Saddles in the Energy Landscape Probed by Supercooled Liquids

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We numerically investigate the supercooled dynamics of two simple model liquids exploiting the partition of the multidimensional configuration space in basins of attraction of the stationary points (inherent saddles) of the potential energy surface. We find that the inherent saddle order and potential energy are well-defined functions of the temperature T. Moreover, by decreasing T, the saddle order vanishes at the same temperature (T_{MCT}) where the inverse diffusivity appears to diverge as a power law. This allows a topological interpretation of T_{MCT}: it marks the transition from a dynamics between basins of saddles ($T > T_{\mathrm{MCT}}$) to a dynamics between basins of minima ($T < T_{\mathrm{MCT}}$).

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The study of the properties of the free energy landscape or/and of the potential energy surface (PES) in disordered systems is a topic of current research [1]. The universality in the dynamics of systems as different as disordered spin glasses and structural glasses [2] supports the possibility that some universal features at the landscape level control the slow dynamics in these systems [3]. Along this line, several recent works have attempted to connect both dynamics and thermodynamics of glass-forming liquids to landscape properties.

Numerical investigations of the sampled configuration space have been performed for several models of liquids [4–9]. An important outcome of these studies is the demonstration that on cooling the system populates basins of the PES associated with local minima [the so-called inherent structure (IS) [10]] of deeper and deeper depth [4]. The number of distinct basins with the same depth in bulk systems has also been evaluated [8]. This information has been incorporated into a detailed description of the thermodynamics of supercooled liquids [5,6,8,11].

In the landscape framework, the dynamics of the system in configuration space is conceptually decomposed in a "fast" oscillatory motion (dynamics within a basin) and a slow diffusive motion (dynamics among different PES basins). Quantitative calculation of the diffusion coefficient D based on landscape properties has been formulated within the instantaneous normal mode (INM) theory [12]. The INM approach focuses on the properties of the local curvature of the PES sampled by the liquid, calculated by diagonalizing the Hessian ($\mathcal{H}$) matrix of the potential energy V. Analysis of the resulting eigenvalues and eigenvectors [13] allows one to evaluate the number of independent directions in configuration space associated with basin changes, i.e., to diffusion. For the cases where such analysis has been performed, strong evidence has been presented for the existence of proportionality between D and the number of diffusive directions [14–17]. It has also been shown that the number of diffusive directions decreases with T and appears to vanish at the so-called mode-coupling [18] transition temperature T_{MCT} [15,17], i.e., at the T where an apparent divergence of the inverse diffusivity is observed.

A major difficulty in quantitatively pursuing the idea of a connection between the diffusivity and topology of configuration space is that no transparent mapping has been yet proposed to associate equilibrium configurations with the "closest" configuration on the border between different basins.

In this Letter we propose such a mapping and present an analysis of the properties of the closest *stationary points* (saddles) of the potential energy. The proposed mapping, which can be considered as an extension of the Stillinger-Weber mapping [10,19], partitions the configuration space $\mathbf{R}^{3N}$ of a three-dimensional N particle system in basins of attraction of the saddles, characterizing the saddle with their order and their potential energy. The dynamics of the system is then described as dynamics between different saddles' basins. We apply the proposed mapping to two different models of simple liquids and find that (i) the order of the sampled saddle is a well-defined function of T, (ii) on cooling the liquid populates basins associated with saddles of lower and lower order, (iii) the location in potential energy of the saddles is much smaller than the system potential energy, providing evidence that the diffusion process is entropy driven, even below T_{MCT}, and (iv) at T_{MCT}, the saddle order appears to vanish, indicating that, at this T, the system populates the basins of potential energy minima, confirming that T_{MCT} marks the crossover between two different dynamical processes.

To partition $\mathbf{R}^{3N}$ in basins of saddles we search for the basins of attraction of an auxiliary potential function, namely, $W = \frac{1}{2}|\vec{\nabla} V|^2$ [20] (for a similar approach, see also [21]). The function W is never negative and it is zero at all saddle points, i.e., at all points where all forces are zero (stationary point configurations). The saddle points are classified according to their order n_s (the number of negative eigenvalues of $\mathcal{H}$) and their potential energy e_s. Saddles of order zero coincide with the local minima of the

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PES (i.e., with IS). The complete description of the energy landscape would require the calculation of the densities of states for each n. However, by investigating two model systems we find that, similar to the case of minima [8], the saddle's energy and order are well-defined functions of T. Hence, all relevant information is contained in the functions $e_s(T)$ and $n_s(T)$.

