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Efficient statistical mapping of energy surfaces of nanoclusters and molecules

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Abstract

A statistical technique to efficiently map out the energy surfaces of nanoclusters and molecules is described. Global energy minimizations are performed to reach of the catchment basins of the lowest energy stationary points. Saddle points are located by using a large value of the iterative energy change as the stopping criterion of a final local relaxation. Minima are derived from saddle points by simply tightening the stopping criterion and continuing the relaxation. A statistical approximation to the widths of the paths in phase space between saddle points and minima is obtained. Application is made to argon clusters of 7 and 38 atoms.

1. Introduction

Understanding the dynamical behavior of small clusters of atoms and molecules in nonzero temperature environments is indispensable to their eventual utility in nano-chemical, nano-electronic, and nano-optic applications [1,2]. Equilibrium molecular dynamics is normally employed to model the thermodynamical behavior of an ensemble of such systems by employing the ergodic hypothesis. However, a time averaged, or even an ensemble description is not very useful for predicting the time local dynamical behavior of a single nanocluster or molecule. Such behavior can only be obtained by knowing the initial state and by detailing the local free energy surface of the system in the neighborhood of that state. Furthermore, molecular dynamics cannot readily identify particular reaction paths, these can only be delineated by directly mapping the topography of the energy surface.

Even if the interest is in the average behavior of an ensemble in thermodynamic equilibrium, calculation of the forces in molecular dynamics is computationally expensive, and it can be expected that a typical trajectory, even for small clusters, will only visit a small fraction of the allowed phase space, making a poor approximation to ergodicity. The need for statistically based methods to characterize the potential energy surface for large systems has been previously emphasized [3,4].

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Periodic quenching along molecular dynamic traces to find minima, and eigenvector following to find associated saddle points, has been the technique of choice to statistically map out potential energy surfaces [5–8]. This technique samples efficiently the potential energy minima and some of the lowest energy connecting saddle points, thereby allowing construction of 'disconnectivity graphs' [9–11] which characterize the global nature of the energy surface. However, this method does not provide a very detailed map of the lowest energy topography, since, for reasons of computational economy, normally only the path determined by the smallest positive eigenvalue of the Hessian, evaluated at the minimum, is explored. All other paths available from one given minimum to another are usually ignored. The resulting map is thus only a skeleton of the real multi-dimensional topography, defining the path of likely least activation energy. Even in exceptional cases where all of the saddle points are obtained [12], information needed for describing the dynamics or thermodynamics is still lacking since no measure is obtained of the widths of the paths in phase space, or, in other words, of the most important part of the enthropic contribution to the free energy.

Another proposed technique, also employing molecular dynamics, is to raise the total energy starting from a given minimum until the potential energy drops below this minimum. Quenching finds the second minimum, and the saddle point connecting the two is then obtained by quenching from the point of maximum potential energy on the molecular dynamic trace using a large cutoff value for the kinetic energy [13]. As with the eigenvector following approach, this method obtains a path which may be the most probable reaction path in phase space, but little information is provided on the possible range of paths and their probabilities and thus on the spectrum of allowed dynamical behavior.

2. Statistical characterization of the energy surface

In this Letter, we present an efficient technique for mapping out in detail the topography of the lowest energy regions of the potential energy surface. This is achieved through a statistical sampling of the probability of passing from saddle point to saddle point, or from saddle point to minimum by enumerating the trajectories taken by a fast conjugate gradient local relaxation, once an effective global search has put the system within reach of the lowest energy saddle points and minima. Saddle points are located by using a large value of the relative energy change per iteration, $|\Delta V/V|$, as the convergence criterion of the local relaxation. Minima are obtained from saddle points by simply tightening the criterion for convergence and continuing the relaxation. Saddle points can be obtained from saddle points by tightening the convergence criterion and relaxing it once again if the potential energy has decreased by more than a few percent. The relative volume in phase space of the attraction basin associated to a particular minimum or saddle point at the site of a saddle point can thus be statistically estimated and probabilities for reaction paths assigned. No calculation of the forces in the global relaxation, nor of the Hessian in the local search, is required. With moderate computational resources, the low-energy regions of systems of up to approximately 100 atoms can be routinely mapped out (with somewhat lower efficiency for short range potentials since these give a more complex energy surface [14]).

