Communication: Designed diamond ground state via optimized isotropic monotonic pair potentials

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We apply inverse statistical-mechanical methods to find a simple family of optimized isotropic, monotonic pair potentials (that may be experimentally realizable) whose classical ground state is the diamond crystal for the widest possible pressure range, subject to certain constraints (e.g., desirable phonon spectra). We also ascertain the ground-state phase diagram for a specific optimized potential to show that other crystal structures arise for pressures outside the diamond stability range. Cooling disordered configurations interacting with our optimized potential to absolute zero frequently leads to the desired diamond crystal ground state, revealing that the capture basin for the global energy minimum is large and broad relative to the local energy minima basins. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4790634]

Advances in the field of self-assembly, devising building blocks (e.g., nanoparticles and polymer chains) with specific interactions to form larger functioning materials, are proceeding rapidly and hold great promise to produce unique colloidal and polymer systems.[1–4] In the past several years, inverse statistical-mechanical methods have been formulated that yield optimized interactions that robustly and spontaneously lead to *targeted* many-particle configurations with desirable or novel bulk properties.[5] This inverse approach provides a powerful and systematic means of directing self assembly with exquisite control. Recent studies have used inverse methods to find optimized isotropic (non-directional) interactions, subject to certain constraints, that yield novel targeted ground states, such as low-coordinated crystal structures.[5] This includes the three-fold coordinated honeycomb (or graphene) structure in two dimensions[6] and the tetrahedrally-coordinated diamond crystal in three dimensions,[7] initial studies of which involved isotropic pair potentials with multiple wells.

Are multiple wells required to achieve low-coordinated crystal ground states with isotropic pair interactions? We have recently shown that inverse statistical-mechanical techniques allow one to produce unequivocally both the square lattice and honeycomb crystal in two dimensions via monotonic convex pair potentials.[8,9] Here, we use inverse techniques to obtain a simple family of optimized isotropic, monotonic pair potentials (that may be experimentally realizable by colloids[5]) whose ground states for a wide range of pressures is the diamond crystal. This possibility is counterintuitive since the diamond crystal is commonly thought to require directional (covalent) interactions.

Using the *forward* approach,[10] it was established over a decade ago that the diamond crystal can be stabilized for a range of densities by an isotropic, monotonic pair potential devised to model star polymers.[11] These authors used free-energy calculations to find the phase diagram and validate their conclusions. Moreover, the potential possessed stable phonon spectra over the predicted ground-state parameter regime.[12] A forward approach was used in another study[13] to examine only lattice energy sums at zero temperature for a relatively small set of Bravais and non-Bravais lattices for an isotropic, monotonic pair potential. It was found that the diamond crystal was stable for a certain pressure range. These authors recognized the limitations of this restricted investigation, which excluded both phonon spectra calculations and annealings to zero temperature from liquid-like initial conditions in order to validate that the diamond was indeed the ground state.

Here we use a simpler functional form for a monotonic radial (isotropic) pair potential function $v(r)$ that obeys certain important conditions on its second derivative with respect to the radial pair distance r established in Refs. 8 and 9. Specifically, we propose a potential function of the form

$$v(r) = \varepsilon \left(1 + a_1 \frac{r}{\sigma} + a_2 \left(\frac{r}{\sigma}\right)^2\right) e^{-(r/\sigma)^2}, \qquad (1)$$

where ε and σ, respectively, define the energy and length units, and a_1 and a_2 are dimensionless parameters. Equation (1) is chosen for its simplicity and because it allows for the desirable features of the second derivative described below. The potential function (1) is strictly convex for all r beyond a small cutoff distance for a large range of parameters. In this study, we restrict ourselves to such potentials that are convex for $r > 0.1\sigma$.[14]

We introduce here an iterative two-step inverse procedure to determine the optimized parameters of the potential function (1) under certain constraints that yields the diamond ground state for a range of pressures. Let $p^* = p\sigma^3/\varepsilon$

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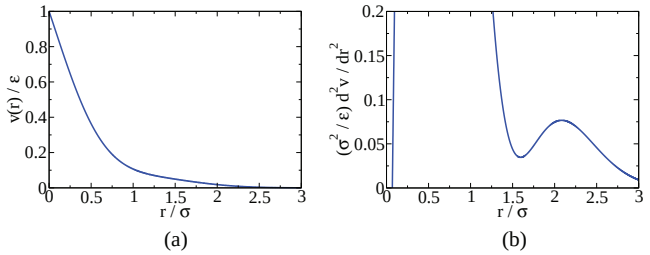

FIG. 1. (a) Optimized monotonic pair potential $v(r)$ from Eq. (1) using the parameters from (2): the D1 potential. (b) Second derivative d^2v/dr^2 of the versus the radial distance r.

