Relation between the Dynamics of Glassy Clusters and Characteristic Features of their Energy Landscape

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(Received 12 June 2013; published 26 February 2014)

Based on a recently introduced metric for measuring distances between configurations, we introduce distance-energy (DE) plots to characterize the potential energy surface of clusters. Producing such plots is computationally feasible on the density functional level since it requires only a few hundred stable low energy configurations including the global minimum. By using standard criteria based on disconnectivity graphs and the dynamics of Lennard-Jones clusters, we show that the DE plots convey the necessary information about the character of the potential energy surface and allow us to distinguish between glassy and nonglassy systems. We then apply this analysis to real clusters at the density functional theory level and show that both glassy and nonglassy clusters can be found in simulations. It turns out that among our investigated clusters only those can be synthesized experimentally which exhibit a nonglassy landscape.

DOI: 10.1103/PhysRevLett.112.083401 PACS numbers: 36.40.-c, 61.20.Ja, 61.43.Fs, 64.70.P-

The features of the potential energy surface (PES) [1] and the resulting consequences for the physical properties of a system is the subject of intensive research. Because of the technological importance of glassy bulk materials, extended glassy systems have been studied extensively [2–4]. During the last few decades or so a number of advances have been made in understanding the nature of the glass transition using powerful simulation and analytical methods [5–7]. However, a number of issues such as nonexponential relaxation processes, rapid growth of relaxation times with decreasing temperatures, the role of PES and configurational entropy, and spatial heterogeneity continue to be debated [8,9]. The qualitative understanding is based on the nature of the energy landscape [1]. It was shown [10] that glassy systems have a large number of local minima of similar energies which are separated by barriers of various heights.

Turning to finite size systems, the electronic structures, equilibrium geometries, and many properties of atomic clusters have also been studied extensively at various levels of theory. The PES and related properties of the Lennard Jones (LJ) clusters containing up to 1000 atoms are well understood [1]. Atomic clusters are known to display size sensitive properties. For example, some clusters such as the LJ_{55} (LJ cluster of 55 atoms of same type) are structure seekers, that exhibit a strong tendency to fall into their unique ground state [11], whereas others such as LJ_{75} have a multifunnel character which makes it much harder to fall into the ground state [11]. By ground state we denote the geometrical configuration corresponding to the global minimum of the PES. For gold clusters the basic structural motif of the ground state can for instance be changed by the addition of a single atom [12]. The ground state geometries frequently exhibit amorphous structures. [13–15]. This can lead to a flat heat capacity vs temperature curve in gallium and aluminum clusters, whereas highly symmetric clusters of the same material give a peaked heat capacity curve [16,17].

Though it is believed that a glassy landscape would also lead to glassy dynamics in clusters, the reported work has been rather sporadic and evidence in terms of dynamical behavior at low temperature is missing [18–20]. One of the early attempts to seek glassy behavior in clusters was by Rose and Berry in their study of $(KCl)_{32}$ [18], and by Nayak, Jena, and Berry [19]. In a more recent work, Banerjee and Dasgupta have investigated the dynamics of glass forming liquids using a master equation approach within a network model [20]. Unfortunately their cluster was a structure seeker with a well-defined ordered structure. Nevertheless they did obtain clear indications of glassy behavior by removing the low energy part of the spectrum. The standard approach to probe the glassy nature is via very long molecular dynamics (MD) runs at various temperatures. Although feasible for LJ clusters, this is prohibitively expensive for a realistic treatment using density functional theory (DFT). An alternative is to characterize the PES using the associated disconnectivity graphs [21] which show the relation between the energy differences of the local minima and the barrier heights. However, the determination of a large number of saddle points is also computationally very expensive at the DFT level. For this reason studies on glassy clusters based on a realistic description, such as DFT, are virtually nonexistent.

The present work has two main objectives. First we introduce a novel approach based on distance-energy (DE) analysis [22], and show that a DE plot represents the essential characteristics of a potential energy landscape. To establish this, we carry out long time MD and compute

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relevant dynamical susceptibility for two model LJ clusters. Second, we demonstrate the utility of our approach by applying it to four clusters at the DFT level and show that one cluster has a glassy character whereas the other ones are structure seekers.

The basic idea is illustrated for a one-dimensional model in Fig. 1, where a glassy landscape is transformed into the landscape of a structure seeker by lowering the energy region around the global minimum with respect to the regions further away. During this transformation the energy differences between the global minimum and the low energy local minima are obviously increased and some barriers disappear which in turn causes some local minima to disappear as well. This can be explained mathematically by the Tomlinson model [23]. The DE plots for the PES at the four stages of the transformation are given by the locations of the local minima and shown by discs of the same color as the corresponding PES. Obviously the distance of a disk along the x axis is the distance of this local minimum from the global minimum in configuration space whereas the distance along the y axis is the energy of the local minimum with respect to the global minimum. For the structure seeker (red PES) the energy increases more rapidly with distance and has fewer points which are close according to the configurational distance compared to the case of the glassy landscape (black PES).

