Optimized Interactions for Targeted Self-Assembly: Application to a Honeycomb Lattice

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We devise an inverse statistical-mechanical methodology to find optimized interaction potentials that lead spontaneously to a target many-particle configuration. Target structures can possess varying degrees of disorder, thus extending the traditional idea of self-assembly to incorporate both amorphous and crystalline structures as well as quasicrystals. For illustration purposes, our computational technique is applied to yield an optimized isotropic (nondirectional) pair potential that spontaneously yields the three-coordinated honeycomb lattice as the ground state structure in two dimensions. This target choice is motivated by its three-dimensional analog, the diamond lattice, which is known to possess desirable photonic band gap properties.

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''Self-assembly'' typically describes processes in which entities (atoms, molecules, aggregates of molecules, etc.) spontaneously arrange themselves into a larger ordered and functioning structure. Biology offers wonderful examples, including the spontaneous formation of the DNA double helix from two complementary oligonucleotide chains, the formation of lipid bilayers to produce membranes, and the folding of proteins into a biologically active state. Molecular self-assembly is a potentially powerful method to fabricate atomically precise materials and devices. Whitesides and Grzybowski [1] have produced intricate 2D patterns via self-assembly of organic molecules on an inorganic surface. Jenekhe and Chen [2] have devised ''smart plastics'' that assemble into photonic crystals. Stellacci *et. al.* [3] have assembled gold nanowires by functionalizing nanoparticles with organic molecules. Manoharan *et. al.* have self-assembled unique, small clusters of microspheres [4]. These examples provide glimpses into the materials science of the future, i.e., devising building blocks with specific interactions that can self-organize on a set of larger length scales. Theoretical work has mainly focused on finding the structure and macroscopic properties of many-body systems given the interactions — what we refer to as the ''forward'' problem of statistical mechanics. The forward problem has been extensively studied in the context of the freezing transition both analytically [5] and numerically [6], and more recently by Kamien [7], who uses geometric arguments to obtain crystal entropy.

The purpose of this Letter is to introduce an *inverse statistical-mechanical* methodology to find optimized interaction potentials that lead spontaneously to a target many-particle configuration. The so-called ''reverse'' Monte Carlo (MC) method [8,9] has been used to obtain interactions in liquids given the pair correlation function, which only has partial configurational information. Our inverse methodology distinguishes itself in that we apply it to self-assembly of a given *N*-particle configuration, which may be crystalline, quasicrystalline, or amorphous. We envision target structures possessing varying degrees of disorder, which enables us to extend the traditional idea of self-assembly.

The idea of *tailoring* potentials to generate targeted structures is motivated by the rich array of fundamental issues and questions offered by this fascinating inverse statistical-mechanical problem as well as our recent ability to identify the structures that have optimal or desirable bulk properties. The latter includes novel crystal structures for photonic band gap applications [10], materials with negative or vanishing thermal expansion coefficients [11], materials with negative Poisson ratios [12], materials with optimal transport and mechanical properties [13], and mesoporous solids for applications in catalysis, separations, sensors, and electronics [14].

Colloids are the ideal system to test our optimized potentials, since both repulsive and attractive interactions can be experimentally manipulated (e.g., via depletion forces, dipole-dipole interactions, electrostatic interactions, etc., [15]) and therefore offer a panoply of possible potentials that far extends the range offered by molecular systems.

Because there is a vast class of many-body potentials, we will focus on isotropic pairwise additive interactions for simplicity here. There are many open questions even for this simple class of potentials. For example, the limitations of isotropic pairwise additivity for producing target structures are not known. We know that such interactions cannot produce thermodynamically stable chiral structures with a specified handedness; equal amounts of left-handed and right-handed structures would result. When is anisotropy in the potential required? An answer based on intuition from molecular systems would fail here. For instance, the diamond lattice is thought to require directional interactions because such structures found in Nature result from cova-

lent bonding. In fact, it is not known whether a diamond lattice could be created from an isotropic pair potential. This structure has a special status in photonics research because a diamond lattice of dielectric spheres exhibits a photonic band gap across the Brillouin zone [10].