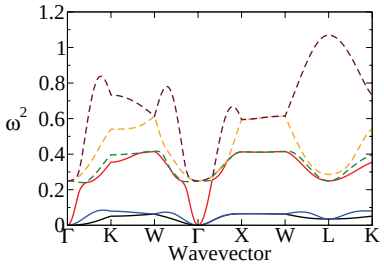

FIG. 2. Phonon spectrum in reduced units of the D1 potential for the diamond at dimensionless pressure $p^* = 0.078$ and density $\rho^* = 0.271$. Only a representative subset of wave vectors that lie on paths connecting high-symmetry points (Γ, K, W, X, and L) of the Brillouin zone[7] is shown. The D1 potential is chosen such that the lowest phonon frequency relative to the highest one at the X point is maximized.

and $\rho^* = \sigma^3\rho$ be a dimensionless pressure and dimensionless density, respectively. The first step of the optimization procedure involves choosing an initial set of "competitor" configurations. Then we find the parameters a_1 and a_2 that maximize the ratio p_{max}/p_{min} (maximum to minimum pressure) for which the diamond has a lower enthalpy than any competitor configuration. This use of the pressure range as an optimization variable is new to our knowledge. The second step involves a rapid cooling procedure within a simulation box under periodic conditions in the isobaric ensemble, implying that the box is deforming and changing volume. We start this step by choosing initial lattice vectors that define the box within which are N particles initially Poisson distributed in space interacting via the potential (1) with parameters from the first step. Cooling is achieved using a quasi-Newton method, which has similar basins of attraction as obtained from steepest-descent methods or Metropolis schemes at zero temperature. The basis number N for the periodic cell is varied from 1 to 16 (i.e., we sample over variable-basis crystals) over the entire pressure range defined by p_{min} and p_{max}. If we find a lower enthalpy configuration than that for the diamond crystal, we add that configuration to the competitor list and the two-step procedure is iterated. If we find no other states with lower enthalpy, we terminate the procedure. Knowledge of the final set of competitors allows us to choose a potential (without a full-blown optimization) that has other useful qualities at the cost of only a small decrease in the pressure range over which diamond is the ground state, e.g., for the system to be relatively stiff mechanically as measured by the phonon spectrum.

After optimization under the aforementioned constraints (e.g., relative stiffness and convexity for $r > 0.1\sigma$), we obtain the following optimized parameters for the potential (1):[15]

$$a_1 = -1.42324, \qquad a_2 = 0.713012. \tag{2}$$

Henceforth, we will refer to the potential function (1) with parameters defined by (2) as the diamond-1 or D1 potential;[16] see Fig. 1(a). The diamond crystal is the ground state of the D1 potential from $p^* = 0.0554$ to $p^* = 0.1010$. At these pressures, the corresponding densities and nearest-neighbor (NN) distances are, respectively, $\rho^* = 0.235$ and $\rho^* = 0.303$, and $r_{NN} = 1.403\sigma$ and $r_{NN} = 1.290\sigma$. The second derivative d^2v/dr^2 is designed to meet two simultaneous objectives: (a) to stabilize the low-coordinated target structure, and (b) to discriminate against all competitors. Specifically, using the generalized coordination function formalism,[9] we determined that to obtain low-coordinated ground states with monotonic convex potentials, $|d^2v/dr^2|$ must be large both below and close to the NN distance. It also must be small up to the NN distance of the close-packed crystals and large up to the next NN distance of the targeted low-coordinated ground state, after which it goes to zero.

We also tried to find a monotonic potential of the form (1) that has the closely related tetrahedrally-coordinated wurtzite crystal as its ground state, but concluded that such a potential does not exist. Wurtzite and diamond crystals have the same first and second coordination shells, and so the only way potential functions of the form (1) can distinguish between the two is from its longer-range behavior. However, such potentials decrease very rapidly at these larger distances due to the dominant Gaussian factor. Thus, wurtzite for potential (1) has higher energy than that of diamond, since its third nearest neighbors are slightly closer.

The mechanical stability of the diamond crystal for the D1 potential is confirmed by phonon calculations, as done in Ref. 7, over the entire Brillouin zone.[17] Figure 2 shows the phonon spectrum (reflecting strengths of the restoring forces for deformations for given wave vectors) at a pressure in the middle of its stability range. The optimized D1 potential is selected among those potentials that yield nearly optimal pressure range for the diamond ground state such that the lowest phonon frequency relative to the highest one at the X point is maximized. But it is also optimal for other wave vectors that we studied.

