Taming the Rugged Landscape: Techniques for the Production, Reordering, and Stabilization of Selected Cluster Inherent Structures

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Taming the rugged landscape: Techniques for the production, reordering, and stabilization of selected cluster inherent structures

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We report our studies of the potential energy surface (PES) of selected binary Lennard-Jones clusters. The effect of adding selected impurity atoms to a homogeneous cluster is explored. Inherent structures and transition states are found by combination of conjugate gradient and eigenvector-following methods while the topography of the PES is mapped with the help of a disconnectivity analysis. We show that we can controllably induce new structures as well as reorder and stabilize existing structures that are characteristic of higher-lying minima. © 2003 American Institute of Physics. [DOI: 10.1063/1.1562621]

I. INTRODUCTION

The minimization/optimization problem is one of the more ubiquitous and challenging in computational science.1 Central to researchers in the physical sciences and engineering, this problem is also of primary importance to social, biological, and economics investigators.

Driven in large measure by such widespread interest, there has been appreciable progress on the minimization problem. Especially notable have been algorithmic advances in the form of annealing and stochastic relaxation approaches1–6 as well as basin-hopping techniques.7,8 In both classical and quantum form, these methods offer valuable, complementary alternatives to traditional, gradient or pseudogradients approaches.1

In addition to algorithmic developments relevant to the minimization problem, there have also been notable advances in the tools to classify and analyze the topography of the underlying objective functions. In chemical applications, the principal focus of the remainder of our discussion, the objective function of interest is typically a specified potential or free energy surface. Following Stillinger and Weber,9,10 it is useful to perform an “inherent structure” decomposition of the associated configuration space by employing the minima (local and global) of this surface. These inherent structures, their relative orderings, and their connectivity provide important information concerning the structure, function, and dynamics of the associated physical system. Disconnectivity analysis introduced by Czerminski and Elber,11 discussed by Becker and Karplus,12 and developed by, among others, Wales, Doye, and Miller13–15 has proved especially valuable with respect to these latter tasks.

As evidenced by the development of classical and quantum annealing methods, there is an important interplay between minimization and the Monte Carlo sampling problem. Both applications, for example, are concerned with overcom-

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dependence of selected physical properties, and provide valuable test beds for the development and application of emerging computational techniques. This combination of formal, computational, and technological interest has produced a vast and growing cluster literature.31–33

The remainder of the paper is organized as follows: In Sec. II we outline the computational details of the present study. We discuss the methods we use to determine the inherent structures and transition states of a specified cluster’s PES. Using these methods, we examine specific results for two prototype systems in Sec. III. These particular results are designed to demonstrate “proof of principle” with respect to the basic objectives of the present study for selected systems. Finally, in Sec. IV we summarize our results and speculate about likely future research directions.

II. COMPUTATIONAL DETAILS

The present section describes the computational details of our investigations involving binary clusters of the form $X_nY_m$. Our overall interest will be to explore the extent to which we can utilize the “adatoms” (i.e., the $Y$ system) to induce, reorder, and stabilize selected inherent structures in the “core” $X$ system. While one can easily imagine applications involving both more and more complex components, we feel these relatively simple, two-component clusters are a convenient starting point for an initial study of the issues we raise.

We shall assume in what follows that the total potential energy is composed of a pairwise sum of Lennard-Jones interactions. Specifically, we assume that the total potential energy, $V_{\text{tot}}$, for an $N$-particle system is given by

$$V_{\text{tot}} = \sum_{i<j}^N v_{ij}(r_{ij}),$$

where the pair interaction as a function of the distance between particles $i$ and $j$, $r_{ij}$, is given by

$$v_{ij}(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right].$$

In Eq. (2) the constants $\varepsilon_{ij}$ and $\sigma_{ij}$ are the energy and length-scale parameters for the interaction of particles $i$ and $j$.

For a two-component system, we must specify both the “like” ($X-X$, $Y-Y$) as well as the “mixed” ($X-Y$) interactions. With an eye toward studying trends in the results as opposed to results for particular physical systems, it is convenient to reduce the number of free parameters. To do so, we shall assume in the present study that the “mixed” Lennard-Jones values are obtained from the “like” Lennard-Jones parameters via usual combination rules

$$\sigma_{XY} = \frac{1}{2}(\sigma_{XX} + \sigma_{YY}),$$

$$\varepsilon_{XY} = \sqrt{\varepsilon_{XX}\varepsilon_{YY}}.$$  

Furthermore, we note that with the mixed Lennard-Jones parameters specified as in Eqs. (3) and (4), the inherent structure topography of the “reduced” potential energy surface of the binary system (i.e., $V_{\text{tot}}/\varepsilon_{XX}$) is a function of only two parameters, $(\sigma, \varepsilon)$, the ratios of the corresponding adatom/core length and energy parameters,

$$\sigma = \sigma_{YY}/\sigma_{XX},$$

$$\varepsilon = \varepsilon_{YY}/\varepsilon_{XX}.$$  

If necessary for a discussion of a specific physical system, the absolute bond lengths, energies, activation energies, etc., can be obtained from the corresponding “reduced” results by a simple rescaling with the appropriate core-system Lennard-Jones parameters.

