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Are there localized saddles behind the heterogeneous dynamics of supercooled liquids?

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Abstract. – We numerically study the interplay between heterogeneous dynamics and properties of negatively curved regions of the potential energy surface in a model glassy system. We find that the unstable modes of saddles and quasi-saddles undergo a localization transition close to the Mode-Coupling critical temperature. We also find evidence of a positive spatial correlation between clusters of particles having large displacements in the unstable modes and dynamical heterogeneities.

The dynamics of supercooled liquids is often described as a complex trajectory across their Potential Energy Surface (PES) [1]. This approach traces its origin back to the pioneering work of Goldstein [2], who argued that at low temperature these systems get trapped in the basins of attraction of local minima of the PES and hence the atomic dynamics is slowed down. In the last decade, several authors have addressed a quantitative study of the PES through numerical simulations of model systems. The original picture has evolved into a refined description of the dynamics in terms of collections of local minima (*metabasins* [3]) and transitions between them [4–6].

Other works have focused on the properties of the Hessian matrix of the potential energy, revealing even a more complex scenario, where not only local minima but also higher-order stationary points (saddles) and more general points characterizing regions of negative curvature of PES (quasi-saddles) play an important role in the structural slowing-down of the liquid [4–15]. Indeed, it has been shown [12, 13] that some information about the liquid-like diffusive dynamics is encoded in the imaginary spectrum of the Hessian matrix: the number of unstable modes n_{im} of saddles is correlated with the diffusivity of supercooled model systems and decreases as the liquid is cooled. Attempts have been made [10–13] to identify the temperature at which the thermal average of n_{im} extrapolates to zero with the critical

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temperature T_c where the purely dynamical Mode-Coupling Theory (MCT) [16, 17] predicts a structural arrest of the liquid. The residual relaxation exhibited by both real and simulated systems below T_c is to be attributed, within this scenario, to "activated processes", *i.e.* rare transitions over finite energy barriers, ignored in the mean-field approach of MCT.

However, the idea that the slowing-down of the liquid around T_c reflects a geometric transition [11] in the PES has been recently criticized. Careful studies have in fact put in doubt the existence of a sudden change in the sampling of saddles at T_c [4, 15] and there are indications that saddles do not disappear completely below T_c [14, 18]. Most worrying, perhaps, is that a saddle-based approach appears unsuitable [19] for the description of *dynamical heterogeneities* [20–22], *i.e.* rearrangements involving localized subsets of mobile particles, which have been recognized in the last years as the hallmark of the supercooled dynamics and whose evidence is hard to glimpse on a $3N$-dimensional PES.

In this letter, we analyze the localization properties of the unstable modes of saddles and quasi-saddles sampled by a supercooled Lennard-Jones (LJ) mixture. We provide quantitative evidence that the spatial structure of these unstable modes change from extended to localized around T_c. We establish for the first time the existence of a direct connection between saddles and dynamical heterogeneities in a supercooled liquid. In fact, the regions of the system where unstable modes are localized are statistically correlated with clusters of particles which are highly mobile on the β-relaxation timescale. Our results thus indicate that a crossover in the nature of the sampled saddles is indeed underlying the emergence of dynamical heterogeneities and the failure of mean-field theories below T_c.

Our model is the binary LJ mixture introduced by Wahnstrom in [23]. This mixture has been shown to be a good glass-former and its properties have been analyzed in-depth [9, 23], especially as far as dynamical heterogeneities are concerned [24]. Our system is an equimolar mixture of 500 particles interacting via the LJ potential $u_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}]$, with $\alpha, \beta = 1, 2$ indexes of species, and enclosed in a cubic box of side $L = 7.2779\,\sigma_{11}$ with periodic boundary conditions. Reduced units will be used in the following, assuming σ_{11}, ϵ_{11}, and $(m_1\sigma_{11}^2/\epsilon_{11})^{1/2}$ respectively as unit of distance, energy and time. The interaction parameters are $\sigma_{11} = 1.0$, $\sigma_{22} = 0.833$, $\sigma_{12} = 0.917$, $\epsilon_{11} = \epsilon_{22} = \epsilon_{12} = 1.0$. The masses are $m_1 = 1.0$, $m_2 = 0.5$. Two different cut-off schemes for the potential have been considered, cut and shifted (CS) and cut and quadratically shifted (QS) at $r_c = 3.0$. The QS cut-off is obtained adding a term $a+br^2$ with a and b determined to ensure continuity to both $u(r)$ and its first derivatives at r_c. This cut-off scheme has been used to check any bias in the determination of the properties of the PES due to discontinuities in the force at the cut-off [25]. Molecular Dynamics (MD) simulations have been performed in the canonical ensemble using the Nosé-Poincaré thermostat [26, 27]. At the lowest temperature corresponding to an equilibrated supercooled liquid ($T = 0.575$), the length of the run was 2×10^7 time steps with $\delta t = 0.008$, equivalent to a total simulation time two orders of magnitude larger than the structural relaxation time. Our best estimate of the MCT critical temperature, obtained from an analysis of the intermediate scattering functions, is $T_c = 0.55 \pm 0.01$, which is slightly lower than the previously reported ones [9].

