Geometry, interaction range, and annealing

Xiao-yan Chang and R. Stephen Berry
Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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A method introduced by Stillinger for finding global minima of potential surfaces and for achieving the optimization objectives of simulated annealing is shown to require caution in some of its applications. In particular, a range parameter is varied to eliminate secondary minima on the potential surface or hypersurface of the objective function of interest. We show that in some cases, using minimizations on the simplified surface to reveal minima on the more complex surface require scrutiny of the sequences of low-energy minima, as functions of the range parameter whose variation controls the complexity of the surface.

I. INTRODUCTION

The shape of a multidimensional potential surface of a homogeneous cluster of atoms is much governed by the range of the range of the pairwise attractive forces between the atoms. Specifically, within the range of realistic pairwise potentials, the shorter the range, the more high-energy local minima the surface supports.[1-3] Stillinger and Stillinger have used this as an illustrative device for executing a general method of simplifying a search for global minima by simulated annealing, the "ant lion" method:[2] A complicated surface with many high-level minima is parametrized (and transformed from a discrete point set to a continuous surface, if necessary) so that the parameter mimicking the range of long-range, attractive pairwise interactions can be tuned. This range is extended, eradicating high-energy minima, until the surface is simple enough that straightforward annealing takes the system with high probability to the global minimum. If the method is successful in its simplest form, the global minimum for the system with long-range pairwise attractions is the adiabatic transformation from the realistic potential of the global minimum of the realistic system, with its shorter-range attractive interactions. This is clearly a powerful method, and will be very useful in making complex simulated annealing problems tractable. However, its success, at least in its simplest form, depends on the global minimum of the potential based on long-range attractions surviving as the global minimum when the range parameter is tuned to shorter-range interactions. Here, we present a cautionary note to illustrate two related points. First, that this adiabatic survival condition is not always met. Second, the sequence of low-lying minima can depend on the range of the pairwise potential so that the global minimum of the simplified surface need not be the range-shortened, adiabatic transformation of the global minimum of the complex, realistic surface. Consequently, adiabatic range tuning, as we shall call this procedure, must be done cautiously with checks of which minimum is the lowest, especially when it is apparent that the surface has more than one kind of very low-lying minimum.

We demonstrate this limitation of adiabatic range-tuning with a cluster of fourteen particles bound by pairwise Morse potentials, which we call M_{14}. If the range parameter is fixed to make the curvature of the pair potential match that of the Lennard-Jones potential, this becomes a moderately good model for Ar_{14}. In contrast to Ar_7[3] and Ar_{13},[2] the global minimum of M_{14} does depend on the value of the range parameter. We show here that the sequence of the lowest two minima of the multidimensional potential of this system changes with the value of the range parameter, so that the Stillingers' method is not universal, and must be used with appropriate checks.

II. METHOD

We briefly review the method as we used it. The realistic set of states for which the global minimum is sought is modeled by a smooth potential surface. The surface is made as simple as feasible by making the range of pairwise interactions very long. The surface is explored by a molecular dynamics or Monte Carlo search and minima are found by now-standard quenches of the kinetic energy, followed by determination of the energy of the local potential minimum, either by steepest descents (which we used here) or by the conjugate gradient method. The lowest minimum of the surface based on long-range interactions can then be used as the starting geometry for finding, by the same minimization algorithms, the minimum energy and the structure that yields that energy on the surface based on realistic short-range interactions.

The potential itself is derived from a sum of pairwise potentials with a long-range attraction and a short-range repulsion, e.g., a Morse potential,

$$V(r_{ij}) = \epsilon \sum_{i<j} \{\exp[2\beta(r_{ij}-r_0) - 2\exp[-\beta(r_{ij}-r_0)]\}, \quad (1)$$

where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ is the distance between atoms i and j, ϵ is the well depth (which would be 1.684×10^{-21} J for argon), β regulates the range of the well and r_0 is the equilibrium diatomic separating (3.76 Å for Ar). This potential can be expressed in scaled units and thereby be reduced to only one parameter, designated ρ_0, which determines the range of the interactions[3] (see Fig. 1). Systems with large value of ρ_0 are narrowly bound systems with high vibra-