The computational task in our study is thus one of exploring and characterizing the (reduced) potential energy surface of our binary cluster systems as a function of the number of (core, adatom) particles, $(n,m)$, and for given $(\sigma, \varepsilon)$ ratios. In typical applications the lowest $N_{\text{IS}}$ inherent structures and the associated disconnectivity graphs are determined. For the applications reported here, $N_{\text{IS}}$ is generally of the order of a few hundred (thousand) or less. Depending on the size of the cluster, inherent structures are found either via conjugate gradient methods starting from randomly chosen initial configurations, or by more systematic surface exploration methods such as those outlined by Wales and co-workers14 and by Jordan et al.35 In all cases, the inherent structures that are located are confirmed to be stable minima via a standard Hessian analysis. To reduce the chance we miss particular local or global minima, we monitor the number of times individual inherent structures are found and demand that each of the $N_{\text{IS}}$ inherent structures be located a minimum number of times (at least 10) before we terminate our search. Once we are satisfied we have located the relevant inherent structures, transition states linking these stable minima are obtained using the eigenvector following methods outlined by Cerjan and Miller36 and further developed by Simons et al.,37–39 Jordan et al.,35 and Wales.40 Finally, with the requisite inherent structures and barriers in hand, we perform a disconnectivity analysis using methods outlined by Czerminski and Elber,11 Becker and Karplus,12 and Miller et al.13

III. NUMERICAL RESULTS

In the present section, we wish to illustrate the general themes we introduced in Sec. I. We do so by demonstrating that we can accomplish three basic objectives. Specifically, we show that by adding selected “impurity” atoms to bare “core” systems, we can:

1. induce new “core structures,”
2. reorder the energies of existing core inherent structures, and
3. stabilize selected inherent structures by controlling the activation energies that determine their isomerization kinetics.

For purposes of illustration, we shall examine numerical results for a few, simple Lennard-Jones systems involving five and seven core atoms, systems well-known from previous studies to have one and four energetically distinct inher-
ent structures, respectively. The inherent structures and their associated energies for these core systems are illustrated in Figs. 1 and 2.

We first consider mixed clusters of the generic type $X_5Y_2$. Here two impurity $Y$ atoms are added to the parent, five-atom $X$ core. We have chosen this system because it builds upon the very simple five-atom core, a system that has only a single inherent structure, and because the total system has a total of seven atoms, a magic number for icosahedral growth in homogeneous systems. Using the techniques of Sec. II, we then determine the lowest several inherent structures for a range of $(\sigma, \epsilon)$, c.f. Eqs. (5) and (6). As can be seen from Fig. 3, the total potential energy [Eq. (1)] of the lowest inherent structure for the $X_5Y_2$ system shows no appreciable structure as a function of the $(\sigma, \epsilon)$ parameters.

On the other hand, we see in Fig. 4 that the core potential energy, defined as the potential energy of interaction for only the core $X$ atoms, of the minimum (total) energy cluster clearly breaks into extended regions, each corresponding to a well-defined core structure. The reader should notice that each region in Fig. 4 contains the same “kind” of core structure but their core energies are slightly different. We have chosen a single “average” core energy value to represent all energies in the corresponding domain for plotting convenience.

The distinct core structures, shown in Fig. 4, have been identified by examining their core energies ($E_{core}$) and their
principal moments of inertia. For each structure a triplet of
values \((E_\text{core}, I_2, I_3)\) has been associated, where \(I_2\) and \(I_3\)
are the moments of inertia about the principal axes 2 and 3,
respectively. We have defined \(I_2\) and \(I_3\) in the following way:
\(I_2 = I_2'; I_3 = I_3'; \) where \(I_2', I_3'\), and \(I_3'\) are the principal
moments of inertia obtained by diagonalizing the inertia ten-
sor of the system. If the triplet of values has not been suffi-
cient to identify a core structure then we have examined the
structure visually.