The two-dimensional analog of this open three-dimensional crystal is the three-coordinated honeycomb lattice. Accordingly, our general optimization procedure (described below) will be illustrated by applying it to produce an optimized circularly symmetric pair potential $V(r)$ that spontaneously yields the honeycomb lattice as the ground state (zero-temperature) structure in a positive density range. In contrast to previous approaches that have claimed to produce open lattice structures, our procedure incorporates the phonon spectrum, which is a crucial ingredient. Because the honeycomb is an open lattice that is a subset of the triangular lattice, it is inherently challenging to assemble using isotropic potentials. Indeed, such a potential has never been found before.

The potential energy for a system of N classically interacting particles at positions $\mathbf{r}^N \equiv \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ in the absence of an external field is given by

$$\Phi(\mathbf{r}^N) = \sum_{i<j} V_2(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i<j<k} V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \cdots \quad (1)$$

where the V_n's are n-body potentials. In this study, we consider only isotropic pair potentials and therefore

$$\Phi(\mathbf{r}^N) = \sum_{i<j} V(|\mathbf{r}_i - \mathbf{r}_j|). \quad (2)$$

A central feature of our inverse approach is a computational algorithm that searches for and optimizes a functional form for $V(r)$ that leads to self-assembly of a given target structure. To find an optimized $V(r)$ for a given target structure, we make an initial guess for that function. We require that this initial potential have real frequencies for each of its normal modes (for a lattice, this means real phonon frequencies for all wave vectors in the Brillouin zone). Thus, the structure is mechanically stable at zero temperature. We then parametrize the potential, establishing a family of functions $V(r; \{a_0 \ldots a_n\})$ of which our initial guess is a member. The parametrization must be chosen so that an overall rescaling is not possible. For each a_i, we choose a range of values that it can take, namely $[a_i^{\min}, a_i^{\max}]$. We then optimize this family of functions for self-assembly. Specifically, the program runs a molecular dynamics simulation (MD) at volume (or area) per particle α, initially in the target structure configuration and interacting via the initial guess potential. The initial root mean square speed in the MD corresponds to about 90–95% of the melting temperature, where the system is in a non-harmonic regime and liquid nucleation and/or structural phase transition is beginning to set in. The root mean square deviation from the target structure, defined as

$$L = \sqrt{\frac{1}{N} \sum_i (\mathbf{r}_i - \mathbf{r}_i^{(0)})^2 - \left(\frac{1}{N} \sum_i (\mathbf{r}_i - \mathbf{r}_i^{(0)})\right)^2}, \quad (3)$$

is computed and averaged over a number of simulations. Here $\mathbf{r}_i$ is the position of the ith particle after an appropriate amount of simulation time, $\mathbf{r}_i^{(0)}$ is its initial position, and N is the number of particles. The quantity L is thus minimized in parameter space by simulated annealing. The program outputs the set of parameter values that corresponds to the minimum value of L, presumably giving the potential that best suppresses liquid nucleation and/or a possible structural phase transition. This is the idea of the algorithm: we postulate that if the potential is modified in such a way that deformations of the target structure are suppressed near (but below) the phase coexistence region, the structure will self-assemble from a random configuration in a MC simulation. In the case that the melting temperature rises significantly over the course of the optimization, the initial temperature can be increased such that the system again approaches coexistence. A more detailed description of this optimization procedure, as well as a different one, will be given in Ref. [16].

We now apply our methodology to obtain an optimized circularly symmetric interparticle potential, $V(r)$, that will spontaneously favor the self-assembly of randomly placed particles in two dimensions into the honeycomb lattice upon simulated annealing from high to zero temperature. A claim was made that the honeycomb lattice was favored by a hard-core plus linear-ramp potential for certain parameter values [17], but we have now shown conclusively that this is not possible because the phonon spectra of such $V(r)$ have imaginary frequencies. Thus, it would be a significant accomplishment for our procedure if it assembled the honeycomb lattice.

For lattice self-assembly, we make another restriction on the initial function: that the target should be energetically favored among the four principal 2D lattices, (the triangular, square, honeycomb and kagomé) over a significant range of area per particle α. This is the second of our two necessary conditions for lattice self-assembly, the first being that all phonon frequencies are real.