As a demonstration of this technique, we present the topography mapping of the potential energy surface of argon clusters of 7 and 38 atoms, modeled with a Lennard–Jones (LJ) potential of form

$$V = \sum_{i<j} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right], \qquad (1)$$

with $\sigma = 3.4$ Å and $\epsilon = 1.671 \times 10^{-14}$ erg [7]. The potential energy surface of this system has been studied through the conventional technique of molecular dynamics and eigenvector following [7,11–13,15–18]. It is known that, within the LJ model, Ar_7 has four minima and at least 838 saddle points [12]. The low-energy minima and their connections through the lowest energy saddle points for Ar_7 have been enumerated by Wales and

Berry [7] through the eigenvector following method, providing a convenient check of our proposed technique. Ar_{38} has a much more complicated potential energy surface topography due to the larger number of degrees of freedom. The global minimum is known to be a truncated octahedron fcc structure but an icosahedral structure is almost degenerate in energy and has a much larger catchment basin accessible from higher energy [15]. Ar_{38} is presented here as a demonstration of the efficiency of the proposed technique and of the detail in the topography map which can be obtained.

Our technique employs a hybrid algorithm consisting of a global, 'symbiotic' variant [19] of the genetic algorithm [20], followed by a local conjugate gradient relaxation [21]. The conjugate gradient relaxation (analogous to fast quenching in the molecular dynamics scheme) is initiated if, after a fixed number of generations of the global genetic optimization, the lowest energy obtained for the system has not changed [19]. Since the interest is normally in the lowest energy minima and saddle points, those with significant representation at 300 K for example, for large systems the search algorithm can be tuned to find only these stationary points by prolonging the global part of the search. However, for the case of Ar_7 where the system is relatively small, and to demonstrate the completeness of our approach, we tune the algorithm to find also higher energy stationary points.

The distribution in energy of stationary points, and the number of times each was found in 860 000 distinct runs of the global algorithm for Ar_7 is plotted in Fig. 1. In section (a) of the figure, the convergence criterion, $\Lambda \equiv |\Delta V/V|$, for stopping the conjugate gradient refinement was set very tight, $\Lambda = 10^{-12}$ per iteration, meaning, as explained below, that the stationary points represented in large numbers in Fig. 1a are minima. For example, explicit calculation of the Hessian reveals that of the 55 points plotted in Fig. 1a only the four lowest energy points are minima (as found in [7]), the other 51 points corresponding to saddle points, inflexion points, or partial cluster minima with less than 7 atoms (for example, the spike at -0.207×10^{-12} erg corresponds to the octahedral global minimum of Ar_6 plus 1 atom at a large distance).

The novelty of the approach presented here is that the ratio of finding saddles to finding minima may be increased by increasing the value of the convergence criterion Λ. Section (b) of Fig. 1 corresponds to the results of the runs with the

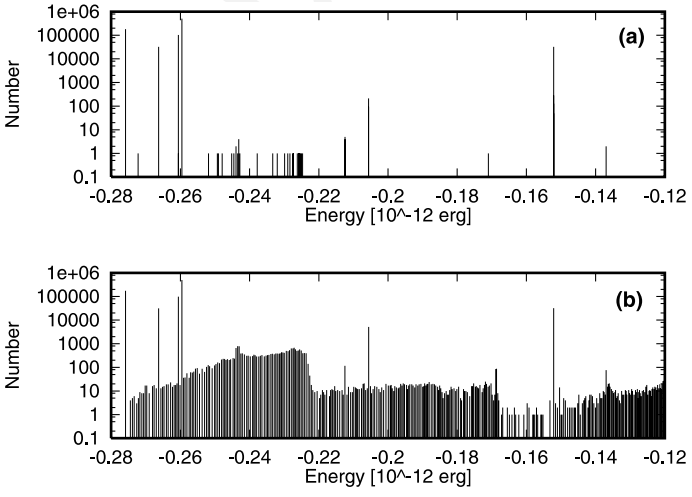

Fig. 1. (a) Energy distribution of the stationary points found for Ar_7 in 860 000 runs of the algorithm using a tight convergence criteria of $\Lambda = 10^{-12}$. (b) The same but for $\Lambda = 10^{-8}$, showing that the algorithm converges more often on points which are not minima (many of which are saddle points). The number of times the point was found is plotted with logarithmic scale on the y-axis.

