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Confinement of the molecular dynamics trajectory to a specified catchment area on the potential surface: Application to clusters

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Abstract. Potentialities of the approach recently proposed in [1,2] are considered in an application to clusters. The approach makes possible a detailed investigation of particular inherent structures of a many-body system, including the transition between them. In contrast to the conventional approach, in which the system is allowed to explore the entire potential energy surface (PES), in this approach it is confined to a catchment area on the PES, which corresponds to the structures of interest. Illustrations are given for the Lennard–Jones (LJ) and carbon clusters.

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1 Introduction

There has been, in modern science and technology, a trend toward the consideration of particular structures and channels of reaction (nanoelectronics, molecular biology, etc.). At the same time, many-body systems such as clusters typically possess a large number of inherent structures (ISs), which present a real challenge for the computer simulation of specific structures and reactions.

The conventional approach to this problem is a combination of a molecular dynamics (or Monte Carlo) simulation with quenching [3–6]: One allows the system to explore the entire potential energy surface (PES) and quenches it at regular intervals in order to find out to which IS the current point in the phase trajectory of the system is related. Accumulating the points for the IS(s) of interest, one can calculate all equilibrium characteristics of a particular IS, the transition rates among certain ISs, etc. However, if the number of ISs is large, the probability that the system will visit a particular IS is generally small. Therefore, the system spends its time in investigating all other ISs rather than the IS(s) concerned. Hence such an approach becomes too time-consuming, even if possible.

In this paper, we consider an alternative approach to this problem, which has been proposed recently in our papers [1,2]. Namely, the system is suggested to be confined to a catchment area on the PES that represents either a single catchment basin (potential well) or a set of connected basins (wells). These two cases correspond to the investigation of a particular IS and of the transitions among certain ISs, respectively. Specifically, the approach is considered in application to the constant-energy molecular dynamics (MD) simulation technique.

A key element of this approach is the procedure of reversal of the phase trajectory of the system at the boundary of the catchment area. This procedure should allow the system to reproduce proper behavior in the area and should be suitable for practical calculations.

Methodologically, the proposed technique is complementary to the methods developed in [4,7–10] for studying PESs for complex systems such as clusters and biomolecules. The objective of these latter methods is to understand how the global PES is organized, whereas the intent of the proposed technique is a detailed investigation of local regions of the PES.

2 The approach

The method of constant-energy MD involves numerical integration of the coupled Newtonian equations for a set of atoms interacting through a given potential.

In the *conventional* approach, the system is allowed to explore all the PESs accessible to it at the given total energy. The system is quenched at regular intervals. Each quench leads to a minimum on the PES, which represents one of the ISs of the system. Thus, if one knows to which IS the current phase point in the MD trajectory is related, one can collect information about the IS(s).

Every IS is characterized by its energy V_0, the normal mode frequencies $\nu_1, ..., \nu_{3n}$, and by the order of the point group h. In the general case of nonlinear atomic configuration, six of the above frequencies (for the translational and rotational degrees of freedom) are equal to zero, and

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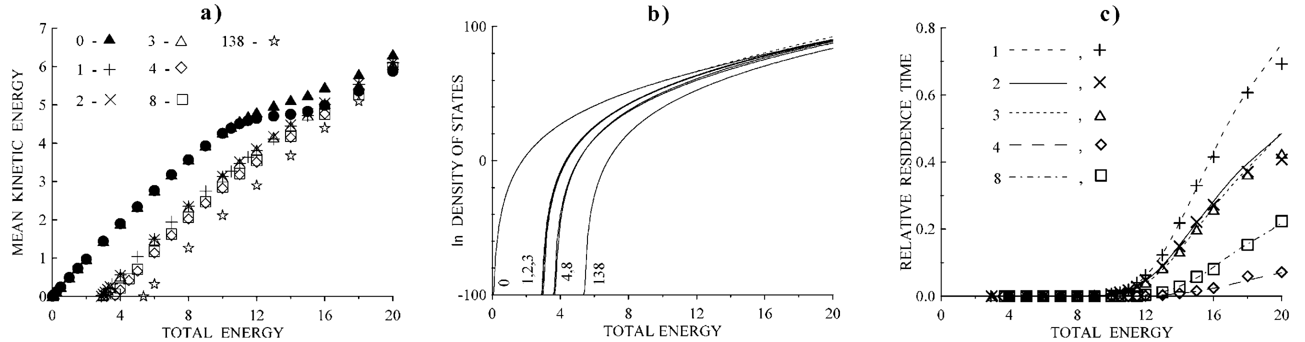

Fig. 1. LJ_{13}; isomers are numbered according to Table 1, and the total energy is counted from the ground-state isomer energy. (a) Caloric curves for particular isomers (solid circles show the total caloric curve). (b) The absolute fractional densities of states (the dashed line shows the total density of states). (c) The relative densities of states (lines) in comparison with the relative residence times (symbols).

the others are real. Permutational ISs are identified by the calculation of the distance in configuration space.