The stable phases for the D1 potential at various pressures outside those for the diamond stability range are shown in Fig. 3. The phases are determined by repeatedly cooling disordered configurations at constant pressure using the aforementioned variable-box energy minimization techniques and retaining the lowest-enthalpy configurations. We find that the diamond is stable for $0.0554 \le p^* \le 0.1010$. Four neighboring phases are particularly interesting. At low pressures, $0.0272 < p^* < 0.0530$, a hexagonal crystal phase, where the distance between hexagonal planes is shorter than the distance between particles in the same plane, is stable. This crystal has an effective coordination number of two. Between this phase and the diamond phase ($0.0530 < p^* < 0.0554$), a low-coordinated rhombohedral graphite phase is stable. It is composed of stacked honeycomb layers where each

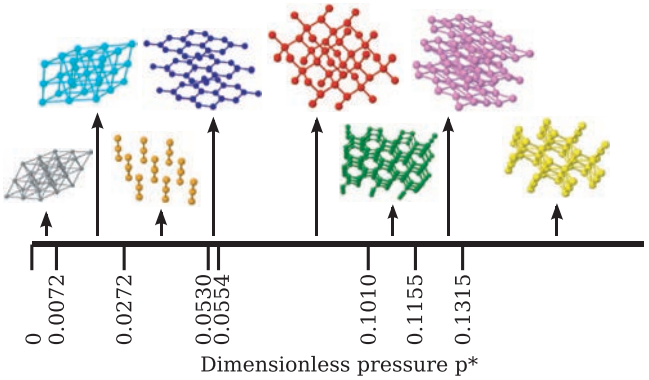

FIG. 3. Ground states of the D1 potential for a range of pressures obtained from steepest descent for a basis up to $N = 16$. The crystal phases indicated from zero pressure to higher pressures are the 12-coordinated face-centered cubic (gray), the 8-coordinated body-centered cubic (cyan), a 2-coordinated hexagonal (orange), a 3-coordinated buckled rhombohedral graphite (blue), the 4-coordinated diamond (red), a 5/6-coordinated deformed diamond (green), a 6-coordinated buckled hexagonal (violet), and a 8-coordinated flattened-hexagonal closed-packed (yellow). "Bonds" are indicated between nearest-neighbor particles for visualization purposes.

successive layer is shifted in the same direction relative to the layer immediately below it (unlike standard graphite where the shift direction alternates between layers). The distance between the planes is about 1.5 times larger than the NN distance within a layer, which is much less than that for actual graphite. At high pressures in the range $0.1155 < p^* < 0.1315$, the opposite happens, since the stable phase is a *buckled* simple hexagonal crystalline, where the NN distance within a hexagonal plane is shorter than that between planes, resulting in a coordination number of six. Unlike the low-pressure hexagonal phase, this phase shows buckling: particles in the same layers are not perfectly aligned, but the distance between nearest neighbors stays constant. The transition between the high-pressure buckled hexagonal phase and the diamond phase ($0.1010 < p^* < 0.1155$) consists of a highly deformed diamond crystal, for which particles have variable coordination numbers of either 5 or 6. The highest-pressure phase reported is a flattened hexagonal closed-packed crystal in which the NN distances within a layer are larger than that between layers. This is not the stable phase for all $p^* > 0.1315$; other phases arise at higher pressures.

We employed the same rapid cooling method used to obtain the phase diagram to quantify how easy it is for the system to reach the ground state. Table I compares the frequency with which the diamond is obtained using the D1 and the star-polymer[11] potentials for various numbers of particles, demonstrating an advantage of the D1 potential. The high frequency with which the D1 potential results in the diamond is evidence that its energy landscape is smooth and possesses a broad global minimum; see Fig. 4(c). The fact that this frequency decreases as N increases is a consequence of the relative crudeness of our rapid cooling method, which is ineffective at resolving large-scale defects. However, it is all the more remarkable that this method is capable of reaching the ground state with reasonable frequency despite using large bases, as opposed to, for example, a carefully-tuned simulated annealing procedure. Nevertheless, we have verified using simulated annealing on a 256-particle system that the diamond crystal emerges as the ground state for the D1 potential.