same initial conditions but with the convergence criterion set loose at $\Lambda = 10^{-8}$. The algorithm now converges with greater probability on stationary points which are not minima. Explicit calculation of the Hessian of 80 points chosen at random from the distribution shows that roughly 64% of these are saddle points, 11% are inflexion like points or shallow valleys, while the rest correspond to minima of less than 7 atoms, saddles of minima of less than 7 atoms, and minima of 7 atoms. The increased probability of converging on a saddle point when using a larger value of Λ is due to the fact that the implementation of the conjugate gradient minimization is necessarily discrete. Therefore, unless the discrete displacement in configuration space is in the direction of the eigenvector corresponding to an eigenvalue of the Hessian which is negative, i.e., on the concave downward part of the saddle, a larger value of Λ leads to a higher probability that the algorithm will converge if the search is in the immediate neighborhood of the saddle point. This probability is related to the number of positive eigenvalues of the Hessian at the saddle point and to the inverse of the magnitudes of these. The convergence probability will be greater for conjugate gradient minimizations than for steepest decent methods which tend to follow directly the eigenvectors corresponding to large negative eigenvalues.

Making the convergence criteria too large leads to preferential convergence on neither a minimum nor a saddle point, but somewhere else, for example, at some point in the basin of a shallow valley or at an inflexion like point. Although such topographical features clearly play an important role in the dynamics, the immediate interest of this Letter is to locate either saddle points or minima. The optimal is thus to converge on as many true low-energy saddle points as possible while at the same time avoid converging elsewhere. A value of $\Lambda = 10^{-8}$ was empirically determined for the LJ potential, and for the cluster sizes presented here, to provide the best compromise in this sense. This rather tight stopping criteria eliminates the possibility of stopping on all slopes which are not almost zero on the potential energy surface. To eliminate inflexion like points from the sample, we require that the stationary point connects directly at least two distinct minima. Finally, we require that the stationary point–minima connections are found at least three or more times for Ar_7, and at least two or more times for Ar_{38} where the statistics are less. Since each run of the algorithm is from a different initial configuration, it is improbable that the algorithm will converge at the same point in energy within a shallow valley in distinct runs. However, the probability of converging at the same point will be much higher if the algorithm is lead to that point by the curvature of the potential energy surface, as in the case of true saddle points. These three saddle point selection criteria eliminate, to a great extent, spurious, shallow valley and inflexion like points.

The algorithm is thus first run with $\Lambda = 10^{-8}$, and, after recording the energy at which the algorithm converges (with significant probability on a saddle point), changing the value of Λ to 10^{-12} and continuing the optimization. This convergence criterion is almost always sufficient to allow the discrete search to leave the saddle point. If the potential energy then drops by more than 2%, Λ is again changed to 10^{-8}, allowing for the possibility of convergence on a second, lower energy saddle point. The process is repeated until the conjugate gradient code converges finally, with $\Lambda = 10^{-12}$, on what must be a local minimum. Since the algorithm is efficient and can be run hundreds of thousands, or millions, of times, each starting from a distinct random initial configuration of the atoms, statistics are accumulated concerning the widths of paths in phase space leading from saddles to minima, or saddle points to saddle points. The same saddle point may be found on the route to various different minima. The reconstructed energy surface thus consists of not only the interconnections between saddle points and between saddle points and minima, but also probabilities associated to these reaction paths. To the extent to which the conjugate gradient relaxation is similar to the relaxation approach taken by Nature, the calculated probabilities provide an approximation to the real attraction basin widths in phase space. It is noted that here we are moving over a surface defined by an empirical potential fitted to experimental data rather than by a quantum first principles calculation incorporating all relevant

degrees of freedom. However, not withstanding the much larger CPU costs involved in the latter, the method is applicable to both approaches.

The detail in the potential energy surface for Ar_7 can be surmised from Fig. 2 which plots the minima, saddle points, and their interconnections (saddle point to saddle point connections are not shown). The connection of a saddle point to a minimum is drawn only if the point was found to connect at least two minima and only if the the connection was found three or more times. Minima were considered to be the same if their energies were within 0.00001×10^{-12} erg and saddle points were considered to be the same if their energies were within $.0003 \times 10^{-12}$ erg. In Fig. 2, the horizontal and vertical positions of the minima correspond to their actual energies. The vertical positions of the saddle points correspond to their actual energies while the horizontal positions were taken to be at the center of the distribution in energy of all the minima they connect. The width of the connecting lines in the figure is drawn proportional to the number of times the connection was found, and represents an approximation to phase space widths. In total, 305 saddle points connecting directly two or more minima, and found three or more times, are shown in the figure. We did not find any points in Fig. 2 which were not either saddle points, or minima of 6 atoms with one atom at a large distance.