In the *present* approach, the system is confined to a catchment area on the PES. Specifically, the system is placed into the area, and the MD run is executed. As in the case of the conventional approach, the system is quenched at regular intervals so that it may be determined whether the system is still in this area or has left it. If the system has left the area, the trajectory is subjected to reversal at the boundary of the area.

In our calculations, the boundary of the area was located with an accuracy of one time step. For this, the last checking interval, as the system approached the boundary, was successively reduced by half until the boundary was fixed. It should be emphasized that the efficiency of the procedure of locating the boundary is of secondary importance for the discussed approach: Even if the checking were performed at every time step, the advantage over the conventional method would generally still be held since the system does not leave the catchment area under consideration. Note also that when one finds the system outside the given catchment area, one knows the basin where the system is located. Therefore one knows the ISs for which the system attempted to leave the given catchment area.

The suggested procedure of reversal [1, 2] involves three steps: The first step is the change of the signs of the velocities of all atoms at the point of reversal; this causes the phase trajectory to be "rejected" to the given area. The second step is the uniform random scattering of the components of atomic velocities within the β part of the mean value of the velocity. This scattering amplifies the effect of divergency of the phase trajectories, and as a result, a proper level of stochastization in the system is provided. We used $\beta = 0.4$ as a regular value. The last step is a correction of the integrals of motion of the system (the total energy and the linear and angular momenta for a free system).

At low and moderate energies, until saddles of high order were involved, the trajectory successfully returned to the basin every time when the reverse procedure was applied. However, as the energy increased, not every act of reversal furnished the desired result: After a few time steps within the true basin, the trajectory attempted to leave it again (this typically happened for the saddle regions in which the number of imaginary frequencies was as large as ten or higher). As a result, a new act of reversal was executed in a short time. Furthermore, at even higher energies, when the system had a pronounced tendency towards a decay, it happened that the phase trajectory cycled within a small part of the saddle region: The same sequence of the basins (but not of the same phase points!) in which the system was found at quenching repeated many times. Since such events were rare (one event to several tens of the attempts at decay), termination of the run was found reasonable in these cases, specifically if the length of the sequence exceeded 80; the points obtained prior to this sequence were taken into account in the statistics.

The proposed approach has been verified for a set of the Lennard–Jones (LJ) and carbon clusters by the comparison with the conventional approach. Specifically, there have been comparisons for the distributions of the kinetic energy and the residence times of the system in the basins, and for rates of transitions between particular isomers [2]. Note that according to the relation for the density of states derived in [1], the reproduction of the kinetic energy distributions ensures the reproduction of all equilibrium properties of particular isomers. All the characteristics were found to be in good agreement. The only small exception is the nonphysical enrichment of the distributions of the residence times at small times (of the order of one tenth of the vibrational period), an effect whose negative consequences for the other characteristics, in particular for the transition rates, have not been perceived.

3 Results and discussion

3.1 Caloric curves for particular isomers

Figure 1a presents the caloric curves for LJ_{13}, which is the smallest magic LJ cluster. The cluster executes no overall translation and rotation. Numerical values are given in the LJ units. Shown are the caloric curve (CC) for the ground-state isomer, the CCs for several excited-state isomers (starting from the lowest one), and the total CC.

Table 1. Characteristics of the isomers for LJ_{13}. The isomers are numbered according to their order in the isomer energy spectrum (among 1012 isomers found in the course of simulations). 0 labels the ground-state isomer. $\overline{\nu}$ is the geometrical mean of the normal frequencies.