From each equilibrated run we extracted between 100 and 200 independent configurations and minimized the mean-squared force $W = 1/N \sum_i f_i^2$ using the LBFGS algorithm [28] to locate the nearest saddle. It has been recognized [12,14,25] that W-minimizations usually stop near quasi-saddles, *i.e.* local minima of W, where the PES displays one inflection mode with non-zero force, and that discontinuities in the cut-off can lead to incomplete minimizations [25]. While other numerical strategies have been proposed for accurately locating saddles [15], there has also been evidence [12,13,29] that quasi-saddles do not differ significantly from true saddles as far as the influence on the dynamics is concerned. In the following we will use the term saddle in a wide sense, without distinction between quasi-saddles and saddles. The Hessian

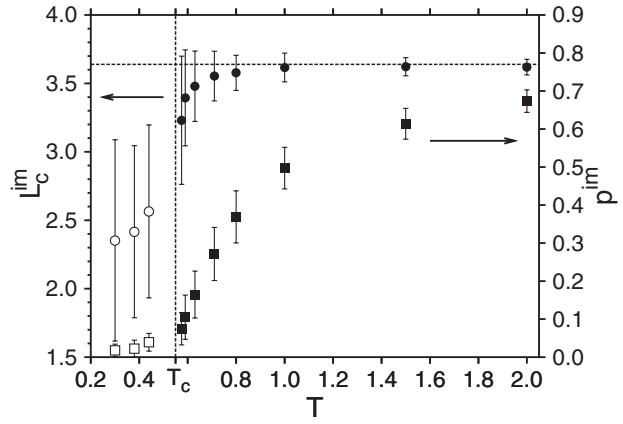

Fig. 1 – Gyration radius L_c^{im} (circles, left axes) and participation ratio p^{im} (squares, right axes) as a function of T, both in the supercooled liquid (black) and glass (white). Error bars represent one standard deviation of the distribution of values. The horizontal dashed line is drawn at $L_{box}/2$.

matrix at each saddle was diagonalized yielding the eigenvalues ν_α^2 and the eigenvectors $\boldsymbol{e}_i^\alpha$, where $\alpha = 1, \ldots, 3N$ is an index of mode and $i = 1, \ldots, N$ an index of particle. The order n_{im} of a saddle is then defined as the number of imaginary frequencies in its spectrum.

To have a better understanding of the localization properties of the unstable modes, we consider the average

$$E_i^{im\,2} = \frac{1}{n_{im}} \sum_{\alpha=1}^{n_{im}} \boldsymbol{e}_i^{\alpha\,2} \tag{1}$$

of the squared displacements $\boldsymbol{e}_i^{\alpha\,2}$ of atom i over the n_{im} unstable modes. The vector $E^{im} = (E_1^{im}, \ldots, E_N^{im})$ contains averaged information about the distribution *in real space* of the instabilities associated with the saddle. By construction E^{im} is normalized so that we can define a participation ratio for the unstable modes of a given saddle in the usual way [26],

$$p^{im} = \left(N \sum_{i=1}^{N} E_i^{im\,4} \right)^{-1}. \tag{2}$$

p^{im} will be roughly 1 for extended instabilities and $\mathrm{O}(1/N)$ for a single, localized one. Further insight can be gained considering the gyration radius [30]

$$L_c^{im\,2} = \sum_{i=1}^{N} |\boldsymbol{r}_i - \boldsymbol{r}_g|^2 E_i^{im\,2}, \tag{3}$$

where $\boldsymbol{r}_g = \sum_i \boldsymbol{r}_i E_i^{im\,2}$. For extended instabilities $L_c^{im} \approx L_{box}/2$. Both p^{im} and L_c^{im} refer to a given configuration and quantify the degree of localization of the unstable modes of a saddle as a whole. They will overestimate the size of localized instabilities when the system is large enough that several independent ones are present, but we will show that this should not be the case for the mixture in consideration.