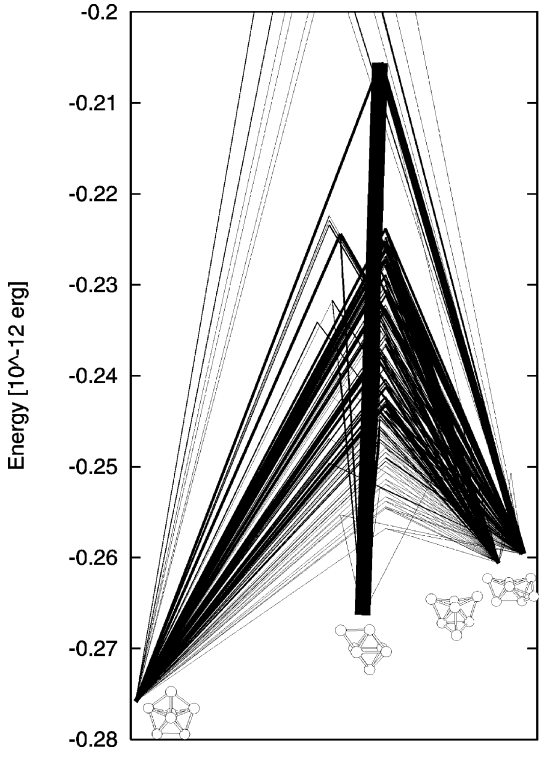

Fig. 2. Plot of saddle points and connections to minima for Ar_7. The saddle points were obtained with a convergence criterion $\Lambda = 10^{-8}$ while the minima were obtained with $\Lambda = 10^{-12}$. Only saddle points which connect at least two minima, and only connections obtained at least three times are plotted. The thickness of the connecting lines is proportional to the number of times the connection was found.

Note that the lowest energy saddles connect isomer 1 with isomers 3 and 4, and not with isomer 2. The number of saddle points which connect more than two minima is substantial, and these connect isomer 1 with isomers 3 and 4. Note that isomer 2, which is the capped octahedron, is fed only substantially from the Ar_6 octahedron plus one atom (energy -0.207×10^{-12}). Even though such a point is not a traditional saddle point, neither is it an inflexion point (since the potential energy surface is asymptotically flat in the configuration coordinates of the single atom) nor a shallow valley (since it connects in fact three distinct minima directly). Its delineation, however, is important to the thermodynamics of the system. For example, it predicts that the capped octahedron will be stable with respect to thermal excitation since the only reaction path of substantial phase space volume consists of essential evaporation of the capping atom (occurring at a rather high total energy, or temperature).

For Ar_{38}, 100 000 runs of the algorithm were performed. Here, in order to obtain good statistics for the different paths leading to the very lowest energy minima, the results of the global optimization are augmented by a factor of 10 by applying light, stochastic perturbations, 'shakes', of the low-energy configurations found. Local optimization, with the conjugate gradient relaxation, then proceeds for each shake in the same manner as described above. In Fig. 3 only those saddles which connect at least two minima of low energy ($< -2.83 \times 10^{-12}$ erg), and found two or more times, are shown (4803 saddle to minima connec-

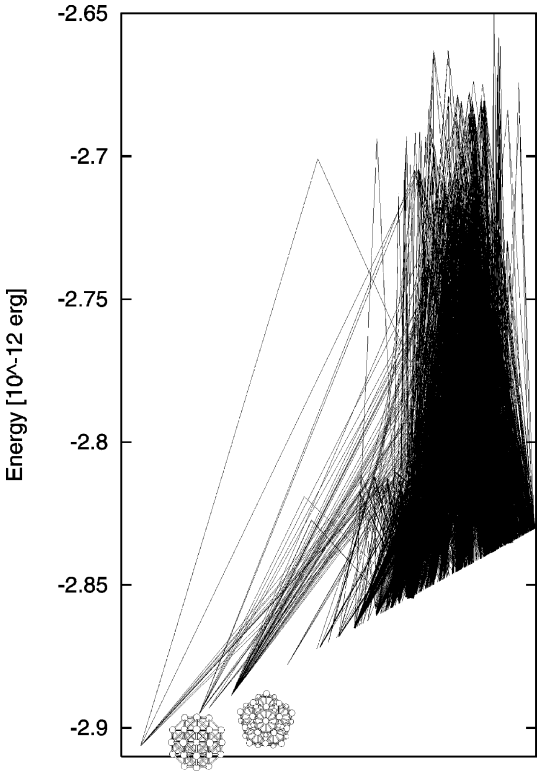

Fig. 3. The same as for Fig. 2 but for Ar_{38}. Only saddle points which connect at least two minima with energies below -2.83×10^{-12} erg, and which were obtained two or more times, are plotted.