For realistic PESs which are very high dimensional, a suitable generalization of the distance is needed. A global fingerprint describing a cluster can be obtained from the eigenvalues of an overlap matrix of atom centered Gaussians, whose widths are given by the covalent radius of the atom on which it is centered. The root mean square of the difference vector between two fingerprint vectors is then a distance measure which fulfills all the properties of a metric [22]. As we shall see, it is this distance between the ground state and all the metastable states along with their energies that reveals the character of a PES. Since for the LJ model systems, the bond length cannot be approximated by the sum of the covalent radii, we use the following slightly modified matrix for the calculation of the eigenvalues of the LJ systems: $C_{i,j} = \exp[-r_{i,j}^2/(2\sigma_{ij}^2)]$, where $r_{i,j}$ is the distance between atoms i and j, and σ_{ij} the parameter of the LJ potential (specified in the Supplemental Material [24]) which takes on three different values depending on whether the atoms i and j are of A or B type. Since all the matrix elements used for the calculation of the configurational distance are scaled with respect to the equilibrium bond lengths, the configurational distance is independent of the bond length and systems with different bond lengths can be compared. Our results are rather insensitive to the exact functional form chosen for the calculation of the matrix elements $C_{i,j}$ and it is to be expected that even distances based on other descriptors of the chemical environments [25] will lead to similar results.

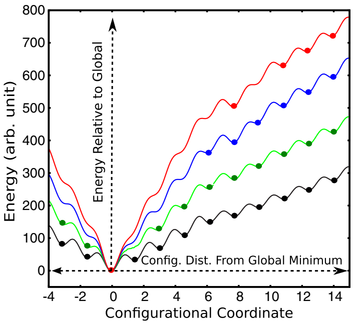

FIG. 1 (color online). Simple one-dimensional model for the transformation of a glassy into a nonglassy energy landscape. The movement of the local minima, indicated by the discs, shows the evolution of the DE plots during this transformation.

The high dimensional character of the true PES leads to an important modification of the simple picture shown in Fig. 1. Because local minima can be found in so many directions around the global minimum the number of minima within a certain configurational distance will be much larger than in our one-dimensional model and the density of points in the plot will be much higher. An even larger increase occurs for the saddle points which lead to neighboring minima. The global minimum of the LJ_{13} cluster, for instance, is surrounded by 535 local minima which are connected to the global minimum by 911 saddle points [26]. Furthermore, there are 911 structurally distinct transition states connecting those 535 local minima.

We will next show that DE plots convey all the necessary information to judge whether a system has glassy character or not. To do so we study two binary LJ (BLJ) systems having 45 atoms (13 of type A and 32 of type B) and 55 atoms (13 of type A and 42 of type B). The LJ potential parameters used for these clusters and the coordinates for the ground state geometries are given in the Supplemental Material [24]. Then we establish the glassy nature of the 55 atom cluster using standard tools such as disconnectivity graphs and dynamical susceptibilities obtained from molecular dynamics. The same analysis, carried out on the 45 atom cluster, shows that it is a structure seeker. We next compute and examine the DE plots and will demonstrate that they give information which is in agreement with the information obtained by the previous methods.

In order to compute long time dynamical properties we have performed constant temperature MD using DLPOLY [27] at five temperatures in the range [0.20,0.31]. The dynamics was studied via a two point correlation function [8], $Q(t)$,

$$Q(t) = \int d\vec{r}\rho(\vec{r},t_0)\rho(\vec{r},t+t_0) \sim \sum_{i=1}^{N} w(|\vec{r}_i(t_0) - \vec{r}_i(t+t_0)|),$$

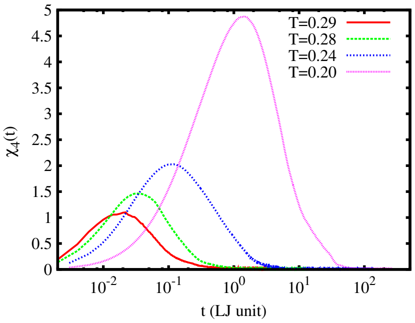

FIG. 2 (color online). Dependence of the dynamical susceptibility χ_4 on time for different temperatures in the case of BLJ_{55}

