Nonaffine Deformation of Inherent Structure as a Static Signature of Cooperativity in Supercooled Liquids

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We unveil the existence of nonaffinely rearranging regions in the inherent structures (IS) of supercooled liquids by numerical simulations of model glass formers subject to static shear deformations combined with local energy minimizations. In the liquid state IS, we find a broad distribution of large rearrangements which are correlated only over small distances. At low temperatures, the onset of the cooperative dynamics corresponds to much smaller displacements correlated over larger distances. This finding indicates the presence of nonaffinely rearranging domains of relevant size in the IS deformation, which can be seen as the static counterpart of the cooperatively rearranging regions in the dynamics. This idea provides new insight into possible structural signatures of slow cooperative dynamics of supercooled liquids and supports the connections with elastic heterogeneities found in amorphous solids.

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When a liquid is cooled down to its glass transition temperature, particle motion slows down enormously and becomes highly cooperative [1]: The more the system becomes glassy, the more the relaxation requires cooperative rearrangements of a large number of particles. Experimental and theoretical investigations as well as simulation results on dynamical heterogeneities strongly support the presence of cooperatively rearranging regions of growing size [1–4]. However, it is still debated whether and how the onset of such cooperative dynamics can take place without any apparent or straightforward connection to structural changes. Such links have been searched for in various directions. For example, different connections between the local propensity of particles to motions and the underlying structural features of the system have been investigated, but they still remain quite elusive [5].

An alternative (and so far complementary) description of the dynamics of supercooled liquids is based on the way the system explores its potential energy surface [6]. When the system enters the supercooled regime, the presence of local minima, or inherent structures (IS), turns out to be extremely important and to produce complex trajectories in the potential energy landscape: The time evolution of the system samples the basins associated to the local minima, or groups of such basins, on a relatively short time scale, whereas transitions between different groups of basins separated by major energy barriers take a much longer time and imply a slow aging process, during which the system is out-of-equilibrium. Such a description, however, does not fully account for the cooperative dynamics associated to dynamical heterogeneities. Yet, possible connections have been discussed [6] and recent works have gathered additional insights [7–12].

In the present Letter, we report about a signature of the onset of cooperative dynamics in the structural features of supercooled liquids from a novel perspective. The approach is motivated by a recent theory [13]—based on a general framework of nonequilibrium thermodynamics—which relates the response of a glassy system to an applied deformation to the corresponding change of its IS. In contrast to previous approaches, here it is suggested that the *reversible* part of the dynamics changes considerably when approaching the glass transition. Since the reversible dynamics basically mirrors the space transformation behavior of the system, the suggestion in [13] guides the way toward investigations of *static* rather than dynamical properties. Accordingly, the most important feature of IS transformation is a hindrance to affine deformation: The typical linear size of the regions where nonaffine deformations take place is roughly the particle size in the liquid and is expected to become larger upon approaching the glass transition.

We explore these theoretical considerations by computer simulations of different model systems for supercooled liquids subject to static shear deformations with small amplitudes. In the liquid phase, a broad distribution of rearrangements is found, centered around a rather large mean value. Instead, when the system enters the supercooled regime, its IS displays the onset of an enhanced collective behavior with much smaller displacements. This feature, which does not depend on the particular model or deformation considered, has been detected here for the first time and indicates the existence of nonaffinely rearranging regions of relevant size in the IS of supercooled liquids. The presence of such collective rearrangements in the IS response is strongly evocative of the cooperativity characterizing the dynamics, and it is in fact observed in the same range of temperatures. On this basis, we propose that these nonaffinely rearranging regions are the IS counterpart of the cooperatively rearranging regions observed so far only in the dynamics.

