

Dimensionality and Design of Isotropic Interactions that Stabilize Honeycomb, Square, Simple Cubic, and Diamond Lattices

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We use inverse methods of statistical mechanics and computer simulations to investigate whether an isotropic interaction designed to stabilize a given two-dimensional lattice will also favor an analogous three-dimensional structure, and vice versa. Specifically, we determine the 3D-ordered lattices favored by isotropic potentials optimized to exhibit stable 2D honeycomb (or square) periodic structures, as well as the 2D-ordered structures favored by isotropic interactions designed to stabilize 3D diamond (or simple cubic) lattices. We find a remarkable “transferability” of isotropic potentials designed to stabilize analogous morphologies in 2D and 3D, irrespective of the exact interaction form, and we discuss the basis of this cross-dimensional behavior. Our results suggest that the discovery of interactions that drive assembly into certain 3D periodic structures of interest can be assisted by less computationally intensive optimizations targeting the analogous 2D lattices.

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Material properties are intimately linked to structural characteristics featured at various length scales. Thus, discovering new ways to create materials with prescribed morphologies is a key challenge in their design for specific applications. In addition to the development of top-down material fabrication strategies, there has been considerable progress in bottom-up approaches in which the primary components (molecules, nanoparticles, colloids, etc.) are engineered to promote their self-assembly into targeted structures. Examples of the latter include assembly of lithographic masks [1], polymer membranes [2], magnetic nanostructures [3], and colloidal superlattices [4] for photonic materials [5,6], to mention a few.

A critical part of any self-assembly design problem is understanding how tunable aspects of the interactions affect the thermodynamic stability of competing assembled states with different morphologies. For nanoscale to microscale

particles, this understanding has been guided in part via exploratory experiments and simulations to characterize the structures that spontaneously form from systems with various particle chemistries [7,8], shapes [9–15], and surface properties [16–19], as well as different dispersing solvents [20] and mixtures of assembling particles [21,22]. Highly coordinated lattices with, e.g., face-centered cubic or hexagonal symmetries in three dimensions [7] and triangular symmetry in two dimensions [23] are commonly observed in the experimental assembly of monodisperse particles with short-range, isotropic interactions. A broader array of thermodynamically stable 3D structures—including low-coordinated diamond and simple cubic (Sc) lattices of interest for technological applications [24,25]—has also been demonstrated by computer simulations of monodisperse particles with softer, repulsive potentials [26–30], including those that model the interactions between elastic spheres [31] or star polymers [32]. Similar interactions favor open 2D structures as well, including honeycomb and square lattices [33–39] with, e.g., sterically stabilized magnetic particles in the presence of an external field [40] providing one novel experimental realization. Finally, low-coordinated lattices can also be stabilized by particles with patchy surfaces or faceted

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shapes, as demonstrated by experiments (mostly in 2D [41,42]) and simulations (in both 2D [43,44] and 3D [16,18,45,46]). For a given application, the choice of self-assembling components often hinges on practical considerations including the complexity and expense associated with particle synthesis and the kinetics of assembly.

Despite the fact that various interaction models are known to stabilize specific lattices of interest in a given spatial dimension (2D or 3D), much less is understood about how spatial dimension affects the design rules for assembly. For example, to what extent will an interaction designed to stabilize a given 2D lattice also favor an analogous 3D structure, and vice versa [47]? The answer is of fundamental interest and may also have important practical implications because finding interactions that stabilize lattices in 2D is a simpler and less computationally demanding material design problem than in 3D. Here, we study this question using computer simulations and model potentials designed by inverse statistical mechanical optimization [48,49].

In particular, we determine the 3D-ordered lattices favored by models with isotropic potentials φ_{hc} (φ_{sq}) optimized to exhibit stable 2D honeycomb (square) periodic structures, as well as the 2D-ordered structures favored by isotropic interactions φ_{dia} (φ_{sc}) designed to stabilize 3D diamond (simple cubic) lattices [50]. As we show, the isotropic potentials optimized for either 2D or 3D target structures also do surprisingly well at stabilizing the analogous lattices in the other dimension.