We show in fig. 1 the thermal average of the participation ratio p^{im} and gyration radius L_c^{im} as a function of T. At high T saddles are extended: p^{im} tends to saturate around 0.7 and

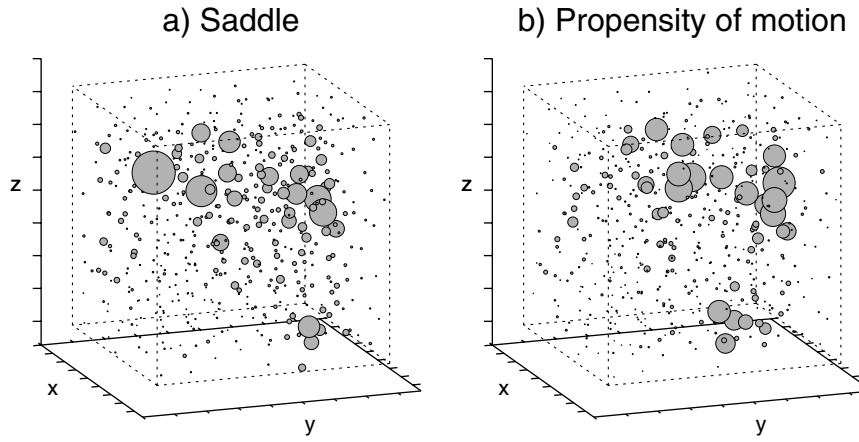

Fig. 2 – Plot a): distribution of average displacements E_i^{im} on the unstable modes of a saddle sampled at $T = 0.575$. Plot b): normalized propensity of motion E_i^p of the MD configuration from which the saddle in plot a) has been located. A sphere proportional to E_i^{im} and E_i^p is drawn around each particle, in plot a) and b), respectively.

L_c^{im} approaches its limiting value of $L_{box}/2$. In the *landscape-influenced* range [8], roughly between T_c and $2T_c$, the instabilities of saddles have a mixed character. In fact, while p^{im} decreases markedly, the gyration radius L_c^{im} still fluctuates around $L_{box}/2$, indicating that most of the instabilities of saddles are percolating through the system despite their enhanced localization. On approaching T_c saddles become strongly localized and the average L_c^{im} decreases abruptly. Figure 1 thus shows that the localized nature of saddles becomes pronounced exactly in the same temperature range where dynamical heterogeneities first appear [19] and in correspondence to the break-down of mean-field approaches.

The degree of localization of the instabilities of saddles can be inspected directly in the snapshot of fig. 2a, which displays the spatial distribution of E_i^{im} in the simulation box for a saddle sampled at $T = 0.575$, slightly above our estimated T_c. A sphere of radius proportional to E_i^{im} is drawn around each particle. We see that particles involved in the unstable modes, *i.e.* those with a large E_i^{im}, are strongly clustered. As counterparts, extended regions of stable particles are observed. The spatial structure of saddles like that in fig. 2a, for which $n_{im} = 7$, casts some new light on a common assumption about the nature of saddles sampled by supercooled liquids, namely that saddles of low order may originate from non-interacting subsystems, each experiencing a saddle of order one [13, 15, 31]. Figure 2a shows that the 7 unstable modes have a strong spatial overlap, being concentrated on a rather compact cluster of particles. Similar features are present in the whole landscape-influenced range, while in the hot liquid the fraction of extended unstable modes increases so that particles are essentially involved in all of them. Thus, the independent subsystems interpretation does not seem to hold for saddles sampled by LJ systems in the $T > T_c$ range([1]).

The emerging scenario seems to mirror the observations of dynamical heterogeneities [19]. The question arises naturally whether there is a direct mapping between saddles and dynamical heterogeneities, *i.e.* whether unstable clusters like that in fig. 2a are also the mobile ones.

To address this issue we followed the approach of [33], who introduced the *propensity of motion* of particles as a measure of dynamical heterogeneities. A configuration is selected

([1])Similar results were in fact obtained for the BMLJ of [32]. We have also checked that this is the case also for the true saddles we have sampled, for which $W \approx 10^{-10}$.

from the MD trajectory at a given temperature T. Then several short runs at the same T are performed, monitoring the square displacements $\Delta r_i^2(t)$ from the reference configuration. We evaluate the propensity of motion as $\langle\, \Delta r_i^2(t^*)\,\rangle$, where $\langle\, ...\,\rangle$ indicates an average over independent sets of initial velocities and t^* corresponds to the maximum of the non-Gaussian parameter $\alpha_2(t)$, which lies in the late β-relaxation regime and is a characteristic timescale for dynamical heterogeneities [20]. Using this procedure it is possible to identify the dynamical heterogeneities that a single configuration will, on average, give rise to. We have considered up to 500 sets of initial velocities, drawn from the appropriate Maxwellian distribution. Since the timescales for diffusion are slightly different for the two species (roughly a factor of 2), we have also tried to choose different values of t according to the species, but the picture was essentially unaltered, so we simply used the value of t^* for the small particles.

