

Mosaic Multistate Scenario Versus One-State Description of Supercooled Liquids

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According to the mosaic scenario, relaxation in supercooled liquids is ruled by two competing mechanisms: surface tension, opposing the creation of local excitations, and entropy, providing the drive to the configurational rearrangement of a given region. We test this scenario through numerical simulations well below the Mode Coupling temperature. For an equilibrated configuration, we freeze all the particles outside a sphere and study the thermodynamics of this sphere. The frozen environment acts as a pinning field. Measuring the overlap between the unpinned and pinned equilibrium configurations of the sphere, we can see whether it has switched to a different state. We do not find any clear evidence of the mosaic scenario. Rather, our results seem compatible with the existence of a single (liquid) state. However, we find evidence of a growing static correlation length, apparently unrelated to the mosaic one.

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It is common opinion that in finite dimension a divergence of a relaxation time τ at nonzero temperature is associated to a diverging characteristic length ξ . The idea is that when this length increases, relaxation proceeds through the rearrangement of ever larger regions, taking a longer and longer time. The relation between τ and ξ depends on the physical mechanism of relaxation. Two main mechanisms are activated relaxation of a ψ -dimensional droplet of size ξ , giving $\tau \sim \exp(A\xi^\psi/T)$, and critical slowing down, where $\tau \sim \xi^z$ [1].

Glass-forming liquids are tricky: relaxation times grow spectacularly (more than ten decades) upon lowering the temperature, without clear evidence of a growing *static* cooperative length. In particular, density fluctuations are thought to remain correlated over short distances close to the glass transition (although there are some indications that energy fluctuations might develop larger correlations [2,3]). Thus the concept of *dynamic* heterogeneities is central to several theories of the glass transition [4–7], where the role of order parameter is played by dynamic quantities such as local time correlators, which become correlated over the growing dynamic length scale ξ_{dyn} . No thermodynamic singularity is present in these theories. Dynamic singularities are also typically absent at finite temperatures, with the notable exception of Mode Coupling Theory (MCT) [8], recently recast in terms of dynamic heterogeneities [9]. Note, however, that the experimental values of ξ_{dyn} [10–13] are barely in the nm range, the same as density correlations [14].

The mosaic scenario (MS) [15–17], working within the conceptual framework of nucleation theory, identifies, on the other hand, a *static* correlation length. Deeply rooted in

the physics of mean-field spin glasses, the MS crucially assumes the existence of exponentially many inequivalent states $\exp(N\Sigma)$, below the Mode Coupling temperature T_{MC} (Σ is called complexity or configurational entropy, and N is the size of the system). Suppose the system is in a state α and ask: what is the free energy cost for a region of linear size R to rearrange into a different state β with the same free energy? According to the MS, there are two opposing contributions: a surface cost due to the mismatch of α and β , proportional to YR^θ , where Y is a generalized surface tension ($\theta \leq d - 1$), and an entropic gain proportional to $T\Sigma R^d$, arising from the fact that the larger the region, the higher the number of possible rearrangements. This is similar to nucleation theory, with $T\Sigma$ playing the role of the free energy difference between the two phases. For small droplets, the surface contribution dominates, whereas for large R the volume contribution wins, and eventually the rearrangement occurs. Thus, similarly to nucleation theory, a length scale emerges, $\xi_{\text{mos}} \equiv (Y/T\Sigma)^{1/(d-\theta)}$ fixed by the balance of the two contributions. A droplet with $R < \xi_{\text{mos}}$ may flip to a different state, but the pinning field provided by the surrounding system will make it flip back; for $R > \xi_{\text{mos}}$ the region is *thermodynamically* favored to flip, but the larger R the longer the *time* the rearrangement takes. ξ_{mos} thus acts as the typical cooperative length. Furthermore, by noting that ξ_{mos} diverges at the temperature T_0 where Σ vanishes, the MS provides a rationale for the Vogel-Fulchmer-Tamman (VFT) law for the relaxation time, $\tau \sim \exp[\Delta/(T - T_0)]$.