A specified target lattice is the ground state for a given pair potential φ and pressure p if, and only if, it is mechanically stable at this condition and its zero-temperature chemical potential (i.e., molar enthalpy) is lower than that of all other mechanically stable competing structures. Here, we use a stochastic optimization approach (described in detail elsewhere [30]) to discover new model pairwise interactions φ_{target} that maximize the range of density ρ for which a 2D target lattice is the ground state. In our optimizations, we consider isotropic, convex-repulsive pair potentials that qualitatively mimic the soft, effective interactions of sterically stabilized colloids or nanoparticles [51]. The form we adopt can be expressed as [30]

$$\varphi(x) = \epsilon \left\{ Ax^{-n} + \sum_{j=1}^2 \lambda_j \{1 - \tanh[k_j(x - \delta_j)]\} + f_{\text{shift}}(x) \right\} H[x_{\text{cut}} - x]. \quad (1)$$

Here, $x = r/\sigma$ is a dimensionless interparticle separation, ϵ and σ are characteristic energy and length scales, x_{cut} is the dimensionless potential range, H is the Heaviside step function, and $f_{\text{shift}}(x) = Px^2 + Qx + R$ is a shifting function with fitting constants P, Q, R chosen to ensure $\varphi(x_{\text{cut}}) = \varphi'(x_{\text{cut}}) = \varphi''(x_{\text{cut}}) = 0$. All together, there are nine dimensionless parameters that can be varied in the

optimization algorithm $(x_{\text{cut}}, A, n, \lambda_1, k_1, \delta_1, \lambda_2, k_2, \delta_2)$; however, one is not independent of the others because we also require $\varphi(1)/\epsilon = 1$. From here forward, we report quantities implicitly nondimensionalized by appropriate combinations of ϵ and σ .

To identify the ground-state phase diagram for a given pair potential φ , we compare the p -dependent, zero-temperature chemical potentials of a wide variety of Bravais and non-Bravais lattices in a “forward” calculation. Several methods for identifying candidate ground states are available, including evolutionary optimization [52,53] and shape matching and machine learning algorithms [54]. In this study, we use simulated annealing optimization [30] to determine free-lattice parameters, which minimize the chemical potentials of the structures subject to the constraint of mechanical stability, as determined by phonon spectra analysis [55]. In 2D, the Bravais lattices consist of oblique, rhombic, square, rectangular, and triangular symmetries; here, we limit our consideration of non-Bravais lattices to honeycomb, kagome, and other five-vertex semiregular tilings, namely, snub-hexagonal, snub-square, and elongated-triangular. For 3D, we consider the following Bravais and non-Bravais lattices identified in a previous study on closely related model interactions [56]: fcc, bcc, Sc, diamond, pyrochlore, body-centered orthogonal, hexagonal, rhombohedral, cI16, oC8, β Sn, A7, A20, and B10. While the methods employed both to determine the interaction potentials optimal for a target lattice and to compute the corresponding ground states are identical in 2D and 3D, we note that calculations are significantly faster in 2D than in 3D due to the smaller number of competing structures to consider in 2D and the reduced dimensionality of the lattice sum and the phonon spectra evaluations.

For computational efficiency of inverse optimizations in 2D or 3D, only a limited set of competing structures can be considered for a specific target lattice, ideally consisting of the lattices that have the lowest chemical potentials for the interaction type over the density range of interest. Here, we use a simple iterative process for determining the competitive lattice pools. Specifically, we (1) begin with a trial set of competitive structures, (2) carry out an inverse optimization calculation using this competitive pool to obtain parameters for a trial optimal potential, (3) perform an extensive forward calculation to determine the ground-state phase diagram of the trial potential, and (4) as necessary, refine the competitive pool based on the lattices that appear in the forward calculation in step (3) and return to step (2). The final pools determined from this method contain a diverse array of structures in 2D and 3D [57].

To obtain information about the thermal stability of the target lattices, we also perform Monte Carlo quench simulations in which a high-temperature fluid is instantaneously cooled down to a much lower temperature to observe assembly of the target structure. Our simulation sizes are chosen such that larger systems do not affect the

