Designed Diamond Ground State via Optimized Isotropic
Monotonic Pair Potentials

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Abstract

We apply inverse statistical-mechanical methods to find a simple family of optimized isotropic, monotonic pair potentials, under certain constraints, whose ground states for a wide range of pressures is the diamond crystal. These constraints include desirable phonon spectra and the widest possible pressure range for stability. We also ascertain the ground-state phase diagram for a specific optimized potential to show that other crystal structures arise for other pressures. 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.
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. In the past several years, inverse statistical-mechanical methods have been formulated that yield optimized interactions that robustly and spontaneously lead to a targeted many-particle configuration with desirable or novel bulk properties. 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. This includes the three-fold coordinated honeycomb (or graphene) structure in two dimensions and the tetrahedrally-coordinated diamond crystal in three dimensions, 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 robustly both the square lattice and honeycomb crystal in two dimensions via monotonic convex pair potentials. In the present work, we employ inverse techniques to obtain a simple family of optimized isotropic, monotonic pair potentials whose ground states for a wide range of pressures is the diamond crystal.

Using the forward approach, 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. 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. A forward approach was used in another study 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 the second derivative with respect to the radial interparticle distance $r$ established in Refs. and . Specifically, we propose a
potential function of the form

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

(1)

where \( \varepsilon \) and \( \sigma \), 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 \( r > 0.1\sigma \).

We use 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. We define the dimensionless pressure \( p^* \) and density \( \rho^* \) as follows:

\[ p^* = p \sigma^3 / \varepsilon, \quad \rho^* = \sigma^3 \rho. \]  

(2)

The first step of the optimization procedure involves choosing an initial set of “competitor” configurations. Then we determine the parameters \( a_1 \) and \( a_2 \) that maximize the ratio between the maximum and minimum pressures \( p_{\text{max}} \) and \( p_{\text{min}} \) for which the diamond crystal has a lower enthalpy than any competitor configuration, since we are working in the isobaric ensemble. The second step involves a rapid cooling procedure within a simulation box under periodic conditions in the isobaric ensemble, implying that the simulation box is deforming and changing volume. We start by choosing initial lattice vectors that define the simulation box within which there is a Poisson distributed set of \( N \) particles interacting with the potential function (1) and the parameters from the first step. Cooling is then carried out using a quasi-Newton method, which has similar basins of attraction as obtained from steepest-descent methods or the Metropolis algorithms at zero temperature. The basis number \( N \) for the periodic cell is varied from 1 to 16 to allow the sampling of variable-basis crystals over the entire pressure range defined by \( p_{\text{min}} \) and \( p_{\text{max}} \). If we find a lower enthalpy configuration than that for the diamond crystal, we add that configuration to the competitor list and repeat the two-step procedure. If we find no other states with lower enthalpy, we terminate the procedure. Using the final set of competitors, we have access to a large family of potentials that stabilize the diamond crystal with nearly-optimal pressure ranges. This allows us to choose a potential that has other useful qualities at the cost of only a small decrease in the pressure range over which the potential’s ground state is the diamond crystal. One
such desirable property is for the lowest modes in the phonon spectrum to have the highest possible energies (i.e., the system is relatively stiff mechanically).

After optimization under the aforementioned constraints (e.g., lack of floppy modes and convexity), we obtain the following optimized parameters for the potential function (1):

\[ a_1 = -1.42324, \quad a_2 = 0.713012. \]  

(3)

Henceforth, we will refer to the potential function (1) with parameters defined by (3) as the diamond-1 or D1 potential, 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 distances are, respectively, \( \rho^* = 0.235 \) and \( \rho^* = 0.303 \), and \( r_{NN} = 1.403\sigma \) and \( r_{NN} = 1.29\sigma \). The magnitudes of the second derivative at different distances have two simultaneous objects: (a) to stabilize the low-coordinated target structure, and (b) to discriminate against all competitors. Specifically, using the generalized coordination function formalism described in Ref. 9, we determined that to obtain low-coordinated ground states with monotonic convex potentials, the magnitude of the second derivative must be large both below and near the nearest-neighbor distance of the low-coordinated ground state. It also must be small up to to the nearest-neighbor distance of the close-packed crystals and large up to the next-nearest-neighbor distance of the targeted low-coordinated ground state, after which it goes to zero.

FIG. 1: [a] Optimized monotonic pair potential \( v(r) \) from Eq. (1) using the parameters from (3): the D1 potential. [b] Second derivative \( d^2v/dr^2 \) of the same optimized pair potential versus the distance \( r \).
We also have attempted to use the same procedure to find a monotonic potential of the form (1) that has the closely related tetrahedrally-coordinated wurtzite crystal as its ground state. However, we have found that such a potential does not exist. This can be readily be explained by the fact that wurtzite and diamond crystal have the same short-range interparticle distances (first and second coordination shells), so the only way a potential of the form (1) can distinguish between the two is from its longer-range behavior. However, potentials of the form (1) decreases very rapidly at such distances, since they are dominated by the Gaussian factor. Therefore, the wurtzite crystal for the potential (1) has higher energy than the diamond crystal due to its third nearest neighbors being slightly closer.