Methods and numerical simulations.—We consider three well-established model systems for supercooled liquids: (a) The three-dimensional (3D) binary Lennard-Jones mixture of Ref. [14]; (b) The 3D soft spheres binary mixture studied in Ref. [15]; (c) The 2D soft spheres binary mixture in Ref. [16]. In all three models, the densities have been chosen such that crystallization is prevented. Upon cooling, these systems therefore go from the liquid to the supercooled and glassy regime. In order to investigate the response of IS to an applied deformation, we have designed the following procedure [13]. First, starting from a particle configuration $X = \{\mathbf{r}_i\}$ equilibrated at a given temperature T, we deform it affinely $\mathbf{r}_i \to \mathbf{r}_i^d$ and subsequently find the inherent structure of the deformed configuration $X^{dq} = \{\mathbf{r}_i^{dq}\}$. For the energy minimization, we use a conjugate gradient algorithm. Second, starting from the same initial configuration X, we first find the IS corresponding to the initial configuration $X^q = \{\mathbf{r}_i^q\}$ and subsequently apply the same affine deformation to obtain $X^{qd} = \{\mathbf{r}_i^{qd}\}$. All subsequent analysis is based on the comparison between the two configurations X^{dq} and X^{qd}, which is quantified by the mismatch, i.e., the nonaffine displacement field $\{\mathbf{d}_i = \mathbf{r}_i^{dq} - \mathbf{r}_i^{qd}\}$. In the limit of a flat energy landscape, $\{\mathbf{d}_i\}$ is identically zero. By lowering the temperature into the supercooled regime, we expect the presence of basins and barriers in the energy landscape to introduce collective contributions to the displacement field. We carefully chose the deformation amplitudes sufficiently large to make the system typically leave a basin. Supplementary information is given in the EPAPS document [17]. We have considered two different kinds of deformation: (*i*) The spatially modulated shear deformation $\mathbf{r}_i \to \mathbf{r}_i^d = \mathbf{r}_i + \gamma \sin(k_n y_i)\mathbf{e}_x$, where γ denotes the maximum amplitude of the deformation and $k_n = 2n\pi/L$ the wave vector with L the size of the simulation box; (ii) The homogeneous shear $\mathbf{r}_i \to \mathbf{r}_i^d = \mathbf{r}_i + \gamma y_i \mathbf{e}_x$, where Lees-Edwards boundary conditions are used. We have applied the deformations (i) and (ii) to the systems (a), (b), and (c) with γ varying between 10^{-4} and 10^0. All quantities are given in reduced Lennard-Jones units. For all the systems, we have prepared 20 to 50 independent samples of N particles (N varying from 500 to 8000) [17] which have been carefully equilibrated [18]. All quantities discussed are averaged over the independently prepared samples and the error bars obtained from sample-to-sample fluctuations. Some simulations were performed using the LAMMPS code [19]. The following analysis concerns temperatures T in the range from the high T Arrhenius dependence of dynamic quantities to the onset of caging and cooperative dynamics.

Results.—A first, qualitative understanding can be obtained via a simple visualization of the mismatch field $\{\mathbf{d}_i\}$ at different temperatures and for different amplitudes of deformation. In Fig. 1, $\{\mathbf{d}_i\}$ vectors are plotted for the system (c) and deformation (ii) at high temperature $T = 1.0$ (left) and low temperature $T = 0.46$ (right). The length of the vectors are suitably enlarged for clarity. At high T, for a fixed amplitude of deformation, the mismatch vectors display a relatively large magnitude as well as uncorrelated directions. This indicates that, at these temperatures, the local changes to the IS induced by our procedure are in fact dominated by the thermal fluctuations of the system. At low temperatures, instead, $\{\mathbf{d}_i\}$ have much smaller magnitudes for the same γ (see figure caption for details) but, at the same time, they appear rather spatially correlated in magnitude and in direction. These two kinds of behavior are ubiquitous in our numerical study and appear systematically for a wide range of γ values [18]. Interestingly enough, in all cases considered, the transition from the one to the other behavior is coupled to the onset of the supercooled regime (for example, for the system (c) in Ref. [16], the onset of the glassy dynamics can be set around $T \approx 0.46$). These findings support the idea that a qualitative change of the response of IS to deformation is strongly correlated to the onset of the cooperative dynamics [7].

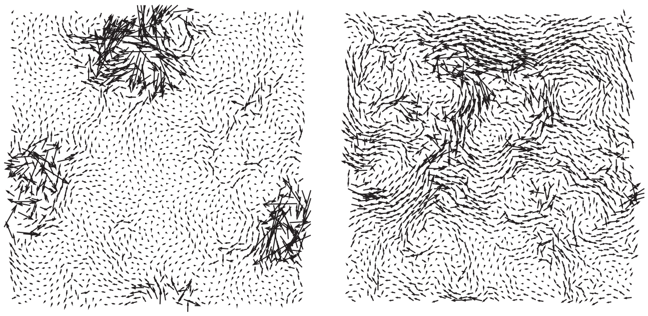

FIG. 1. Mismatch field $\{\mathbf{d}_i\}$ for the 2D soft spheres binary mixture of Ref. [16] at $T = 1.0$ (left) and $T = 0.46$ (right) for homogeneous shear deformation with amplitude $\gamma = 0.001$. For better visibility, the lengths of the vectors are multiplied by a factor 14 and 600 for $T = 1.0$ and $T = 0.46$, respectively.