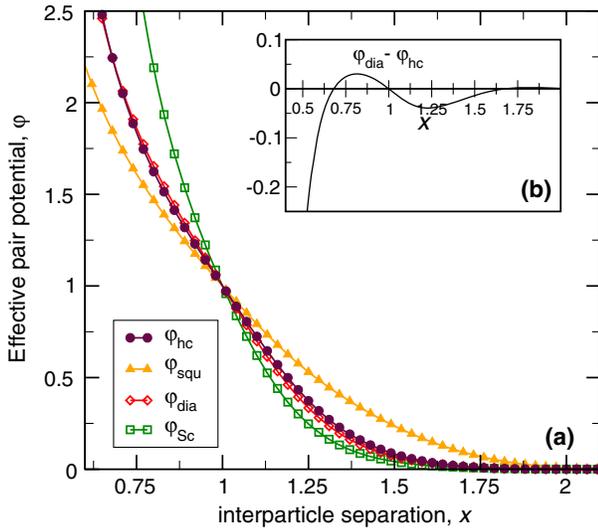


FIG. 1. Isotropic, convex-repulsive potentials, φ_{hc} and φ_{squ} (described in the text), which maximize the density range of mechanically stable 2D honeycomb- and square-lattice ground states, respectively. Also shown are previously designed potentials, φ_{dia} and φ_{sc} [30], that maximize the density range of mechanically stable 3D diamond- and simple cubic-lattice ground states, respectively. The inset highlights subtle differences between φ_{dia} and φ_{hc} .

results (for more details, see Table S1 and discussion in the Supplemental Material [58]). We note that interactions previously optimized to stabilize 3D target ground states of diamond (φ_{dia}) and simple cubic (φ_{sc}) lattices over a wide range of density—using methods identical to those employed here—lead to target crystalline phases with good thermal stability [59].

The interaction potentials we obtain for maximizing the density range of 2D honeycomb- and square-lattice ground states [60] together with previously optimized interactions for diamond- and simple cubic-lattice ground states [30],

are shown in Fig. 1. Notice that interactions φ_{hc} and φ_{dia} are remarkably similar to one another, despite the fact that they were obtained from optimizations favoring different (albeit analogous) structures in different spatial dimensions. As shown in the inset of Fig. 1, significant discrepancies between these potentials (i.e., the steeper repulsions of φ_{hc}) are present only for interparticle separations $x < 0.6$ that, as we confirm below, are closer than the nearest-neighbor distance for the honeycomb or diamond lattices in the density range where the structures are stable for either model. Based on the similarity of these interactions, one might already expect that φ_{hc} and φ_{dia} would stabilize similar lattices in 2D and 3D. On the other hand, we see appreciable differences between the potentials φ_{squ} and φ_{sc} optimized to stabilize 2D square and 3D simple cubic lattices, respectively. Of the four interactions studied here, φ_{squ} has the softest repulsive core and the longest range, while φ_{sc} has the steepest core repulsion and the shortest range.

In Fig. 2, we show the results of our forward calculations, i.e., the 2D ground states for the four optimized potentials as a function of density [61]. Shaded regions represent densities where the ground state comprises two neighboring lattices in coexistence. First, we note that the 2D inverse optimization calculations succeed in their goal: stable honeycomb- and square-lattice ground states appear for φ_{hc} and φ_{squ} , respectively, over very wide density ranges, especially when compared to those of other repulsive, isotropic interaction models [36,39,62] known to form these phases. Perhaps more noticeable is not only that the 2D honeycomb lattice is stabilized over a similar density range by the 3D-optimized φ_{dia} (a result now expected based on the similarity to φ_{hc} shown in Fig. 1), but also that the square lattice is stabilized over a wide density range by φ_{sc} (despite significant differences compared to φ_{squ}). In other words, for both cases, stable 2D