Selected cluster structures illustrating the core arrange-
ments corresponding to various \((\sigma, \epsilon)\) values are shown in
Fig. 5. We see from Figs. 4 and 5 that the \(X_5Y_2\) cluster
exhibits core \(X\)-atom structures that include trigonal bipyra-
midal, planar, and square pyramidal core geometries. Of
these, only the trigonal bipyramidal form is stable in the
parent \(X_5\) system. This illustrates that a suitable choice of the
\((\sigma, \epsilon)\) parameters can controllably induce core geometries not
present as stable minima in the bare cluster. For example, the
square pyramid core structure, seen in Fig. 5.2 as a stable
system, corresponds to a transition state in the bare \(X_5\) clus-
ter.

Figure 6 represents the \(X_6Y_2\) cluster at four points in
Fig. 4 defined by the \((\sigma, \epsilon)\) coordinates \((0.4,0.5), (0.4,1.0),\)
\((0.4,1.5),\) and \((0.4,2.0)\). Here the pairs of coordinates corre-
spond to (a), (b), (c) and (d) of Fig. 6, respectively. In other
words, we keep value of \(\sigma=0.4\) fixed, while increasing the
value of \(\epsilon\). Each disconnectivity graph shows all inherent
structures available to the system for the given \((\sigma, \epsilon)\) values.
The global minimum of each system is labeled by number 1
and contains as a recognizable component the square pyra-
mid core structure (see Fig. 5.2). In Fig. 6(a) the square
pyramid core structure is connected to two inherent struc-
tures, labeled 2 and 3, by pathways whose energies do not
exceed \(-13.8\) (in units of \(\epsilon_{XX}\)). Since isomer 2 contains the
same core structure (the square pyramid) as the global mini-
mum the corresponding isomerization thus does not lead to a
change in the core structure of the cluster. For present pur-
poses, therefore, the barrier that connects them is not a “re-
levant” barrier. The relevant barriers are those that connect
inherent structures that contain different core structures. The
inherent structure 3 contains as the core structure a (dis-
torted) trigonal bipyramid (see Fig. 5.3). Therefore, the
isomerization barrier that connects the inherent structure 3
with global minimum is the lowest relevant isomerization
barrier and its value is \(\Delta E_{1,3} = 0.986\epsilon_{XX}\). Figures 6(b) and
6(c) show that increasing the value of \(\epsilon\) increases isomeriza-
tion barriers that connect inherent structure 1 (the square
pyramid core structure) with inherent structure 2 (the dis-
torted trigonal bipyramid core structure). Numerically, these
barriers are \(\Delta E_{1,2} = 1.227\epsilon_{XX}\) and \(\Delta E_{1,2} = 1.431\epsilon_{XX}\), respec-
tively. In Fig. 6(d) the square pyramid core structure is con-
ected by an isomerization barrier of \(\Delta E_{1,2} = 1.647\epsilon_{XX}\) with
two (almost degenerate in energy) distorted trigonal bipyra-
mid core structures. As illustrated in Fig. 6 and discussed
earlier, the barriers that determine the isomerization kinetics
of these newly induced structures are sensitive to the \((\sigma, \epsilon)\)
values and can thus be at least partially controlled. These two
simple results are specific demonstrations of goals (1) and
(3) stated earlier.

As a second illustration, we consider mixed clusters of
the type \(X_7Y_3\). This system builds upon a parent, seven-
atom, “magic number” system known to exhibit a set of four,
ergontically distinct inherent structures. The core in-
herent structures and associated energies for the stable \(X_7\)
inherent structures are presented in Fig. 2. Figure 7, a \((\sigma, \epsilon)\)
contour plot of the core-atom potential energies of the lowest
total energy \(X_7Y_3\) clusters, again reveals the presence of
definite “core-phases.” As illustrated in Fig. 8, some of these
regions correspond to various core structures present in the
parent \(X_7\) system while others correspond to new structures
not seen in the original, single-component cluster. We can
see from Figs. 7 to 9 that the impurity \(Y\) atoms provide us
with significant control over the relative ordering of the core
energies of the parent \(X_7\) system. Specifically, by choosing
an appropriate range of \((\sigma, \epsilon)\) values, we can generate \(X_7Y_3\)
clusters in which the lowest (total) energy inherent structure
can have core structures that are either pentagonal bipyra-
mid, capped octahedral, or bicapped trigonal bipyramidal in
nature. Moreover, since we can manipulate the isomerization
barriers in these systems, we can at least partially stabilize
clusters that exhibit selected core structures with respect to
isomerization. This is illustrated in Fig. 9.