where $\rho(\vec{r}, t_0)$ are space-time dependent particle densities. $w(r) = 1$, if $r \leq a$ and zero otherwise. The averaging over the initial time t_0 is implied. The window function w of width $a = 0.30$ treats particle positions separated by an amplitude smaller than 0.3 as identical. The dynamical susceptibility, $\chi_4(t)$ is defined as the fluctuation in $Q(t)$, $\chi_4(t) = (1/N)[\langle Q^2(t)\rangle - \langle Q(t)\rangle^2]$. It is well established, that for glassy systems, $\chi_4(t)$ has a nonmonotonic time dependence, and peaks at a time τ_4, which is proportional to the structural relaxation time. The time dependence of $\chi_4(t)$ is shown in Fig. 2 for BLJ_{55}. The noteworthy feature is the increase in τ_m by 2 orders of magnitude as the temperature decreases. The behavior is very similar to the behavior of a glassy extended system [8] and quantitatively establishes the glassy character of the BLJ_{55} cluster. On the other hand applying the same analysis to the BLJ_{45} cluster does not give such a temperature dependence (see Supplemental Material [24]).

We also looked at an experimentally measurable fingerprint of glassy systems, namely, heat capacity. As shown in Fig. 3, it is rather flat for BLJ_{55} and shows no well-defined peak, indicating the absence of a first-order-like transition. For comparison Fig. 3 also shows the specific heat for another cluster of the same size, namely LJ_{55}, which is known to be a strong structure seeker. These calculated heat capacities are quite similar to the experimentally observed specific heats of Ga_{30} and Ga_{31} cations [16], which were termed as melters and nonmelters. The phenomenon has been explained on the basis of their respective geometries, the magic melters being relatively more ordered and nonmelters being disordered [17]. The same explanation applies in this case. The nonglassy LJ cluster is a icosahedral structure, whereas the glassy system is disordered.

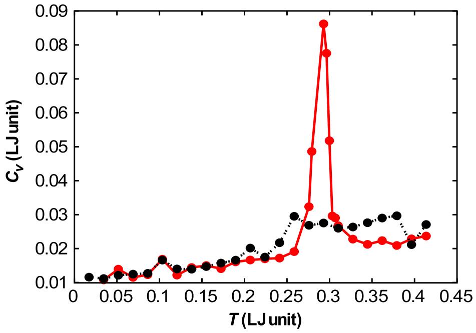

FIG. 3 (color online). The heat capacity C_V as a function of temperature for the glassy cluster BLJ_{55} (black curve) and the nonglassy LJ_{55} one (red curve).

Figure 4 shows the disconnectivity trees for our two model BLJ clusters. The differences are obvious. The structure seeker has a ground state which is considerably lower in energy than the next metastable configurations. In the case of the glassy system there are many metastable configurations which are close in energy to the ground state and the barriers that have to be surmounted to get from one metastable configuration into another one are of variable height and frequently much larger than the energy difference between the local minima.

Now we present and discuss the DE plots (Fig. 5) for both systems. The differences are striking and by comparison with our model PES of Fig 1, it is clear that BLJ_{55} has a glassy PES whereas BLJ_{45} does not have a glassy character. As has already been seen from the disconnectivity plot, for the structure seeker, the global minimum is much lower in energy than any other metastable states. In addition, the first metastable structure also has a rather large configurational distance from the global minimum. For the glassy system, on the other hand, there exists a large number of local minima close to the global minimum which implies that the density of structures in the configurational space is higher for the glassy system. Indirectly the large

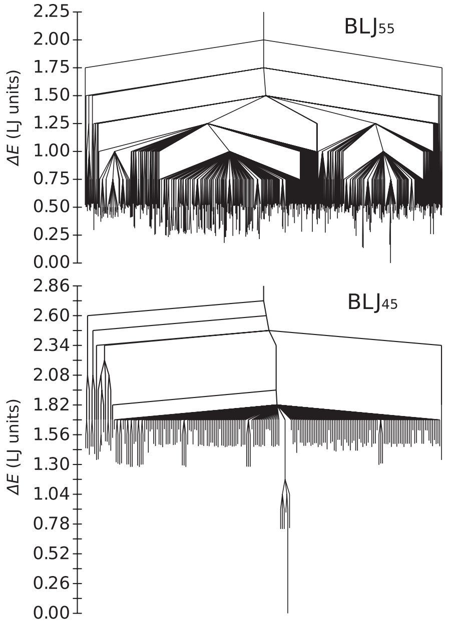

FIG. 4. Disconnectivity graphs for the glassy BLJ_{55} (top) and nonglassy BLJ_{45} (bottom) clusters. The graphs were produced with the disconnectionDPS software [28].

number of close-by minima also indicates that low energy saddle points exist around the global minimum. This is related to the Bell-Evans-Polanyi principle [29] which states that barriers are low if the educt and product of a chemical reaction are similar. Hence the system has a distribution of low and high barriers, which is the characteristic of glassy systems.