In this Letter we report a numerical test of the MS. For this purpose, the formulation of Ref. [18] is particularly convenient. Imagine picking a reference equilibrium con-

figuration and freezing all particles except those within a sphere of radius R (containing M particles). This region is thus embedded in a very large box of frozen particles which act as a pinning field. The key point of the MS is that a sufficiently large sphere will be thermodynamically favored to flip to a different state. If the reference configuration is in state α , and calling β one of the exponentially many different states, the MS gives [18]

$$p_{\alpha\alpha}(R) = \frac{1}{Z} \exp(YR^\theta/T), \quad p_{\alpha\beta}(R) = \frac{1}{Z} \exp(\Sigma R^d) \quad (1)$$

as the probabilities for the sphere to remain in the reference state α and to flip to β , respectively [the normalization is $Z = \exp(YR^\theta/T) + \exp(\Sigma R^d)$]. The mosaic fragmentation of a state into regions of size ξ_{mos} corresponds to an exponentially sharp jump from $p_{\alpha\alpha} \sim 1$ to $p_{\alpha\alpha} \sim 0$ at $R \sim \xi_{\text{mos}}$ [18]. Let us call the configuration of the sphere thermalized with a given environment the *pinned* equilibrium state of the sphere. If we define a suitable overlap q to measure the similarity in phase space between this pinned state and the reference state α , the MS predicts

$$q_{\text{MS}}(R) = p_{\alpha\alpha}(R)q_{\alpha\alpha} + p_{\alpha\beta}(R)q_0, \quad (2)$$

where $q_{\alpha\alpha}$ is the self-overlap of state α and q_0 is the typical overlap between different states. Thus within the MS one expects a first order transition [19], where $q_{\text{MS}}(R)$ drops (or at least makes a crossover) at ξ_{mos} from $q_{\alpha\alpha}$ to q_0 . Note finally that for large R the overlap decays exponentially, $q_{\text{MS}}(R) - q_0 \sim \exp[-(\Sigma R^d - YR^\theta/T)]$.

We have realized this *gedanken* experiment for the soft-sphere binary mixture [20], a simple fragile glass former (see Ref. [21] for an attempt to find a mosaic length scale in spin models using this formulation). We used the swap Monte Carlo algorithm [22] (for simulation details, see Ref. [23]). Equilibration time is considerably shortened, so we can perform equilibrium simulations of large systems well below $T_{\text{MC}} = 0.226$ [20,24]. This is important, since in the standard MS T_{MC} acts like a spinodal temperature [15], above which there are not many states and the surface tension is zero [25]. We first equilibrated systems both of 2048 and of 16384 particles, then picked reference configurations used to equilibrate M particles within the sphere while keeping the remaining frozen. We studied $M = 5, 20, 50, 100, 200, 400, 800, 1600, 3200$, and 5500 at temperatures $T/T_{\text{MC}} = 4.42, 2.13, 1.54, 1.15, 0.94$, and 0.89. The largest R was 10.95, 1 order of magnitude larger than the particle size. Though reminiscent of the work of Ref. [27], we focus on static rather than dynamic quantities.

To introduce the overlap between the reference state α and the pinned state of a sphere of radius R , we divide the space in cells of side l and define

$$q(R) = \frac{1}{M} \sum_i \langle n_i^{(\alpha)} \rangle \langle n_i^{(\text{pin})} \rangle, \quad (3)$$

where n_i is the occupation number of cell i . The sum runs over all the cells in the sphere and $M = 4/3\pi R^3 \rho$. Occupation numbers are averaged over many independent configurations, both of state α (between 4 and 16) and the pinned state (10 to 100). The overlap of two identical configurations of the sphere is $q = 1$, whereas for two independent configurations $q = q_0 = \epsilon$, with $\epsilon = \rho l^3$. l is such that $\epsilon \ll 1$, but larger than the typical vibrational amplitude of the particles [23]. Here $\epsilon = 0.06$.