Figures 9(a)–9(d) represent the \(X_7Y_3\) cluster at four points
in Fig. 7 with \(X_7Y_3(\sigma, \epsilon)\) coordinates \((0.4,0.5),\)
\((0.4,1.0), \) \((0.4,1.5),\) and \((0.4,2.0)\), respectively. The number
of inherent structures available to the \(X_7Y_3\) cluster varies
from more than 800 in Fig. 9(a) to 400 in Fig. 9(d). Since we
are primarily interested in energetically low-lying inherent
structures we show only lowest 70 inherent structures. The
global minimum of each system is labeled by number 1 and

FIG. 5. Plots of \(X_5Y_2\) structures for selected \((\sigma, \epsilon)\) values. The decimal
number for each figure denotes the corresponding \((\sigma, \epsilon)\) domain in Fig. 4.
contains as a recognizable component the core structure shown in Fig. 8.5. We should mention that for a given range of \(\sigma\) and \(\varepsilon\) values, \((\sigma,\varepsilon)\in[0.1,2.0]\), we have not been able to find a global minimum that would contain as a recognizable component inherent structure 4 of the parent \(X_7\) cluster [see Fig. 2(d)]. This is the reason why none of the domains in Fig. 7 is labeled by number 4. In Fig. 9(a) the global minimum, the core structure 5 (see Fig. 8.5), is linked to inherent

FIG. 6. Disconnectivity graph for \(X_5Y_2\ (\sigma,\varepsilon)\) values demonstrating that we can control barriers for the selected inherent structures. The energy scale is in units of \(e_{XX}\). The \((\sigma,\varepsilon)\) values for panels (a)–(d) are (0.4,0.5), (0.4,1.0), (0.4,1.5), and (0.4,2.0), respectively.
structure 2 which contains the (distorted) capped octahedron core structure (see Fig. 8.2). The isomerization barrier between them is \( \Delta E_{1,2} = 0.494 \epsilon_{XX} \). Figures 9(b) and 9(c) show that increasing the value of \( \epsilon \) increases isomerization barriers, that connect inherent structure 1 (see core structure in Fig. 8.5) with inherent structures 3 and 2 (a distorted capped octahedron core structure), respectively. Numerically, these barriers are \( \Delta E_{1,3} = 0.975 \epsilon_{XX} \) and \( \Delta E_{1,2} = 1.136 \epsilon_{XX} \), respectively. The inherent structure 2 in Fig. 9(b) contains the same core structure as the global minimum and, therefore, has not been considered relevant for the isomerization [see the above-mentioned explanation for Fig. 6(a)]. In Fig. 6(d) the core structure 5 is connected to two, energetically almost degenerate, inherent structures labeled by 2 and 3, by pathways whose energies do not exceed \(-40.5 \) (in units of \( \epsilon_{XX} \)). Similar to the case of Fig. 6(a), isomer 2 contains the same core structure as the global minimum so the corresponding isomerization does not lead to a change in the core structure of the cluster. The barrier that links them is not a relevant barrier. The inherent structure 3 contains as the core structure a distorted capped octahedron. Therefore, the isomerization barrier which connects the inherent structure 3 with global minimum is the lowest relevant isomerization barrier and its value is \( \Delta E_{1,3} = 1.304 \epsilon_{XX} \).

**IV. CONCLUSIONS**

In the present work, we have considered the general task of altering core cluster structures. We are, in effect, attempting to turn the logic of the minimization problem upside down. Rather than seeking the global minimum of complex potential energy surfaces, we are instead attempting to exploit what has been learned about the general minimization problem to controllably alter core cluster structures. Specifically, we are examining the extent to which we can induce new core geometries as well as reorder and stabilize existing, higher-lying, local core structures.

Our approach, in the present discussion, has been thermodynamic in nature. We have utilized selected adatoms to effect our desired core cluster modifications. We have presented results for two simple binary cluster examples, the \( X_5Y_2 \) and \( X_7Y_3 \) systems, to validate our approach.

We speculate that there are at least two important directions for future theoretical development of the present ideas. One direction will be to explore the use of more complex adsorbates to achieve selected core cluster structures. One could, for example, imagine using “exterior” methods in which encapsulating agents of well-defined geometries were utilized to induce desired core structures. Alternatively, “interior” approaches in which complex objects, perhaps even previously engineered clusters, could be utilized as “seeds” or “templates” to produce a desired structure in the surrounding cluster (either globally or locally). Another important direction will be to explore the extent to which previously engineered cluster structures can be assembled using “cluster assembled materials” methods to produce larger scale, macroscopic structures. If this proves possible, it would seem to offer an important direction in the production of novel materials starting from synthetic precursors whose core structures and properties are highly varied and are under user control.
FIG. 9. Disconnectivity graph for \( X_7 Y_3(\sigma, e) \) values demonstrating that we can control barriers for the selected inherent structures. The energy scale is in units of \( e_{xx} \). Only branches leading to the 70 lowest-energy minima are shown.

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