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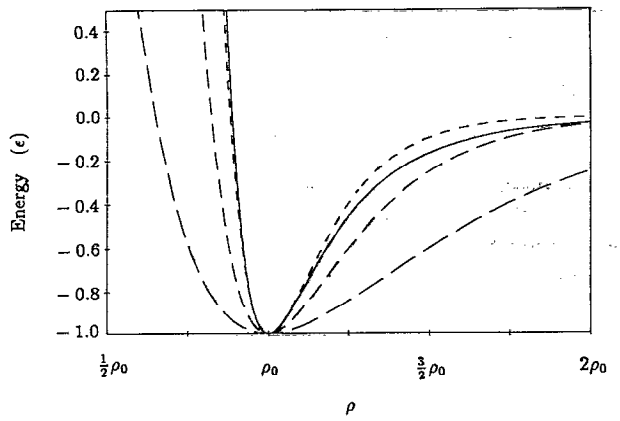

FIG. 1. Curves of the Morse potential $V(r_{ij})$ in units of Eq. (2), i.e., the well depth is -1. The units of ρ_0 are the dimensionless units of $r_0\beta$. The short-dashed curve corresponds to $\rho_0=6$; the intermediate-dashed curve, to $\rho_0=4$; the long-dashed curve, to $\rho_0=2$; the solid line, to the Lennard-Jones potential. This figure is based on Fig. 2 of Ref. 3.

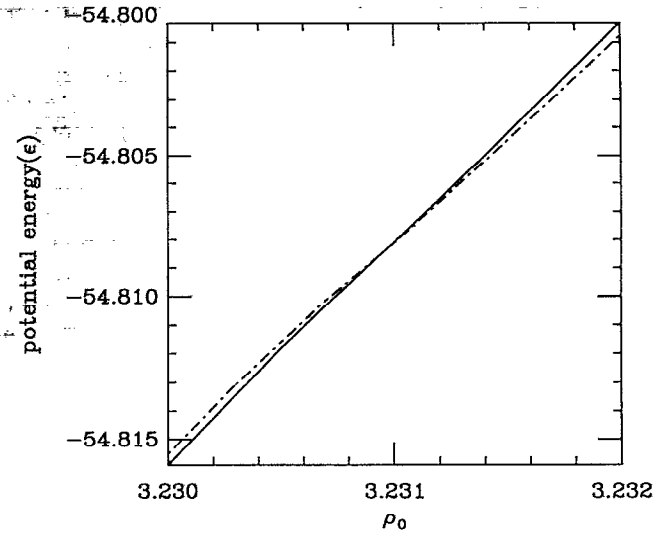

FIG. 2. Dependence of the energies of the two lowest minima of the M_{14} cluster as functions of the range parameter ρ_0 over the range between 3.230 and 3.232, where the energies cross. The energy is in the scaled units of Eq. (2), in which the pairwise attraction has a minimum of -1; the units of ρ_0 are the dimensionless units of $r_0\beta$. The dotted curve applies to the global minimum for short-range pair interactions, (a) in Fig. 3; the solid curve, to the global minimum for long-range pair potentials, the structure (b) of Fig. 3.

tional frequencies. Small values of ρ_0 correspond to long ranges of interaction and low frequencies of vibration. The reduced form is

$$V(\rho_{ij})=\sum_{i<j}\{\exp[-2(\rho_{ij}-\rho_0)-2\exp[-(\rho_{ij}-\rho_0)]\}. \tag{2}$$

The physically relevant range of ρ_0 is approximately 1.5-7[3]. An alternative, used by Stillinger and Stillinger,[2] is an inverse power-law form, $V(r_{ij})=\epsilon[1-(r_{ij}/r_0)^{-n}]^2$. The range parameter of this potential is, of course, the exponent n.

We carried out a combination of molecular dynamics simulations and quenches, to find the geometries and energies of the lowest-energy structures. In our molecular dynamics computations, we used the velocity version of the Verlet "leap frog" algorithm to solve Newton's equations of motion with a step size of 0.5×10^{-14} s, chosen to maintain the constancy of the total energy. The initial structures for M_{14} were constructured by adding one atom to the M_{13} minimum-energy icosahedral structure. The propagation is initiated with all the velocities equal to zero, so the total linear and angular momentum begin (and stay) at zero. The steepest-descent quench technique was used for searching the minimum and saddles according to

$$dq=-\nabla U(q), \tag{3}$$

where q is the coordinate vector for the system. When we carried out the steepest–descent quenches, a value of 10^{-14} for the cutoff variation of potential energies $(V_{\text{new}}-V_{\text{old}})^2/V_{\text{old}}{}^2$ "held" the system at both saddle points and minima. As a check, Hessians were constructured at all saddles. At each, there was at least one negative eigenvalue, confirming that we have located saddles.