Our results for $q(R)$ are shown in Fig. 1 at four different temperatures, two above and two below T_{MC} . The first feature we notice is that $q(R)$ is always a smooth function, with no clear jump nor evident crossover values of R . Yet even at the lowest temperature, q becomes as low as 0.2 at the largest value of R , showing that the sphere has in fact largely decorrelated with respect to the reference state α . This means that whatever the correct relaxation mechanism at low temperatures, this mechanism is at work here, since on average 80% of the particles have rearranged at a temperature well below T_{MCT} . Moreover, $q(R)$ does not seem to decay exponentially to ϵ for large R , but rather as a power law (see later). Finally, there is no clear indication of a plateau corresponding to the self-overlap $q_{\alpha\alpha}$. Not surprisingly, a mosaic fit of the data, using Eqs. (1) and (2), gives unphysical values of the parameters, in particular, a negative value for the complexity Σ and of the surface tension Y .

Three objections can be raised at this point. First, the spheres are not large enough; the mosaic drop takes place for ξ_{mos} larger than our largest R . To this there are two replies: first, ξ_{mos} should *decrease* for increasing T , so it is unclear why we do not see anything while approaching T_{MC} from below; second: as already said, the largest sphere

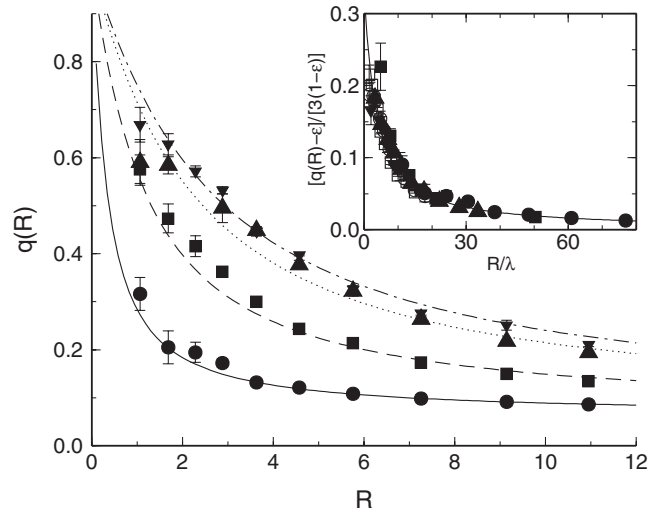


FIG. 1. Overlap $q(R)$ for $T/T_{\text{MCT}} = 4.42$ (circles), 1.54 (squares), 0.94 (triangles), 0.89 (inverted triangles). The largest value of R corresponds to $M = 5500$ particles in the sphere. Lines are the fit from the 1S argument [Eq. (6)]. Inset: data for all temperatures scaled according to Eq. (6).

has largely decorrelated, so if the mosaic bit of decorrelation still has to come, it will contribute only to 20% of the rearrangement. Second objection: the equilibration time of the sphere is longer than our runs, and our results for $q(R)$ are obtained in a *metastable* region. To check this, we have repeated the simulations but initializing the sphere in a different equilibrium state β , having zero overlap with the reference state α . What we find (Fig. 2, right) is that the overlap as a function of time *increases*, thermalizing at the same value as when starting within the same state α . Thus, even for the largest R , the asymptotic value of $q(R)$ does not depend on the initial configuration of the sphere and there is no hysteresis. Third objection: the lowest temperature is not low enough, it is too close to T_{MC} , and the mosaic mechanism is not yet at work. We cannot exclude this. However, at our lowest temperature, standard molecular dynamics is completely stuck, so one would expect the MS to describe the relaxation. Besides, an estimate of T_0 from a VFT fit of the relaxation time gives $T_0 \approx 0.80T_{MC}$ (see Fig. 2, left), so one would really expect the mosaic mechanism to be operating at these temperatures.