We next demonstrate the capability of the method by investigating real clusters treated at the DFT level. We consider four clusters: C_{60}, $B_{12}H_{12}^{2-}$, $B_{16}N_{16}$, and B_{80}. All the low energy metastable configurations required for the DE plots were found using the minima hopping method [30] coupled to the BigDFT electronic structure code [31,32]. The DE plots are shown in Fig. 6. Since the covalent radius of each atom type enters into the calculation of the fingerprint [22], the distances plotted along the x axis can be considered to be in units of the bond length. This scaling allows us to compare systems with different bond lengths. The natural energy scale along the y axis would be the atomization energy per atom. Since the atomization energy for all these covalently bonded systems are comparable (3–4 eV), it would hardly have any visible effect on the logarithmic energy scale of the figure and no such scaling was therefore performed. The DE plots therefore show the energy per atom relative to the global minimum for all systems.

We will first consider the C_{60} cluster, whose experimental synthesis in 1985 [33] was considered a major breakthrough in chemistry. It is well known that the first local minimum corresponds to a Stone-Wales defect [34] and that it is significantly higher in energy than the ground state (≈1.6 eV). A disconnectivity graph based on DFT energies for saddle points that were found by a tight binding scheme has also been constructed for this system [35] and it was found to be of the weeping willow type, indicating that it is a structure seeker at higher temperatures. This explains the necessity of high temperature for its experimental synthesis. In the DE plot, the relatively high barriers can be deduced from the relatively large configurational distance of the lowest metastable structures from the global minimum. The second system is the chemically highly stable icosahedral dodecahydro-closo-dodecaborate dianion $B_{12}H_{12}^{2-}$, which was already synthesized in 1960 [36]. Its structure seeker character can be deduced from the fact that the first metastable structure is much higher in energy than the ground state, but not too far in configurational distance. This suggests that the barrier for jumping from the first metastable structure into the ground state is relatively small and that there is in general a strong driving force towards the ground state. The $B_{16}N_{16}$ has also been observed experimentally [37] and it also exhibits structure seeker features in its DE plot. A system which exhibits a behavior quite opposite to these clusters is the B_{80} cluster for which the lowest structure consists of a 12 atom icosahedron embedded in a disordered half dome structure [38]. This is the only system for which no well characterized experimental structure has been found. Its DE plot is totally different from the other systems. There are numerous metastable configurations, which are both close in energy and close in configurational distance to the ground state. This means that, there are many close-by configurations of similar energies, separated by barriers of different heights. Therefore we predict B_{80} to be glassy.

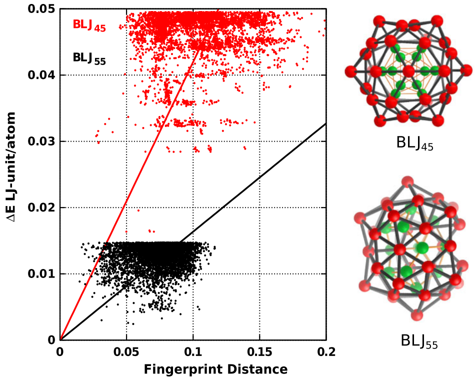

FIG. 5 (color online). DE plots for the investigated glassy (black dots) and nonglassy (red dots) BLJ systems together with their ground state structures. Only the lowest 5000 configurations are considered. The two solid lines show least-square fits to the two data sets. Their slope is a measure for the average driving force towards the ground state. The coordinates of the shown structures can be found in the Supplemental Material [24].

In conclusion, we propose DE plots as a computationally tractable method to characterize a PES on the DFT level. Such DE plots clearly show the strength of the driving force towards the ground state and contain information about the density of metastable configurations in the configurational space. By applying it to several realistic clusters treated on the DFT level, we find clusters with both glassy and nonglassy behavior. All the investigated clusters that were synthesized experimentally exhibit a nonglassy energy

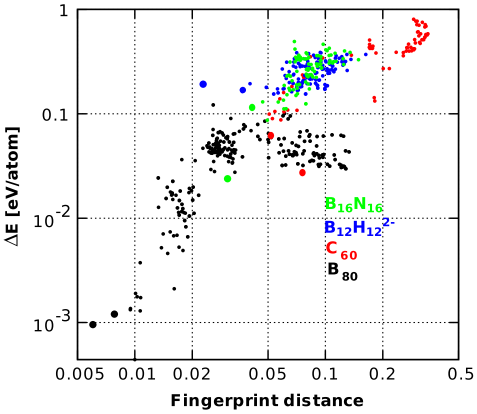

FIG. 6 (color online). DE plots for a B_{80}, C_{60} ,$B_{12}H_{12}^{2-}$ and $B_{16}N_{16}$ cluster. Configurations close to the ground state are shown by larger discs.

landscape. This suggests that a landscape of this type is a prerequisite for experimental synthesis.

We thank the Indo-Swiss Research grant and SNF for the financial support and CSCS (project s142) for computing time. D. G. K. acknowledges a number of discussions with Chandan Dasgupta.

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