Mosaic multi-state scenario vs. 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.

It is common opinion that in finite dimension a divergence of a relaxation time $\tau$ at nonzero temperature is associated to a diverging characteristic length $\xi$. 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 $\tau$ and $\xi$ depends on the physical mechanism of relaxation. Two main mechanisms are activated relaxation of a $d$-dimensional droplet of size $\xi$, giving $\tau \sim \exp(\mathcal{A}\xi^{\nu}/T)$, and critical slowing down, where $\tau \sim \xi^{\nu}$. Thus the concept of dynamic heterogeneities is central to several theories of the glass transition [4, 5, 6, 7], where the role of order parameter is played by dynamic quantities such as local time correlations, which become correlated over the growing dynamic length scale $\xi_{\text{dyn}}$. 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 $\xi_{\text{dyn}}$ are barely in the nm range, the same as density correlations [1].

The mosaic scenario (MS) [12, 13, 14], 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 $T_{\text{MC}}$ ($\Sigma$ is called complexity or configurational entropy, and $N$ is the size of the system). Suppose the system is in a state $\alpha$ and ask: what is the free energy cost for a region of linear size $R$ to rearrange into a different state $\beta$ with the same free energy? According to the MS, there are two opposing contributions: a surface cost due to the mismatch of $\alpha$ and $\beta$, proportional to $\mathcal{Y}R^d$, where $\mathcal{Y}$ 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, $\xi_{\text{mos}} \equiv (\mathcal{Y}/T\Sigma)^{1/d}$, 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 favoured to flip, but the larger $R$ the longer the time the rearrangement takes. $\xi_{\text{mos}}$ thus acts as the typical cooperative length. Furthermore, by noting that $\xi_{\text{mos}}$ diverges at the temperature $T_0$ where $\Sigma$ vanishes, the MS provides a rationale for the Vogel-Fulchheimer-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. [13] is particularly convenient. Imagine picking a reference equilibrium configuration 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 $\alpha$, and calling $\beta$ one of the exponentially many different states, the MS gives

$$p_{\alpha\alpha}(R) = \frac{1}{Z} \exp(\Upsilon R^6 / T), \quad p_{\alpha\beta}(R) = \frac{1}{Z} \exp(\Sigma R^6),$$

as the probabilities for the sphere to remain in the reference state $\alpha$ and to flip to $\beta$, respectively (the normalization is $Z = \exp(\Upsilon R^6 / T) + \exp(\Sigma R^6)$). The mosaic fragmentation of a state into regions of size $\xi_{\text{mos}}$ corresponds to an exponentially sharp jump from $p_{\alpha\alpha} \sim 1$ to $p_{\alpha\alpha} \sim 0$ at $R \sim \xi_{\text{mos}}$.

We have realized this gedanken experiment for the soft-sphere binary mixture (20), a simple fragile glassformer (see ref. 23) 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 $T_{\text{MC}}$ acts as a spinodal temperature (15), above which there are not many states and the surface tension is zero (31). We first equilibrated systems both of 2048 and of 16384 particles, then picked reference configurations used to equilibrate $M$ particles within of 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, one order of magnitude larger than the particle size. Though reminiscent of the work of ref. 23, we focus on static rather than dynamic quantities.

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

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

where $n_i$ is the occupation number of cell $i$. The sum runs over all the cells in the sphere and $M = 4/3\pi R^3 l$. Occupation numbers are averaged over many independent configurations, both of state $\alpha$ (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. Unsurprisingly, 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 $\Sigma$ and of the surface tension $T$.

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

![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. [3]). Inset: data for all temperatures scaled according to Eq. (6).](image-url)
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 $\beta$, having zero overlap with the reference state $\alpha$. 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 $\alpha$. 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 $\eta$ 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 $\epsilon$, 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,

$$q(R) = \frac{1}{\pi R^3 \rho} \int_{0}^{R} dr \frac{4\pi r^2}{R^3} \langle q(r) \rangle = \frac{3}{R^3} \int_{0}^{R} dr r^2 G(r),$$

(4)

where $G(r) = \langle q(r) \rangle/\epsilon$ is the average overlap per unit volume between the state $\alpha$ and the asymptotic pinned state, at distance $r$ from the centre of the sphere. The effect of the pinning border at the centre of the sphere is expected to decay as $\exp(-R/\lambda)$, where $\lambda$ is a correlation length [24]. If we say that the unpinned state (the liquid) is 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:

$$G(r) = (1 - \epsilon) \exp(-(R-r)/\lambda) + \epsilon.$$  

(5)

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

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

(6)

This function describes the relaxation within a single state with self-overlap $\epsilon$, 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 [32]. The only fitting parameter is the correlation length $\lambda$, which increases by a factor 7 with decreasing $T$ in our temperature span (Fig. 3).

We can test assumption [40] by studying, at fixed $R$, the average overlap as a function of the distance $r$ from the center (Fig. 3 inset). We plot $\log[(G(r) - \epsilon)/(1 - \epsilon)]$ vs. $R - r$, for two different values of $R$, at our lowest $T$. The data are compared to our guess Eq. 5 with $\lambda$ obtained from the fit of $q(R)$. The agreement is reasonable. Another test is to plot $(1 - q_{1S}(R) - \epsilon)/(3 - 3\epsilon)$ vs. $R/\lambda$, 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 [27]. 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.

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:

$$q_{\text{mos}}(R) = p_{\alpha\alpha}(R) q_{1S}(R) + p_{\alpha\beta}(\epsilon)$$  

(7)

where now the limiting self-overlap of $q_{1S}(R)$ for $R \to \infty$ is $q_{\alpha\alpha}$, hopefully larger than $\epsilon$ in a multi-state scenario. Thus, the correct mosaic prediction is that the relaxation of the sphere within state $\alpha$ is ruled for small $R$ by $q_{1S}(R)$, but it is interrupted at $R = \xi_{\text{mos}}$ by the entropic drive kicking in, such that $q(R) \to \epsilon$ for $R > \xi_{\text{mos}}$. We have tried Eq. 7 to fit the data of Fig. 1 leaving $\theta$ fixed to avoid having too many parameters. For $\theta = 2$ and $\theta = 3/2$ (two values one might expect [16]), it 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 $\alpha$ is the (unique) liquid state, with self-overlap $\epsilon$, 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 naive 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 $\lambda$, which increases sharply with decreasing temperature. In the paramagnetic phase of the Ising model, $\lambda$ diverges for $T \to T_c$, just as the standard correlation length $L_c$. This means that $\lambda$ has physical significance and begs for an investigation of the relation between $\lambda$ and $\tau$ 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 $\lambda$ 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 non-compact or fractal, 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 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 multi-state scenario is valid, a version more sophisticated than the 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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[31] Note that according to [30, the mosaic mechanism is ac-
The argument breaks down at low values of $R$, where there is no difference between surface and bulk.