If we give up the key assumption of the MS, that is the existence of many states at low temperature, we can interpret our data as relaxation within a single state with self-overlap equal to ϵ , i.e., the liquid state. The argument goes as follows. Let us divide the sphere in shells of radius r . From Eq. (3) we have

$$q(R) = \frac{1}{\frac{4}{3}\pi R^3 \rho} \int_0^R dr \frac{4\pi r^2}{\rho} \langle q(r) \rangle = \frac{3}{R^3} \int_0^R dr r^2 G(r), \quad (4)$$

where $G(r) = \langle q(r) \rangle / \epsilon$ is the average overlap per unit volume between the state α and the asymptotic pinned state, at distance r from the center of the sphere. The effect

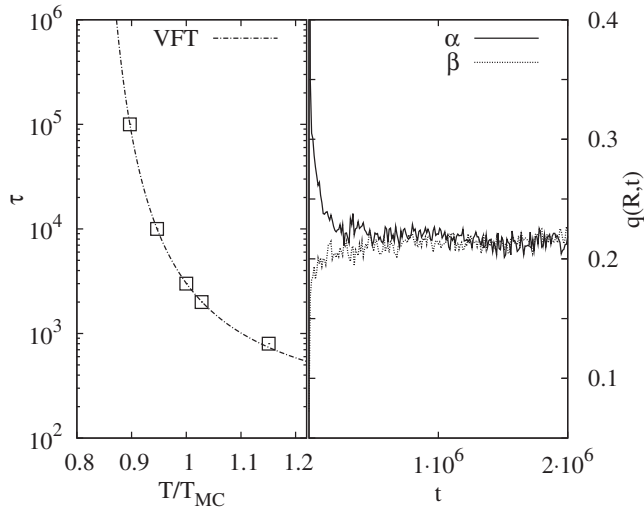


FIG. 2. Left: Relaxation time vs temperature for MC swap dynamics and VFT fit. τ is an integrated relaxation time obtained from the coarse-grained density autocorrelation studied in Ref. [23]. Right: instantaneous overlap vs time for α and β initial configurations of the sphere ($T = 0.89T_{MC}$, $M = 5500$).

of the pinning border at the center of the sphere is expected to decay as $\exp(-R/\lambda)$, where λ is a correlation length [28]. If we say that the unpinned state (the liquid) has self-overlap ϵ and we assume $G(r = R) = 1$ (sticky boundary), a reasonable form for $G(r)$ is given by

$$G(r) = (1 - \epsilon)e^{-(R-r)/\lambda} + \epsilon. \quad (5)$$

Plugging $G(r)$ into Eq. (4), and having defined $x \equiv R/\lambda$, we obtain the one-state (1S) overlap,

$$q_{1S}(R) = 3(1 - \epsilon) \left[\frac{1}{x} - \frac{2}{x^2} + \frac{2(1 - e^{-x})}{x^3} \right] + \epsilon. \quad (6)$$

This function describes the relaxation within a single state with self-overlap, ϵ , and it is quite different from the MS form [Eq. (2)]. In particular, $q_{1S}(R) - \epsilon \sim \lambda/R$, for large R . In Fig. 1 we report the fit to the data obtained with the 1S overlap, which seems quite reasonable [29]. The only fitting parameter is the correlation length λ , which increases by a factor 7 with decreasing T in our temperature span (Fig. 3).

We can test assumption (5) by studying, at fixed R , the average overlap as a function of the distance r from the center (Fig. 3, inset). We plot $\log[(G(r) - \epsilon)/(1 - \epsilon)]$ versus $R - r$, for two different values of R , at our lowest T . The data are compared to our guess Eq. (5), with λ obtained from the fit of $q(R)$. The agreement is reasonable. Another test is to plot $[q_{1S}(R) - \epsilon]/(3 - 3\epsilon)$ versus R/λ , where according to (6) data for all temperatures should fall on a single master curve. Again (Fig. 1, inset) we find a nice agreement. We note that the correlation function $G(r)$ is a kind of the “point-to-set” correlation functions described in [30]. Other than testing the MS, it seems from our results that $G(r)$ may be a useful tool to detect growing spatial correlations in supercooled liquids.