Both the triangular and honeycomb lattices have their first near neighbors (in relative distances) at 1, $\sqrt{3}$, and 2. The coordination numbers for those neighbors are 6, 6, 6 and 3, 6, 3 for the triangular and honeycomb lattices, respectively. Thus, we choose a potential $V(r)$ such that $V(1)$ is not negative, or else there will be a tendency to accumulate as many neighbors as a lattice will permit, and hence it will fall into the triangular lattice. Yet if there is no local minimum at the nearest neighbor distance, the mechanical stability (phonons) will almost certainly be removed (as we have found after trial and error). This motivates the choice of the family of functions

$$V(r; A, \lambda) = \frac{5}{r^{12}} - \frac{6}{r^{10}} + A\lambda^2 e^{-\lambda r}. \quad (4)$$

This is not the function that is finally given to the optimization program; here, we are still approximating the potential form. This is just a Lennard-Jones–type

interaction (12/10 rather than 12/6) added to a soft repulsive exponential tail that is normalized to $2\pi A$ in 2D regardless of the value of λ. We choose the (12/10) Lennard-Jones because it is more sharply distinguished from the exponential tail than is the (12/6). It also has its minimum at unity and has unit depth. For certain choices of A and λ, this potential has one local minimum but with a positive value. To find the best values for A and λ to stabilize the honeycomb, we choose an α at which the honeycomb nearest neighbor is at unit distance and we maximize the interstitial hopping energy (both local and distant) of just the exponential term over λ at a given A. We can then set a lower bound on the value of A by constraining the potential to have a positive hopping energy (hopping into honeycomb interstitial sites is unfavorable). A qualitative upper bound is set on A just by the need for mechanical stability: for large enough values of A, this potential becomes purely repulsive and the honeycomb is mechanically unstable with it. So A is chosen to be its lower bound. This procedure gave the values $A = 3.0$ and $\lambda = 2.677$. The resulting potential gave favorable lattice sums but still imaginary phonon frequencies, so in order to "brace" the lattice, an attractive Gaussian function was added, and so we use the parametrization

$$V(r; a_0, a_1, a_2, a_3) = \frac{5}{r^{12}} - \frac{a_0}{r^{10}} + a_1 e^{-a_2 r} - 0.4 e^{-40(r-a_3)^2}.$$
(5)

For parameter values $a_0 = 6.0$, $a_1 = 21.5$, $a_2 = 2.677$, and $a_3 = 1.829$, the guess potential meets our two necessary conditions. A 500-particle annealed MC simulation using this potential produced a lattice reminiscent of the honeycomb, but with a significant number of defects in the ground state.

In order to demonstrate the effectiveness of the optimization program, we somewhat arbitrarily displaced the parameters from the initial guess function defined by Eq. (5), setting them to be $a_0 = 6.5$, $a_1 = 18.5$, $a_2 = 2.45$, $a_3 = 1.83$. The resulting 500-particle annealed configuration, shown in Fig. 1, is clearly far from the target structure. We then started the optimization program with these values for the parameters, the output of which was the following potential:

$$V(r) = \frac{5}{r^{12}} - \frac{5.89}{r^{10}} + 17.9 e^{-2.49 r} - 0.4 e^{-40(r-1.823)^2}.$$
(6)

This function is plotted in Fig. 2. The phonon spectrum is given in Fig. 3. The lattice sums (not shown there but given in Ref. [16]) demonstrate that while the honeycomb is stable over a wide range of α, the triangular lattice eventually dips below it. The global energy minimum for the triangular lattice occurs at the specific area for which its nearest neighbor is at the second minimum in $V(r)$ caused by the Gaussian function. As long as there is an attractive Gaussian function in $V(r)$, there is no avoiding this effect.
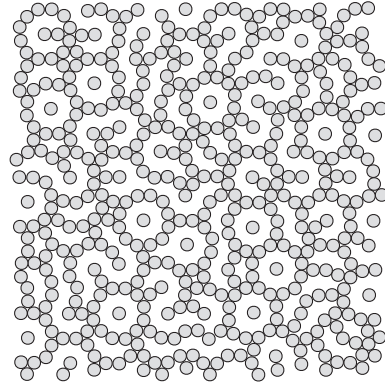

FIG. 1.   500-particle annealed MC results at specific area $\alpha = 1.45$ for a potential with parameters displaced from those given by Eq. (5).

However, it has little relevance for the lattice self-assembly, since it is at relatively high α.

Monte Carlo simulated annealing was carried out on a 500-particle system (at $\alpha = 1.45$) interacting via the potential shown in Fig. 2 [cf. (6)]. The resulting configuration is depicted in Fig. 4. Except for a few defects, the honeycomb has indeed self-assembled. The defects actually seem to be "missing particles," rather than dislocations or pockets of disordering. One might expect that increasing the number of particles to fill the defects (or adjusting α accordingly) would eliminate the defects, but this is not the case. The defects are likely due to the slow dynamics of the MC simulation; i.e., they were "frozen in" during annealing. According to the lattice sums, the perfect honeycomb lattice is lower in energy than the one produced in the MC simulation with defects.