A first, simple characterization is given in terms of the mean length of the mismatch vectors $l_d = \langle N^{-1}\sum_i \mathbf{d}_i^2\rangle^{1/2}$. In Fig. 2, $l_d(\gamma, T)/l_d(\gamma, T = 1)$, obtained in the system (b) using the deformation (i) of amplitude γ and wave vector $k_1 = 2\pi/L$, is plotted as a function of the temperature T. For sufficiently small values of γ, the relative global magnitude of the mismatch field shows a rather steep decrease with decreasing temperature. In fact in Ref. [7], it has also been observed that the critical deformation amplitude to cause IS transitions strongly depends on temperature. Remarkably, there are clearly two well distinguished temperature regimes for the typical length of the mismatch vectors. In addition, the transition between them becomes steeper for small γ and takes place at the onset of the cooperative dynamic regime ($T \simeq 0.4$), i.e., very close to T_{eIS}, where the IS energy starts to strongly depend on temperature, and well above structural arrest ($T_{\mathrm{MCT}} \simeq 0.303$) [15,17].

An estimate of the fraction of particles involved in the rearrangements described by the mismatch field can be obtained by the dimensionless width of the length distribution $\Pi = \langle N^{-1}[\Sigma_i \mathbf{d}_i^2]^2/\Sigma_i[\mathbf{d}_i^2]^2\rangle$ (the participation ratio of Ref. [20]). In the main frame of Fig. 3, Π is plotted as a function of temperature T for $\gamma = 10^{-4}$, 10^{-3}, and 10^{-2}

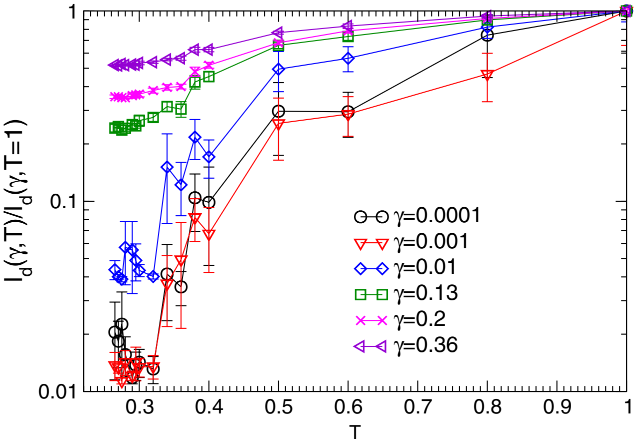

FIG. 2 (color online). Normalized mean length of mismatch field $l_d(\gamma, T)/l_d(\gamma, T = 1)$ as a function of T in the 3D binary mixture of Ref. [15], obtained with the spatially modulated deformation (i) of amplitude γ and wave vector k_1.

for the same system and the same wave vector as in Fig. 2. The width Π increases with decreasing temperature below $T = 0.4$. In particular, for the very small values of γ shown in the figure, Π displays a rather sharp increase and shows that the fraction of particles involved in such nonaffine deformation of the IS increases from 10% to 40–60%. In order to further characterize the nature of the nonaffine rearrangements, we have measured the average degree of correlation $C(r)$ between the directions of the mismatch vectors of different particles i and j separated by a distance r, $C(r) = \langle \mathbf{d}_i \cdot \mathbf{d}_j \rangle / \langle \mathbf{d}_i^2 \rangle$. In the inset of Fig. 3, $C(r)$, obtained for $\gamma = 0.01$ in the system (b) with the deformation (i) is plotted as a function of r. The data show that the low temperature regime is characterized by a definitely larger degree of correlation at the same distance r. Moreover, the distribution of values of $\mathbf{d}_i \cdot \mathbf{d}_j / \langle \mathbf{d}_i^2 \rangle$ for pairs of particles separated by distance $r \pm dr$, plotted in Fig. 4, widens strongly at low temperature, indicating that the extended correlation in the response of IS to deformation corresponds to a high degree of heterogeneity. This feature is strikingly similar to what is observed in the dynamics with the average time correlation and the fluctuations around this average, generally used to quantify dynamical heterogeneities. But it is observed here, in the same range of temperatures [17], in a *static* quantity. On the whole, the emerging new scenario is that the onset of cooperativity in the real-time dynamics corresponds to growth of correlated and heterogeneous domains in the nonaffine deformations of the IS.

The same qualitative behavior is obtained in the entire range $10^{-4} \leq \gamma \lesssim 0.1$ and in the systems (a) and (c) for both deformations (i) and (ii). We have also found in all the systems considered that, when $\gamma \geq 1.0$, the mismatch field always closely resembles the one obtained at high temperature. This indicates that beyond $\gamma \simeq 1.0$, the amplitude of the deformation is sufficient to erase any distinctive feature of the low temperature structure of the IS, as in a sort of Lindemann criterion [6]. Finally, the details of temperature dependence of the different quantities, e.g., the crossover width or the values of Π, depend to some extent on the specific system considered (e.g., the crossover is always smoother in the 2D system) and on the type of deformation [18].