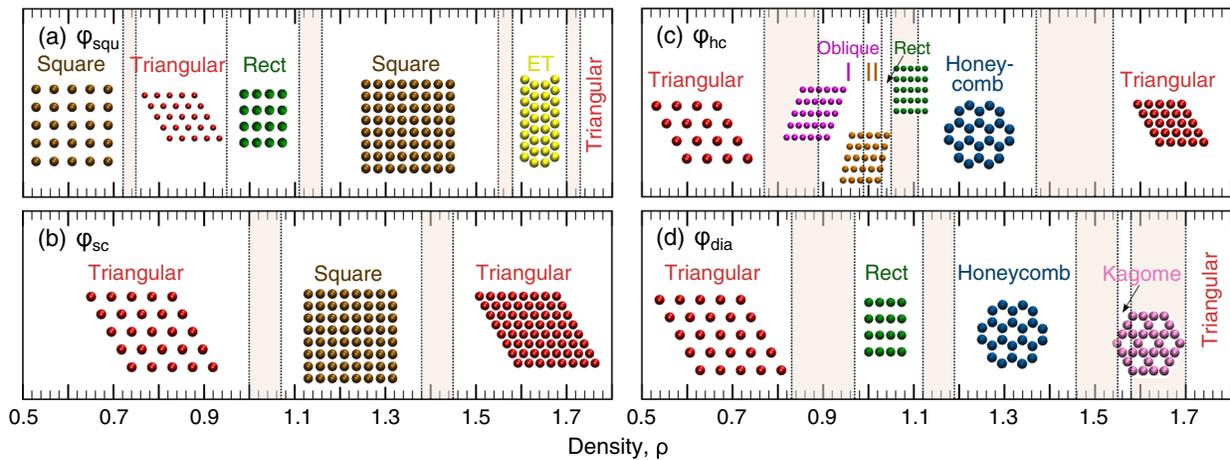


FIG. 2. 2D ground-state lattices as a function of density for (a) φ_{squ} , (b) φ_{sc} , (c) φ_{hc} , and (d) φ_{dia} . Shaded regions represent coexistence between the neighboring lattices on the phase diagram. ET represents the elongated-triangle Archimedean tiling. Parameters for the oblique and rectangular (Rect) lattices are provided in Table S2 in the Supplemental Material [58].

ground states of interest are obtainable by optimizing interactions for a corresponding analogous target lattice in 3D.

To test the same approach in the other direction, i.e., whether optimizing analogous 2D structures stabilizes 3D target lattices of interest, we also determine the 3D ground states for φ_{hc} and φ_{squ} . The results, presented in Table I, show that φ_{hc} and φ_{squ} indeed display wide stability regions for diamond-and simple cubic–lattice ground states, respectively. In fact, not only are the density ranges of the stable diamond lattice comparable for φ_{hc} and φ_{dia} , but the density range of the simple cubic lattice for φ_{squ} is even slightly wider than that of φ_{Sc} [63]. The latter result likely reflects the fact that the faster optimizations targeting 2D ground states enables a more thorough exploration of parameter space during the calculation than is practical in the 3D optimizations.

The fact that particles with isotropic interactions encoded to form 3D diamond (or simple cubic) lattices also display 2D honeycomb (or square) arrays, although nontrivial, is in some sense not surprising. The tetrahedrally coordinated diamond lattice itself consists of undulating interconnected trivalent honeycomb networks, and the simple cubic structure comprises square arrays stacked in registry. However, the outcome that particles with interactions

TABLE I. 3D ground states for φ_{hc} and φ_{squ} with their corresponding density ranges and optimal lattice parameters. Roman numerals denote different structures of the same lattice type. Diamond and simple cubic ground-states are highlighted among other stable phases. Nomenclature is that of an earlier reference [56].

Lattice	Stability range	Lattice parameters
<i>Honeycomb-lattice forming potential, φ_{hc}</i>		
bcc	[0.589, 0.677]	
A7-I	[0.725, 0.777]	$b/a : 2.23, u : 0.075$
A7-II	[0.856, 1.05]	$b/a : 4, u : [0.68, 0.81]$
Diamond	[1.091, 1.376]	
Hexagonal	[1.468, 1.474]	$c/a : 1.38$
A20-I	[1.477, 1.498]	$b/a : 1.72, c/a : 2.8, y : 0.5$
A20-II	[1.54, 1.851]	$b/a : 1.8, c/a : 0.65, y : 0.66$
<i>Square-lattice forming potential, φ_{squ}</i>		
β Sn-I	[0.587, 0.641]	$c/a : 2.67$
B10-I	[0.664, 0.798]	$c/a : 0.4, z : 0.5$
fcc	[0.828, 0.961]	
A20-I	[0.991, 1.047]	$b/a : 1.0, c/a : 0.68, y : 0.8$
oC8-Ga	[1.056, 1.094]	$b/a : 1.0, c/a : 1.5$ $u : 0.75, v : 0.163$
B10-II	[1.1, 1.267]	$c/a : [0.72, 0.73],$ $z : [0.38, 0.39]$
A20-II	[1.282, 1.298]	$b/a : 2.29, c/a : 1.79, y : 0.08$
β Sn-II	[1.322, 1.478]	$c/a : [0.57, 0.64]$
Hexagonal-I	[1.49, 1.592]	$c/a : [0.887, 0.9]$
Simple cubic	[1.606, 1.949]	
β Sn-III	[1.98, 2.106]	$c/a : 2.74$

designed to stabilize 2D honeycomb (or square) lattices also favor diamond (or simple cubic) lattices and not other morphologies containing honeycomb (or square) motifs such as graphite (or body-centered cubic) structures is much more interesting.