TABLE I. Frequency with which the ground-state diamond crystal is obtained from a steepest descent starting from a random configurations of N particles. For each N, the frequency is calculated using 10 000 trials, which results in standard deviations smaller than 0.5%. The D1 potential trials are carried out at $p^* = 0.078$, while the star-polymer potential trials used $p/(\frac{5}{18}k_BTf^{3/2}) = 3.332$ (for which the ground state has a "packing fraction" $\eta = 1.2$) and an arm number $f = 64$ (see Ref. 11 for the definition of these parameters).

N	D1 potential (%)	Star-polymer potential (%)
2	96.89	91.41
4	89.71	77.38
8	62.13	54.28
16	46.32	26.55
32	24.57	8.93
64	5.27	0.30

Our work provides yet another example of the "inverse" statistical mechanical method to identify an appropriate interaction potential whose non-degenerate classical ground state is a pre-selected crystal structure. In general, it is not guaranteed that such a targeted requirement has a solution. But in the present case of the fourfold-coordinated diamond crystal, previous studies have indeed indicated that this can be accomplished with pairwise additive isotropic potentials.[7,11,13] The existence of these examples establish that an infinite family of such interactions will produce the diamond structure as its ground state, each member within some pressure (i.e., density) range.

However, merely stabilizing a given target structure is typically only part of the technical objective. There may be other properties that one wishes simultaneously to satisfy or

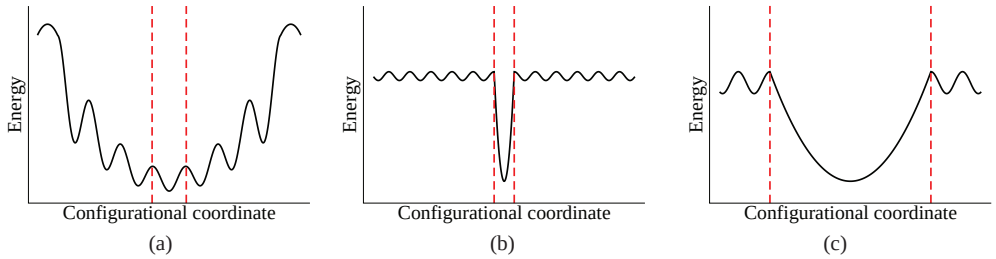

FIG. 4. Schematics of three different types of energy landscapes as a function of the configurational coordinate. Boundaries of the basin of attraction associated with the global minima are indicated by dashed vertical lines. (a) Relatively rough energy landscape. (b) Energy landscape with a deep and narrow global minimum. (c) Energy landscape with a broad and smooth global minimum.

optimize. Here, these have included maximizing the pressure range of ground-state stability for the diamond crystal, constraining the potential to monotonicity and convexity, maximizing the ratio of the highest and lowest phonon frequencies, and optimizing capture probability in the desired crystal basin from random initial configurations. The choice of such constraints and/or optimizations is not unique, but is driven by overall scientific objectives. Distinct choices obviously will identify distinct optimizing potential functions.

The success at constructing diamond potentials naturally raises the question of whether the structure of that other macroscopic crystalline form of elemental carbon, graphite, might analogously be the classical ground state of an isotropic pair potential. This might seem easy, given the existence of potentials that generate the two-dimensional analog, the honeycomb crystal.[6,8,9] However, the layered structure of this three-dimensional graphite allotrope, the stable form of elemental carbon at ambient conditions, with rather large interlayer separation and interlayer relative shift, realistically appears to present a formidable challenge. Ideally, it is desirable to find a potential whose ground state includes both the graphite structure (at low pressure) and the diamond structure (at elevated pressure), thus emulating reality. This ambitious joint requirement might require at least a combination of two-body and three-body interactions, suggesting a direction for future research.

At present there is no known constraint on the complexity (basis of the unit cell) of a single-species target crystal structure that might be stabilized by an isotropic pair potential. But as the unit cell of a target crystal structure increases in size and geometric detail, it is reasonable to suppose that stabilizing isotropic pair potentials, if they exist, will necessarily also have to increase in range and complexity. Establishing such a connection constitutes another direction in which future studies should be focused.

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[14] Since the nonconvexity of the potential is restricted to very small distances, one can add a short-range hard-core repulsion to Eq. (1) to obtain a convex potential, which will behave exactly like the original potential, provided that the pressure or temperature is not extremely large.
[15] The diamond potential function is robust in that its parameters can be perturbed and still produce the diamond crystal as a ground state.
[16] For example, we denote by D2 the potential that has the largest ratio of maximum to minimum stable pressures for the diamond ground state. Its parameters are $a_1 = -1.21189$, and $a_2 = 0.788955$. This potential possesses softer transverse phonon modes compared to the D1 potential.
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