Conclusions.—The presented results reveal for the first time that the onset of the glassy dynamics corresponds to the onset of cooperative heterogeneous rearrangements in the response of IS to external, static deformations. In fact, we have shown that in the liquid state, as a response to the external deformation, the IS displays large and uncorre-

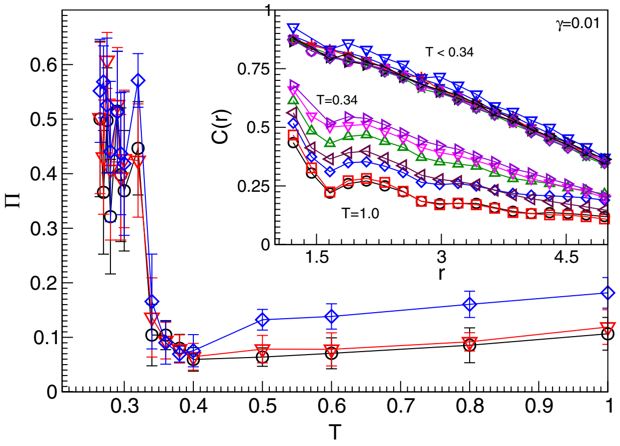

FIG. 3 (color online). Main frame: The participation ratio Π as a function of the temperature for the 3D binary mixture of Ref. [15], in the case of the spatially modulated deformation (i) of amplitude $\gamma = 10^{-4}$, 10^{-3}, 10^{-2}. Inset: Average degree of correlation $C(r)$ of the direction of the mismatch vectors separated by a distance r for $\gamma = 0.01$.

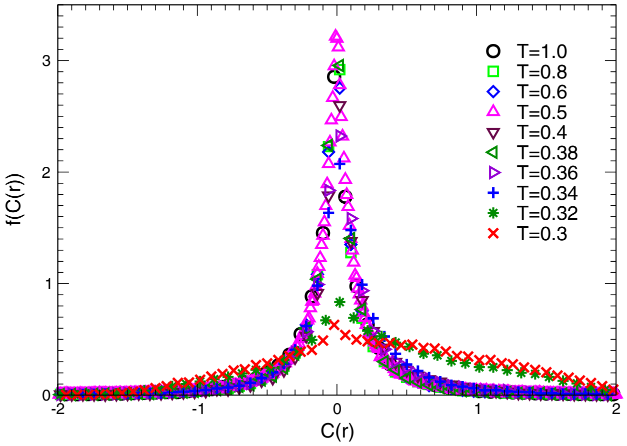

FIG. 4 (color online). Distributions of degree of correlation $C(r)$ between particles at a distance $r = 5$ in particle diameter units. The same system and the same spatially modulated deformation (i) as in Fig. 3 was chosen with deformation amplitude $\gamma = 0.01$.

lated rearrangements, dominated by thermal fluctuations. Near the onset of the cooperative dynamics, the response of the IS to small external deformation is instead characterized by small, collective nonaffine rearrangements involving a relevant fraction of particles [13]. To our knowledge, this feature of the IS had not been recognized until now. It has been possible here, thanks to the procedure designed in Ref. [13] which strongly relies on the many-body nature of the IS construction. An interesting advantage of our approach is in avoiding calculations based on the dynamics, which usually require very long simulation times. The extent of such an advantage can be better quantified by systematically comparing our procedure to the dynamics [18].

The heterogeneous domains of the IS, determined by collective nonaffine displacements, are strongly evocative of the cooperatively rearranging regions observed in the dynamics and are in fact detected in the same range of temperatures. We propose therefore that they are actually the IS counterpart of the cooperatively rearranging regions. If this is the case, they would deliver a *static* correlation length which grows significantly in the supercooled regime, where the dynamic correlation length related to dynamic cooperativity starts to grow. From this point of view, this study suggests a new path for the investigations of structural signatures of glassy dynamics. A more sophisticated analysis of the nonaffine displacement field, for example, adds useful insights in this direction [17]. Finally, our results have also interesting connections with the studies of elastic heterogeneities in amorphous solids [20–27]. Their typical length scale has actually been related to the nonaffine part of the displacement field generated in response to an elastic deformation. In Ref. [26], where a quantitative estimate of this length scale is obtained in a realistic model of amorphous silica, the connection between the typical length scale of elastic heterogeneities in the amorphous solid and the length scale typical of dynamical heterogeneities (which is actually of comparable magnitude) in the supercooled liquid is suggested. Our results support this idea and offer a way to extend those studies to finite temperatures. On approaching the supercooled regime from the high temperature fluid, we find a signature of the onset of dynamic cooperativity in a purely static quantity: the nonaffine, collective rearrangements of the IS show a striking similarity to cooperative, dynamical phenomena.

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