We have found that as long as the salient features of the honeycomb potential are kept (two local minima at distance ratio $\sqrt{3}$, the first being positive and the second negative), self-assembly is unaffected by perturbations in the potential; i.e., the potential is robust. This is essential if this system is to be tested experimentally.

In summary, using an inverse statistical-mechanical approach, we have found an optimized isotropic pair potential that results in the self-assembly of the targeted honeycomb lattice. In many nanoscopic systems, experimental-
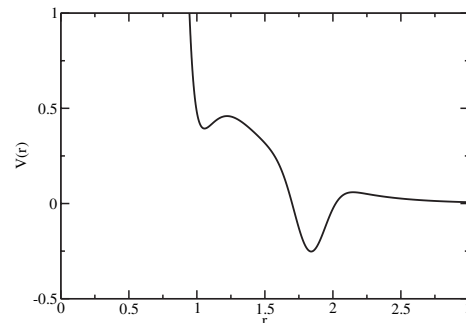

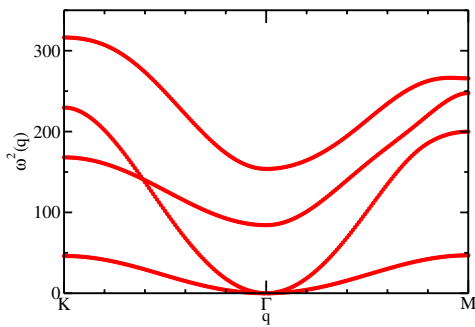FIG. 2.   The optimized pair potential $V(r)$ specified by Eq. (6) for honeycomb-lattice self-assembly.

FIG. 3 (color online). Phonon spectrum (frequency squared) for the optimized honeycomb potential depicted in Fig. 2 at specific area $\alpha = 1.45$.
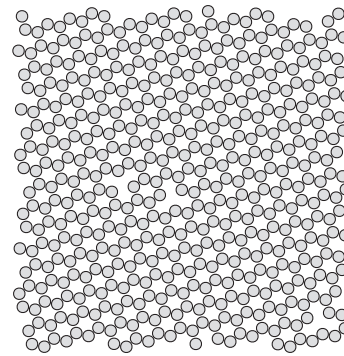

FIG. 4. 500-particle MC results for the optimized potential annealed depicted in Fig. 2 from $k_B T = 0.22$ to $k_B T = 0$ at specific area $\alpha = 1.45$.

ists have increasingly greater control over intercomponent interactions, and hence, optimal design of nanostructures by self-assembly ultimately is always an inverse problem. Our results give some hope to the possibility of self-assembly of the more challenging diamond lattice with isotropic pair potentials. As we indicated earlier, this would have important implications for photonics devices. We are currently searching for a parametrization that upon optimization of an isotropic pair potential will yield the diamond crystal as its ground state. Although the physics of 3D systems can be qualitatively different from 2D, we have already had success in stabilizing bcc and *simple* hexagonal 3D lattices with isotropic potentials using our optimization scheme. Note also that our methodology allows us to minimize the occurrence of defects by maximizing their energy costs.

There are many fascinating research avenues that we can explore using our inverse approach. Our results beg the question of whether more exotic structures can be assembled using only isotropic pair potentials. For example, one might try to assemble a buckyball in a *NVT* annealing simulation with 60 particles with a potential that has sharp minima at the first several neighbor positions. Although we do not know whether this is possible, we have already found a potential that produces small clusters of particles (e.g., simplices), as well as one that produces long chains, or "colloidal wires" [16]. Clearly, there must be limits on the types of structures that can be assembled using only isotropic potentials. We know, for example, that chiral structures with a target chirality cannot be formed, but beyond this specific case we know very little about the limitations of isotropic pair potentials: a fundamentally important problem.

The optimization scheme proposed here is only one approach to the inverse problem, and we expect that others will be needed to search for interactions (isotropic or not, additive or not) that stabilize general systems. Apart from any particular algorithm, however, a central point of this Letter is to propose the use of powerful inverse statistical-mechanical techniques to exquisitely control self-assembly from the nanoscopic to microscopic scales.

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