We investigate numerically two simple model liquids: (*i*) the monatomic modified Lennard-Jones (MLJ) [22], and (*ii*) the standard Lennard-Jones 80/20 binary mixture (BMLJ) [23]. Both models are able to support strong supercooling without the occurrence of crystallization. Standard LJ units are used hereafter. Equilibrium configurations are prepared by standard microcanonical molecular dynamics simulations at constant density ($\rho = 1$ for MLJ and $\rho = 1.2$ for BMLJ) and at Ts ranging from the normal liquid phase ($T \approx 1.6$) down to T_{MCT}. ($T_{\mathrm{MCT}} = 0.475$ for MLJ and 0.435 for BMLJ.) The systems are composed of $N = 256$ (MLJ) and $N = 1000$ (BMLJ) particles enclosed in a cubic box with periodic boundary condition. Truncated ($R_c = 2.6$ and 2.5, respectively) and shifted LJ potentials are used. We analyze 20 independent equilibrium configurations for each T. For each configuration we calculate the associated IS and inherent saddle implementing a steepest descent algorithm which moves in the direction of $-\vec{\nabla}V \equiv \vec{F}$ and $-\vec{\nabla}W = \mathcal{H} \cdot \vec{F}$, respectively (the arrows indicates $3N$-d vectors). Finally, the $\mathcal{H}$ of the starting equilibrium configuration (to evaluate the INM) and of the inherent saddle (to evaluate n_s) is calculated and diagonalized.

Figure 1a shows the average order of the inherent saddle (i.e., the number n_s of negative eigenvalues of $\mathcal{H}$) as a function of the equilibrium T. The average order $n_s(T)$ is a well-defined function of T [24], indicating that the trajectory of the system in the configuration space samples statistically the subspace set up by basins of saddles of a given order $n_s(T)$. Figure 1a also shows that, by decreasing T, $n_s(T)$ vanishes at T_{MCT}.

This finding gives support to the following scenario: T_{MCT} is the T above which the system explores basins of saddles of order $n_s > 0$ and below which the system is mostly confined in a local minimum ($n_s = 0$). The existence of a quantity, $n_s(T)$, that vanishes at T_{MCT} is remarkable. Indeed, this makes $n_s(T)$ a good candidate for the description of supercooled dynamics, for instance, the computation of $n_s(T)$ is an alternative way of determining T_{MCT}.

For comparison with the previous INM studies, Fig. 1b also shows the number of directions characterized by negative eigenvalues n_i as a function of T. As discussed in Ref. [13], a nonzero value of n_i is found at T_{MCT}, when the system is trapped in basins of minima, a clear signature of the presence of nondiffusive unstable modes. Hence, the introduction of the inherent saddle concept offers a way to overcome the difficulties associated with the presence of nondiffusive modes in the standard INM approach. The order of the saddle n_s appears to be a well-defined indicator of the number of diffusive directions.

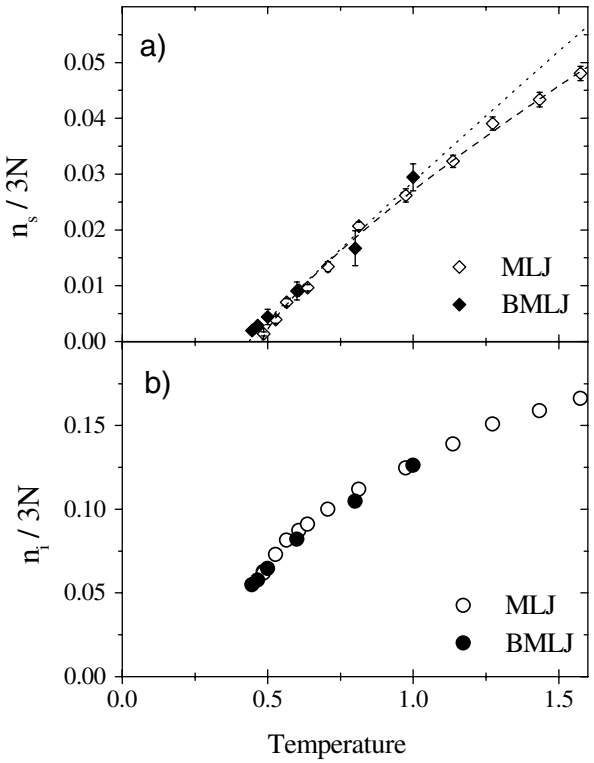

FIG. 1. Temperature dependence of the fraction of the negative eigenvalues of the Hessian calculated at the inherent saddle configurations $n_s/3N$ (a), and at the instantaneous configurations, $n_i/3N$ (b). Open symbols refer to MLJ and solid ones refer to BMLJ. The dashed lines in (a) are the best fit to the data with the function $A(T - T_x)^{\gamma}$ (MLJ: $T_x = 0.48 \pm 0.01$, $\gamma = 0.78 \pm 0.02$. BMLJ: $T_x = 0.435$, $\gamma = 0.94 \pm 0.1$).