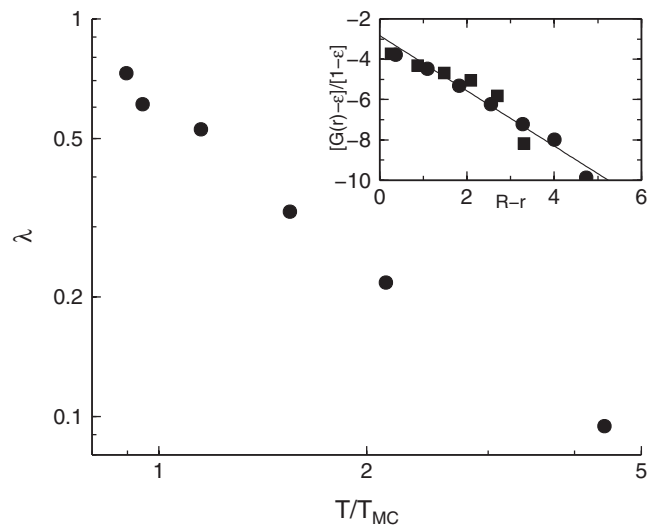


FIG. 3. Correlation length λ vs T . Inset: $[G(r) - \epsilon]/(1 - \epsilon)$ vs $R - r$ for $T = 0.89T_{MC}$ at $M = 400$ and $M = 5500$. The line is our prediction, Eq. (5).

The one-state decay of $q(R)$ described above should in fact be used also in the small R regime of the mosaic scenario. This modifies Eq. (2) as follows:

$$q_{\text{ms}}(R) = p_{\alpha\alpha}(R)q_{1\text{S}}(R) + p_{\alpha\beta}(R)\epsilon, \quad (7)$$

where now the limiting self-overlap of $q_{1\text{S}}(R)$ for $R \rightarrow \infty$ is $q_{\alpha\alpha}$, hopefully larger than ϵ in a multistate scenario. Thus, the correct mosaic prediction is that the relaxation of the sphere within state α is ruled for small R by $q_{1\text{S}}(R)$, but it is interrupted at $R = \xi_{\text{mos}}$ by the entropic drive kicking in, such that $q(R) \rightarrow \epsilon$ for $R > \xi_{\text{mos}}$. We have tried Eq. (7) to fit the data of Fig. 1, leaving θ fixed to avoid having too many parameters. For $\theta = 2$ and $\theta = 3/2$ (two values one might expect [16]), the fits locate the mosaic drop just beyond the largest simulated size, with $q_{\alpha\alpha} \sim \epsilon$. This makes the mosaic fit rather awkward. In our opinion, given the present data, it is more natural to conclude that α is the (unique) liquid state, with self-overlap ϵ , and that there is no mosaic drop beyond our largest R .

We have studied the thermodynamics of a sphere embedded in a frozen equilibrium environment. Our data are compatible with the naïve expectation that the inner shells of the sphere decorrelate and rearrange more than the outer shells close to the border. The penetration scale of the pinning border is given by a length λ , which increases sharply with decreasing temperature. In the paramagnetic phase of the Ising model, λ diverges for $T \rightarrow T_c$, just as the standard correlation length [31]. This means that λ has physical significance and begs for an investigation of the relation between λ and τ also in glass formers. Such an investigation, however, would require a finer resolution of $\lambda(T)$ around and below T_{MC} , which we leave for a future study. The length λ is neatly defined through the novel correlation function $G(r)$. Our study is purely thermodynamic, and for this reason we do not see any crossover at the Mode Coupling temperature.

Our data do not show any clear evidence for the mosaic mechanism. There is the possibility that the experiment or the observable considered are not the most suitable. For example, if the mosaic excitations are highly noncompact or fractal [32], it may be argued that a different experiment would be needed. Having said that, we remain with the impression that the one-state scenario fits reasonably well with our data. Either there is no surface tension or it is very weak and diluted over a wide region across the border. This suggests that, if a multistate scenario is valid, a version more sophisticated than the one here tested is needed. This novel description should not only reproduce the numerical data, but fit them significantly better than the single-state scenario.

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