Figure 2b shows the distribution in the simulation box of the normalized propensity of motion:

$$E_i^p = \frac{\langle\, \Delta r_i^2(t^*)\,\rangle}{(\langle \sum_{i=1}^{N} (\Delta r_i^2(t^*))^2 \,\rangle)^{1/2}} \tag{4}$$

for the MD configuration whose nearby saddle is actually that of fig. 2a. By comparison we see that the localization and essential morphology of the mobile cluster identified by the propensity of motion of the MD configuration are well reproduced in the cluster of average unstable displacements of the nearby saddle. To assess the statistical relevance of the correlation we have analyzed 20 independent configurations at $T = 0.575$. We define as *mobile* (*immobile*) those particles for which the normalized propensity of motion is larger (smaller) than a threshold e^h (e^l). Applying the same cut-off procedure to the average displacements in the unstable modes E_i^{im}, we introduce an analogous separation in *unstable* and *stable* particles. The two threshold values e^h and e^l could vary or even coincide without altering the overall picture. With our choice $e^l = 0.01$, $e^h = 0.045$, the fraction of particles belonging on average to each subpopulation is around 25%.

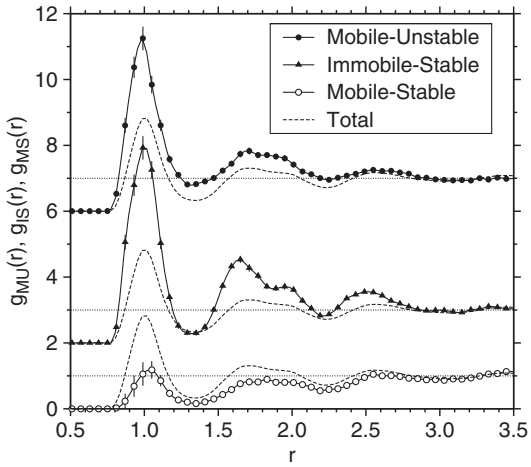

Fig. 3 – From top to bottom: radial distribution functions for mobile-unstable (MU), immobile-stable (IS) and mobile-stable (MS) pairs of particles, compared with the total distribution function (dashed lines) at $T = 0.575$ (see text for definitions). Data related to the IS and MU cases have been shifted for clarity. Error bars represent one standard deviation.

In fig. 3 we show the radial distribution functions at $T = 0.575$ for *mobile-unstable* (MU), *immobile-stable* (IS) and *mobile-stable* (MS) pairs, compared with the total radial distribution function $g(r) = (g_{11}(r)+2g_{12}(r)+g_{22}(r))/4$. The significant enhancement of the first two coordination shells in $g_{MU}(r)$ and $g_{IS}(r)$ clearly shows that particles with a high (low) propensity of motion are surrounded, on average, by particles having large (small) displacements in the unstable modes of the closest saddle. Consistently with such correlation, the $g_{MS}(r)$ (identical to $g_{SM}(r)$) is lower than the total $g(r)$. Moreover, as expected, the effect decreases by increasing temperature. All this provides statistical evidence that dynamical heterogeneities have spatial correlation with compact clusters of particles taking part in the unstable modes of nearby saddles. Interestingly, fig. 3 also suggests that regions of immobile particles possess distinct structural properties, as evidenced by the deeper separation between the first and second shell of neighbours and the enhanced splitting of the second peak in $g_{IS}(r)$ and in agreement with [21].

In summary, by performing MD simulations for a supercooled LJ mixture we have shown that the relaxation channels associated with the unstable modes of saddles and quasi-saddles sampled along the MD trajectory cross over from spatially extended to localized around T_c. These localized unstable modes display non-trivial spatial correlations with the dynamical heterogeneities identified by the propensity of motion [33] in the β-relaxation timescale. The novel finding of such a correlation may represent a step ahead in the understanding of the heterogeneous nature of the supercooled dynamics. Theoretical and computational tools that have been developed for the study of the PES [34,35], may now reveal their utility in a direct analysis of dynamical heterogeneities. We note that other observables, *e.g.* free volume, have been recently addressed as possible origins of dynamical heterogeneities, but their spatial correlation with local mobility has been either found to be poor [36] or investigated below the glass transition [37]. In this perspective, our results point to a key role of saddles and quasi-saddles in bridging the gap between the PES description of supercooled liquids and approaches which focus more directly on the dynamics like the heterogeneity-based picture proposed by Berthier *et al.* [19] or the mean-field MCT.

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