Next we discuss the location in energy of the inherent saddles as a function of the equilibrium T. Figure 2 reports the average instantaneous potential energy, e_i, the average potential energy of the saddle, e_s, and the average potential energy of the IS, e_o, as a function of T for the MLJ potential model. Similar results hold for the BMLJ case. The quantity $e_o(T)$ shows a rapid increase between T_{MCT} and $T \approx 0.8$, reaching a constant value for higher T (see inset of Fig. 2, where e_o is reported in an expanded scale). We notice that the overall variation of e_o is very small on the scale of the variation of e_s and e_i. The quantity $e_s(T)$ shows an intermediate behavior between e_i and e_o. In agreement with the observation that around T_{MCT} the system explores the basin of attraction of saddles of order zero, we find that at $T \sim T_{\mathrm{MCT}}$ the inherent saddle energy curve merges on the IS curve. The data reported in Figs. 1 and 2 allow one to conclude in an unambiguous way that T_{MCT} marks the crossover between two dynamic regimes: at $T < T_{\mathrm{MCT}}$ the system spends most of the time trapped in the local minima, while at $T > T_{\mathrm{MCT}}$ the system explores basins pertaining to saddle points of increasingly higher—but well-defined—energy and order.

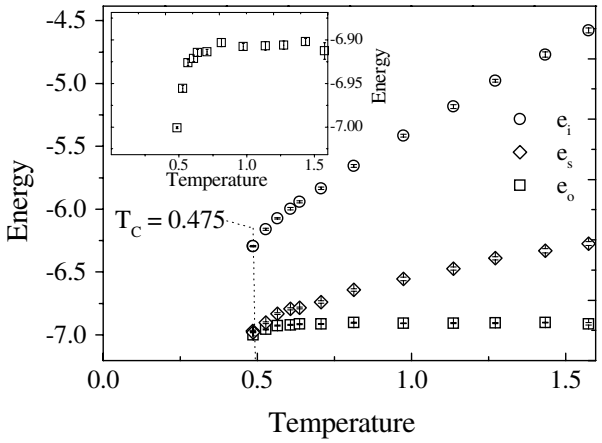

FIG. 2. Temperature dependence of the instantaneous energy [e_i (○)], the inherent saddle energy [e_s (◇)], and the inherent minima energy [e_o (□)] for the MLJ potential model. The vertical dashed line indicates T_{MCT} as derived from the apparent divergence of the inverse diffusivity. The inset shows, in an enlarged energy scale, the T dependence of e_o. A very similar behavior is found for the BMLJ system (not reported here for clarity reasons).

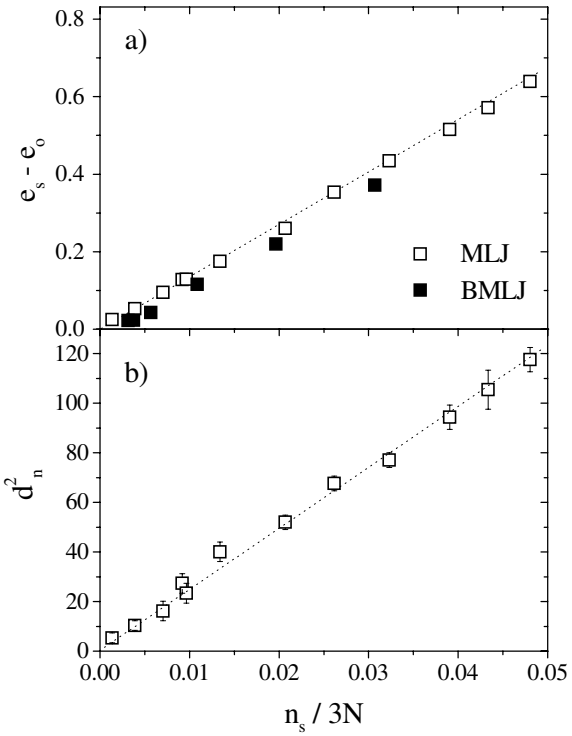

FIG. 3. (a) Saddle elevation energy $e_s - e_o$ as a function of the saddle's order fraction $n_s/3N$ for MLJ (open symbols) and BMLJ (solid symbols). The dashed line, with a slope of ≈ 11 is the best fit to the MLJ data. (b) The mean square distance d_n^2 between minima (IS) reached by quenching the inherent saddle of order n_s is plotted as a function of $n_s/3N$ for MLJ. The dashed line is the best fit to the data