III. RESULTS

We started from $\rho_0=2$, increasing the range slowly; the global minimum structure remained the same until $\rho_0=3.230\,96\pm0.0001$; for ρ_0 larger than this, the structure of the global minimum became the structure that is the second minimum for ρ_0 smaller than 3.230 96. Figure 2 shows the behavior of the two minima as functions of the range parameter. The global minimum structure for ρ_0 less than 3.230 96, i.e., for comparatively long-range interaction, is an icosahedron with one of the faces containing four atoms instead of three, while all the other surfaces contain three atoms, as in the normal icosahedron. For shorter-range interactions, i.e, for ρ_0 larger than 3.230 96, the global minimum structure is an icosahedron with one atom on the center of one of the triangular faces of the icosahedron. The icosahedron is slightly distorted by this extra, superficial atom. The global minimum structure for the shorter-range potential is the second minimum structure for the longer-range potential. We also see similar crossings with respect to the range of the potential for some of the higher minima of both M_{14} and M_{17}. Figure 3 shows the two structures. To illustrate the crossing, at ρ_0 of 3.2307, structure 1 of Fig. 3 has an energy of $-54.810\,310$ and structure II, $-54.810\,120$; at ρ_0 of 3.2310, the energies of structures 1 and 2 are, respectively, $-54.808\,111$ and $-54.808\,138$, making 1 the lower at the smaller ρ_0 and 2 the lower for larger ρ_0.

We now believe that the Stillingers' mapping method may be applicable directly to only selected systems, such as clusters with magic numbers of particles. In such cases, the global minimum is far lower in energy than any of the other. However, it is now straightforward to search for low minima on a surface with only a few kinds of minima, so that a systematic (if inelegant) procedure is easy to construct that makes the Stillinger–Stillinger method more

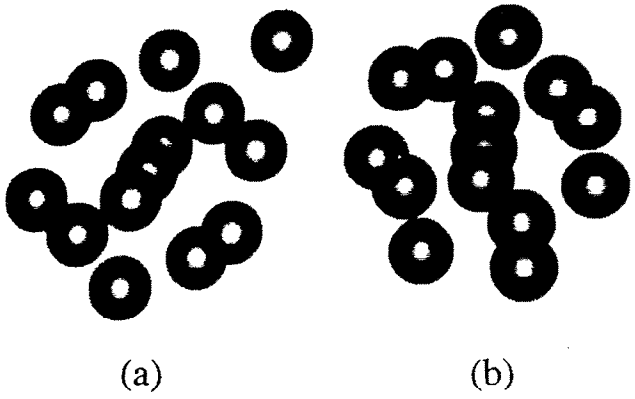

FIG. 3. The two lowest-energy structures of the M_{14} cluster: (a) the global minimum for short-range pair interactions; (b) the global minimum for long-range interactions. The 14th atom, capping a triangular face, is at the top right of (a); the nearly planar set of four atoms making an almost square face of (b) is at the bottom of the figure, angled slightly toward the right.

generally applicable. The multidimensional surface must be checked for low minima at small values of ρ_0; then energy minimizations are carried out for successively larger values of ρ_0, starting with the geometries of the minimum-energy structures for the previous, smaller value of ρ_0. With gradual variation of ρ_0, configurations that are minima for one value of that parameter will almost certainly remain close to and in the same basin as minima for other, nearby values of ρ_0. Used in conjunction with molecular dynamics or Monte Carlo explorations of the potential surfaces, this procedure should pick out even such dramatic crossovers as transitions between icosahedral and face-centered cubic structures, if such can be found to be caused by variations of ρ_0. We conjecture that they will be found, and propose calling them "range-induced transitions." Whether it will be possible to find physical conditions that will yield such transitions is more speculative; in the meantime, we can search for them in simulations.

ACKNOWLEDGMENT

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