T. Keyes, J. Chem. Phys. **91**, 5581 (1989); T. Keyes, J. Chem. Phys. **101**, 5081 (1994).
[10] B. Bernu *et al.,* Phys. Rev. A **36**, 4891 (1987); J.-L. Barrat *et al.,* Chem. Phys. **149**, 197 (1990).
[11] J. N. Roux *et al.,* J. Phys. Condens. Matter **1**, 7171 (1989).
[12] T. S. Grigera and G. Parisi, Phys. Rev. E **63**, 045102 (2001).
[13] G. Parisi, Phys. Rev. Lett. **79**, 3660 (1997).
[14] W. H. Press *et al., Numerical Recipes* (Cambridge University Press, Cambridge, 1992).
[15] For $N = 140$ we could not equilibrate below $u_{\rm th}$, and we had not enough points to perform an extrapolation of $u_b(T)$. However, it has been shown that standard static properties (as the bare energy) do not show significant finite-size effects for $N > 60$ in soft spheres [13] and Lennard-Jones systems [16]. Thus, $u_b^{[N=70]}$ can be compared with $u_{\rm th}^{[N=140]}$, giving $T_{\rm th}^{[N=140]} \approx 0.22$.
[16] S. Buchner and A. Heuer, Phys. Rev. E **60**, 6507 (1999).
[17] U. Bengtzelius *et al.,* J. Chem. Phys. **17**, 5915 (1984); E. Leutheusser, Phys. Rev. A **29**, 2765 (1984).
[18] The distribution of ΔU at fixed u is fairly broad, with a small fraction of barriers much smaller than $k_B T_{\rm th}$. These rare but fast barriers may be connected to nonactivated off-equilibrium dynamics (A. C. thanks D. Kivelson and G. Tarjus for important discussions on this point).
[19] R. Di Leonardo *et al.,* cond-mat/0106214.
[20] W. Kob *et al.,* Phys. Rev. Lett. **79**, 2827 (1997).