![Graph](image)

**FIG. 2:** Phonon spectrum in reduced units of the D1 potential for the diamond crystal at dimensionless pressure $p^* = 0.078$ and density $\rho^* = 0.271$. Only a representative subset of wavevectors that lie on paths connecting high-symmetry points ($\Gamma$, $K$, $W$, $X$, and $L$) of the Brillouin zone is shown. The D1 potential is chosen such that the ratio between the highest and lowest phonon frequencies at the $X$ point is maximized.

Figure 2 shows the phonon spectrum (which shows the strengths of the restoring forces for deformations associated with given wavevectors) of the D1 potential for the diamond crystal at a pressure in the middle of its stability range. Full phonon calculations (not only for the wavevectors shown in Fig. 2) indicate that the diamond crystal is indeed mechanically stable for the D1 potential. The optimized D1 potential is selected among those potentials that produce a nearly optimal pressure range for the diamond ground state in order to achieve a
large ratio between the highest and lowest phonon frequencies at the $X$ point. While only the $X$ point was considered in the optimization, the D1 potential is also optimal for the other wavevectors that we have examined.

![Ground states of the D1 potential for a range of dimensionless pressures](image)

**FIG. 3**: Ground states of the D1 potential for a range of dimensionless 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 drawn between particles that are either nearest neighbors or nearly so as to guide the eye.

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 the variable-box energy minimization techniques and retaining the resultant configurations whose enthalpy are the lowest. We find that the diamond crystal is stable for $0.0554 \leq p^* \leq 0.1010$. Four neighboring phases are particularly interesting. At low pressure, $0.0272 < p^* < 0.0530$, a hexagonal crystal phase, where the distance between hexagonal planes is shorter than the distance between particles from the same plane, is stable. This crystal has an effective coordination number of two, since the potential favors low-coordinated configurations over close-packed ones as long as the nearest-neighbor distance is not too small. Between this phase and the
diamond phase \((0.0530 < p^* < 0.0554)\), a low-coordinated rhombohedral graphite crystalline phase is stable. The rhombohedral graphite crystal is composed of stacked honeycomb crystals where each successive honeycomb 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 \(1.5 \sim 1.6\) times larger than the nearest-neighbor distance within a layer, which is much less than that for actual graphite. At high pressure in the range \(0.1155 < p^* < 0.1315\), the opposite happens, since the stable phase is a \textit{buckled} simple hexagonal crystalline, where the nearest-neighbor distance within a hexagonal plane is shorter than that between planes, resulting in a coordination number of six. Unlike the low-pressure hexagonal crystalline 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 shown in Fig. 3 is a flattened-hexagonal closed-packed crystal, consisting of a distorted hexagonal closed-packed crystal with layer nearest-neighbor distances that are larger than the interlayer nearest-neighbor distance. This is not the stable phase for all \(p^* > 0.1315\); other phases arise at higher pressures.

| \(N\) | 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% |

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 10000 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 \(p/(\frac{41}{18}k_B T f^{3/2}) = 3.332\) (for which the ground state has a “packing fraction” \(\eta = 1.2\)) and an arm number \(f = 64.11\).
FIG. 4: Schematic representations of three different types of energy landscapes as a function of the configurational coordinate. The boundaries of the basin of attraction associated with the global minima are indicated by the dashed vertical lines. (a) A relatively rough energy landscape. (b) An energy landscape with a deep and narrow global minimum. (c) An energy landscape with a broad and smooth global minimum.

We employed the same rapid cooling method used to map out 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 crystal ground state is obtained using the D1 and the star-polymer 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 crystal is evidence that its energy landscape is smooth and possesses a broad global minimum, similar to the schematic illustration in Fig. 4(c). The decreasing frequencies for larger $N$ are the consequence of the relative crudeness of our instant 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 techniques with a 256-particle system that the diamond crystal emerges as the ground state for the D1 potential.

The work reported in this paper 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 at the outset that such a targeted requirement has a solution. But in the present case of the fourfold coordinated diamond lattice previous studies have indeed established that this can be accomplished with pairwise additive isotropic potentials. 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. In addition there tend to be properties that one wishes simultaneously to satisfy or to optimize. For the present study these have included maximizing the pressure range of ground-state stability for the diamond lattice, constraining the potential to monotonicity and convexity, maximizing the ratio of transverse to longitudinal acoustic sound speeds, and optimizing capture probability in the desired crystal basin from random initial configurations. It should be emphasized that 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. At first sight this might seem easy, given the existence of potentials that generate the two dimensional analog, the honeycomb crystal. 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. It may turn out that the graphite structure is unattainable with monotonically decreasing pair interactions. An ideal circumstance would be to find a potential whose classical 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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