This conclusion is consistent with the INM finding that at T_{MCT} the fraction of diffusive directions explored by the liquid goes to zero [14,15,17]. It is also consistent with the interpretation of the transition between different dynamical regimes at T_{MCT} proposed in Ref. [9] and based on the analysis of the decay of the density-density correlation functions evaluated along an inherent structure trajectory.

An important observation stems from the data reported in Figs. 1 and 2: the saddle energies are located well below the instantaneous values. This finding clearly shows that the system trajectory is never close to a saddle point, and dynamics should not be described as saddle-to-saddle motion, but, more correctly as dynamics between basins of attractions of the corresponding saddles. In this respect, one should not discuss the dynamics of the system for $T > T_{\mathrm{MCT}}$ as activated dynamics [25]. It is worth noting that the value e_i at T_{MCT} is larger than $e_s(T)$ for a wide T range. In other words, even at T_{MCT}, the instantaneous potential energy is much larger than the energy value at which saddles are located. Nevertheless at T_{MCT} the system spends a very large fraction of time in a local minimum and only rarely performs jumps between minima. Hence, the diffusion events at low T are not limited by the presence of an energy barrier that must be overcome by thermal activated processes; they are rather controlled by the limited number of directions leading from a basin of a minimum to another basin at (almost) constant potential energy.

Figure 3a shows the relation between n_s and the elevation (in potential energy) with respect to the corresponding local minima ($e_s - e_o$). We discover a remarkable linear relationship between these two quantities. This indicates that—given a minimum—the energy landscape above it is organized in families of equally spaced energy saddle points [to rise one step in the saddle order, the requested energy is $3N\Delta(e_s - e_o)/\Delta n_s \approx 11$ for both systems]. Moreover, this simply linear dependence suggests that the aspects of the landscape above a local minimum is independent from the energy of the minimum itself. We also find a linear relation between the mean square distance d_n^2 between minima that have been reached by quenching the inherent saddles of order n_s and the order of the corresponding saddle [26], as shown in Fig. 3b This linear relation suggests that the descent path from a saddle of order n_s towards the surrounding minima can be interpreted as a sequence of independent random steps, each of them decreasing the order of the saddle by 1 and increasing the (squared) distance between the associated local minima by a fixed amount (random walk among saddle points). It is worth noting that these properties of the energy landscape (i.e., the linear dependence between $e_s - e_o$, d_n^2, and n_s) are ingredients of a model for the landscape introduced by Madan and Keyes [27] and recently revisited [28]. This similarity deserves further investigation.

In conclusion, by the numerical investigation of two different systems, we have pointed out the relevance of the concept of inherent saddle in describing the dynamics of supercooled liquids and we have highlighted same

important characteristics of the energy landscape. In particular we have (I) shown that the inherent saddles' properties (energy and order) are well-defined functions of T; (II) demonstrated the validity of the conjecture that T_{MCT} marks the transition between dynamics among minima ($T < T_{\mathrm{MCT}}$) and dynamics where the systems spend time nearby on high order stationary points; (III) found that $n_s(T)$ is a quantity that can be efficiently used to measure numerically T_{MCT}; (IV) provided evidence that the diffusion processes are entropy driven; and (V) shown that the aspect of the energy landscape "seen" by a given local minimum is highly regular (as demonstrated by the linear dependence of $e_s - e_o$ and of d_n^2 from n_s) and independent from the specific minimum.

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[20] It is worth noting that, for every stationary point of V, W has a minimum (actually $W = 0$ there), while the reverse is not true. There are minima of W that are not stationary points of V (flex points). These points can be easily identified, as the Hessian has one or more eigenvalue(s) much smaller than those found in the "true" saddle points. We find that the number of the flex points is negligible with respect to the number of true saddles of V, and their existence introduces an error of approximately 2% in the estimation of e_s and n_s.
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