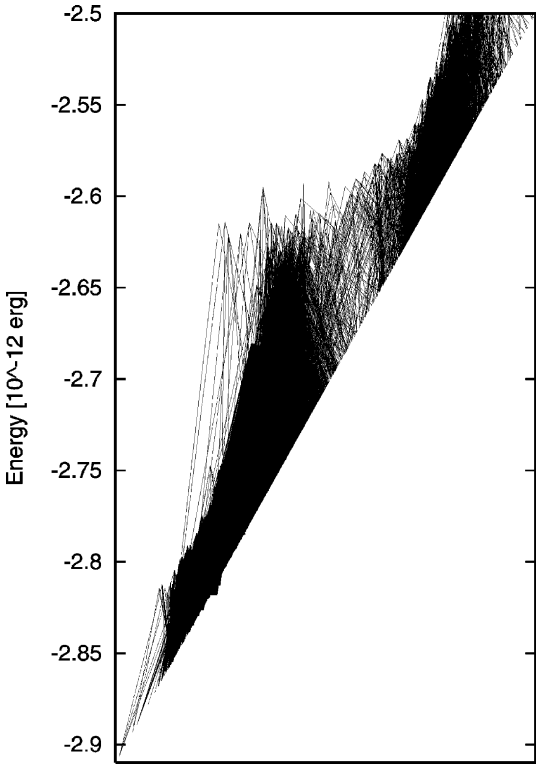

Fig. 4. Saddle point–minima connections found three or more times for Ar_{38}. The width of the lines is proportional to the number of times the connection was found.

tions in total). Note that information used in plotting the figure is, for example, sufficient to delineate the reaction paths between the global minimum fcc and icosahedral isomers, and, additionally, to obtain an approximation of the phase space widths of these paths. In Fig. 4, all of the saddle to minima connections for Ar_{38}, found more than three times, are shown. This figure includes more than 35,780 of the lowest energy saddle to minima connections.

3. Discussion and conclusions

Energy surface maps such as the ones given in Figs. 2–4 contain sufficient information to determine the dynamics and thermodynamics of these finite systems at finite temperature. For example, transition rates between isomers in equilibrium can be estimated from the energies of the minima and connecting saddle points, and a measure of the phase space volume of the local potential wells and saddle points [22]. The volume is usually obtained through calculation of the 'curvature' of the potential energy surface, obtained from the determinant of the Hessian of the potential energy function [22] evaluated at the minimum. Such a description, however, is not very accurate since the curvature at the site of the minimum is not the curvature of the potential energy surface near the saddle point. The statistical approach of enumerating trajectories better approximates the phase space volume of the actual path from a saddle to a minimum. All reaction paths along with their respective probability weights can be considered in the calculation of the transition rate. Such phase space volumes are also adequate for understanding

out of equilibrium processes such as relaxation or nucleation, processes from high to low potential energies. Explicit use of our topography maps to predict the dynamics and thermodynamics of nanoclusters will be the subject of a forthcoming paper.

We have presented a very simple and efficient technique for determining the low-energy topography of the potential energy surface of molecules and nanoclusters. The technique employs an efficient global algorithm, combined with stochastic perturbation, which reaches the lowest energy regions of the potential energy surface, and an iterative conjugate gradient local relaxation which can be biased to converge in the neighborhood of a saddle point by setting the convergence criterion loose enough. The technique not only finds the connections between saddle points and minima, or between saddle points and saddle points, but also approximates the phase space volumes of these paths through statistical sampling.

The approach represents a considerable improvement over eigenvector following techniques in the sense of being more efficient in the determination of the low-energy topography of the energy surface, and of providing widths for the paths in phase space. Most of the reaction paths leading from one low-energy minimum to another can be found and characterized, leading to an accurate determination of the dynamical or thermodynamical behavior of clusters or molecules, in or out of equilibrium.

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