Isomers	U_0	$\overline{\nu}$	h
0	−44.326801	1.750316	120
1	−41.471979	1.636509	2
2	−41.444597	1.635673	2
3	−41.394398	1.635996	2
4	−40.758513	1.638231	4
8	−40.670170	1.632131	1
138	−38.975810	1.553827	6

Each of the CCs for particular isomers was obtained by confinement of the system to one of the basins corresponding to the given isomer. Characteristics of the isomers are given in Table 1. Figure 1a clearly shows that the CCs for the excited-state isomers are very similar in appearance, and that they are remarkably different from the CC for the ground-state isomer. Moreover, if one counts the total energy for each of the isomers from its minimum energy, the CCs for the excited-state isomers follow each other with a good accuracy, even though the inherent structures of these isomers are quite different (cf. in particular the point-group order h, Table 1). A similar picture was observed for another magic cluster LJ_{55} and, surprisingly, for the nonmagic cluster LJ_{14}, which, in contrast with LJ_{13}, has one floating atom on the closed outer shell. On the other hand, the calculations conducted for another nonmagic cluster LJ_{33} showed that in this cluster, all the CCs for particular isomers, both for the ground-state isomer and for the excited-state ones, are similar to the CCs for the excited-state isomers in Fig. 1a. It follows that the form of the CC for a particular isomer is not completely defined by its inherent structure (as one could expect) but is also dependent upon the general structure (morphology) of the cluster. The latter finds its reflection, in particular, in the isomer energy spectra. To this end, it can be noted that the first three clusters (LJ_{13}, LJ_{55}, and LJ_{14}) have a similar isomer energy spectrum, and that this spectrum is quite distinct from that for LJ_{33} [11] (in the latter case, there is no characteristic energy gap between the ground-state isomer and the excited-state ones).

3.2 Absolute fractional densities of states and the "structural" ergodicity of the system

With the characteristics of a specific isomer (U_0, $\overline{\nu}$, and h) and its CC in hand, the absolute fractional density of states for this isomer can be calculated [1], in a manner similar to the calculation of entropy from caloric data in thermodynamics. Figure 1b shows the absolute densities of states thus calculated from the CCs of Fig. 1a (the total density of states was calculated from the total CC, as in [1]).

When calculating the density of states from the CC found by confinement of the system to a catchment basin, one deals with just a local region of the PES. This offers a unique opportunity for addressing the fundamental issue of statistical mechanics: the hypothesis of equal *a priori* probabilities, according to which the probability for the system to visit a given region of the PES is proportional to the fractional density of states corresponding to this region. Specifically, one can calculate the relative density of states for any pair of the isomers and then compare this value with the relative residence time for these isomers found from numerical simulations or experiment. For most systems, this question will likely be addressed to the numerical simulations or experiment and not to statistical mechanics itself, and the positive answer to it will testify that the numerical simulation or experimental data are correct. Figure 1c compares the densities of states for the excited-state isomers from Fig. 1b, which are related to the density of state for the ground-state isomer, with the corresponding relative residence times found by direct counting in the course of the conventional MD simulations. The agreement among the data, on the one hand, testifies to a representative sampling in the MD simulations; and on the other hand, it tells us that the system is "structurally" ergodic, i.e., it visits the isomers according to their fractional densities of states.

A similar comparison has been performed in [5, 6] for LJ_7, but the densities of states were calculated on the basis of a Monte Carlo sampling of the entire PES. In this respect, our approach appears to be more rigorous, since calculation of the density of state for a particular isomer is *a priori* based on the local region of the PES.

3.3 Diffusion in the subsystem of the permutational isomers

It is common that "real" many-body systems are too complex for theoretical study, and clusters are one case. Therefore it may be useful to consider a subsystem which retains many of the characteristic properties of the system, yet is much easier for theoretical consideration. Specifically to clusters, such a problem arises because of a large number of geometrically different isomers: The data obtained in numerical simulations (or experiments) represent some averages over a variety of the isomers. Because of this, comparison of analytical predictions with simulation or experimental data turns out to be a real challenge: On one hand, consideration of all essentially contributing isomers is impractical; on the other hand, introducing some effective average values of parameters in the theory to account for different characteristics of the isomers may disguise possible defects of the theory.

The isomers considered in the previous subsections are, in fact, the simplest examples of such subsystems. Another, more sophisticated subsystem is the manifold of the permutational isomers. In contrast to the individual isomers, kinetic processes are possible in this subsystem, in particular the process of self-diffusion. To illustrate this case, we chose the ground-state isomer of the LJ_{13}, whose permutational copies are directly connected through the transition states with $U = -41.5552$. The MD trajectory was confined to the area of the PES corresponding to the permuta-

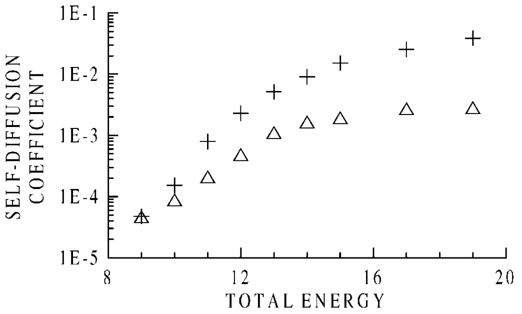

Fig. 2. Self-diffusion in LJ_{13}. $\triangle$: the subsystem of the permutational ground-state isomers; $+$: the system freely exploring all the PES. All values are given in LJ units.

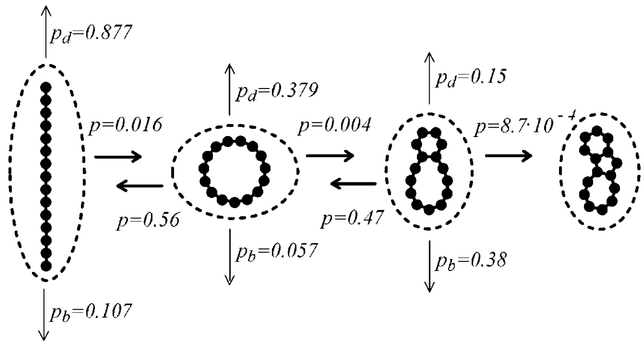

Fig. 3. Schematic picture of estimates of the rates of transition in the sequence of the C_{15} isomers. For details, see the text.

tional copies of the isomer, and the self-diffusion coefficient was estimated in the conventional way (as one sixth of the time derivative of the mean square displacement per atom). Figure 2 shows this coefficient in comparison with the self-diffusion coefficient for the whole system. It can be seen that the behavior of the self-diffusion coefficient in both cases is similar; this testifies that this simple subsystem can be used as a model system for studying diffusion in the whole system, which is incomparably complex.

3.4 Estimation of the rate of a complex transition

As has been shown in [2], the rate of transition from one specific IS to another can be calculated by confinement of the system to the catchment area corresponding to these structures. Moreover, it can successfully be estimated in a more simple and economic way: One confines the system to the catchment basin for the first IS and counts the number of the attempts at leaving this basin for the other IS.

Each of these methods can be used to devise an efficient procedure for estimating the rate of a complex transition when the initial and terminal ISs are separated by a set of the intermediate ISs: The system is successively confined to the catchment areas corresponding to two neighbouring ISs (starting from the first pair), or, more economically, to the catchment basins corresponding to the initial and all the intermediate structures. It is apparent that this procedure, as compared to a straightforward calculation of the transition rate (e.g., using the conventional approach), provides a considerable gain in the computation time. For example, for the second way of estimation, the gain obtained is on the order of $n^{-2}p^{-n}$, where n is the number of the intermediate basins, and p is the probability that the system will leave the basin for the neighbouring basin concerned.

To illustrate this procedure, we considered a 15-atom carbon cluster with the atoms bound by the Brenner potential [12] modified in [13] (Fig. 3). The ground-state isomer for this cluster is the ring ($V_0 = -92.1344\,\mathrm{eV}$). The total energy of the system was taken to be $E = -58.95\,\mathrm{eV}$, which corresponds to the temperature $T \simeq 8800\,\mathrm{K}$.

Starting from the linear chain isomer (V_0=-88.9509 eV), in which the system predominantly resided (because of a larger conformation entropy as compared to the ring), we successively confined it to the catchment basins for the ISs shown in Fig. 3; $V_0 = -87.4679\,\mathrm{eV}$ and $V_0 = -85.3930\,\mathrm{eV}$ for the double- and triple-ring structures, respectively. For each of the basins, the arrows show the probability (the relative number of the events) that the system will leave a given structure, and follow a specific channel (p), dissociate (p_d), or transform into the other bound structures (p_b). The rate of the first stage of the process (the chain-to-ring transformation), which corresponds to $p = 0.016$, is $5.92 \times 10^{10}\mathrm{s}^{-1}$. Then, for example, the rate of the transition from the linear structure to the triple-ring one can be estimated by the multiplication of the above rate and the corresponding values of p for two subsequent forward transitions. It is obtained as $2.1 \times 10^5\mathrm{s}^{-1}$. This process is obviously too slow to be observed in direct simulations.

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