To understand these results, it is helpful to recall that—for isotropic potentials—the zero-temperature chemical potential depends only on the pair interaction and properties of coordination shells located at distances closer than the interaction cutoff, $x < x_{\text{cut}}$. In Fig. 3, we plot the interparticle separations corresponding to the first, second, and third coordination shells $\{x_1, x_2, x_3\}$ for the four lattices of interest here—honeycomb, square, diamond, and simple cubic—considering densities where these lattices are the ground states for the models φ_{hc} and φ_{squ} . First, note that there is considerable overlap between the coordination-shell distances of the honeycomb and diamond structures. Thus, an isotropic potential that stabilizes a honeycomb structure in 2D is expected to be an excellent (if not necessarily optimal) candidate for forming a diamond lattice in 3D, and vice versa. This helps to explain the near identical potentials, φ_{hc} and φ_{dia} , despite their being obtained via optimization of different target structures in different spatial dimensions.

To gain further insight, we also compare the coordination-shell distances of the honeycomb lattice with another related 3D structure, graphite, which consists of

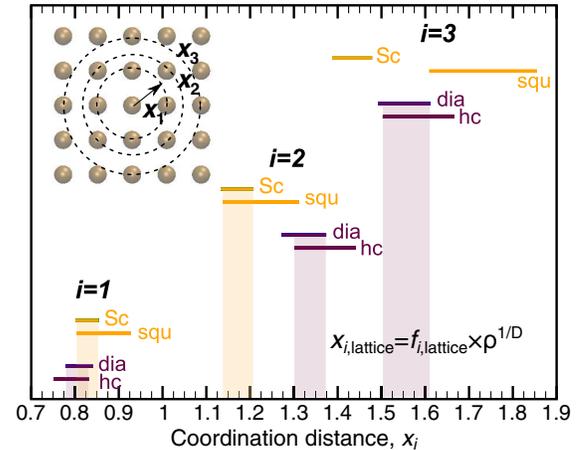


FIG. 3. Separations corresponding to first ($i = 1$), second ($i = 2$), and third ($i = 3$) coordination shells within the stability range of honeycomb (hc) $\rho = [1.11, 1.37]$ and diamond (dia) $\rho = [1.09, 1.38]$ ground states for φ_{hc} , as well as square (squ) $\rho = [1.16, 1.55]$ and simple cubic (Sc) $\rho = [1.61, 1.95]$ ground states for φ_{squ} . The coordination distance (x_i) for shell i is related to density (ρ) by $x_{i,\text{lattice}} = f_{i,\text{lattice}} \times \rho^{1/D}$, where $D = 2$ for hc and squ, and $D = 3$ for dia and Sc. For hc, $f_1 = 0.877383$, $f_2 = \sqrt{3}f_1$, $f_3 = 2f_1$; for squ, $f_1 = 1$, $f_2 = \sqrt{2}f_1$, $f_3 = 2f_1$; for dia, $f_1 = 0.866025$, $f_2 = \sqrt{8/3}f_1$, $f_3 = \sqrt{11/3}f_1$; for Sc, $f_1 = 1$, $f_2 = \sqrt{2}f_1$, $f_3 = \sqrt{3}f_1$. Shaded regions indicate overlap of coordination-shell distances for analogous 2D and 3D stable lattice ground states.

stacks of 2D honeycomb (i.e., graphene) sheets. Note that only the nearest-neighbor distances of mechanically stable 3D graphite lattices align with the first coordination-shell separations of 2D honeycomb structures, and there is substantial mismatch of other relevant coordination distances ($i \geq 2$) (see Fig. S1 in the Supplemental Material [58]). In this important sense, graphite—while closely related to the honeycomb lattice in other ways—is not as *analogous* to honeycomb as the 3D diamond structure is in its relation between interaction and coordination-shell structure, and is thus not favored as a ground state by φ_{hc} at any density. In comparing the other case of square versus simple cubic lattices, we see that the first two coordination shells of these structures similarly overlap, but the third shell positions are not in alignment. This result—together with the ground-state calculations presented above—suggests that, for short-range interactions, the common separation distances between the nearest and next-nearest neighbors for square and simple cubic structures is enough to allow for an optimal 2D square-forming potential to assemble into 3D simple cubic structures, and vice versa. However, the differences in the third-shell distances might help to explain the significant variations in the optimized potentials targeting 2D square (φ_{squ}) versus 3D simple cubic (φ_{sc}) lattices shown in Fig. 1.

In Figs. 4(a)–4(d), we present snapshots of configurations obtained from the Monte Carlo quench simulations for the four potential models. Configurations for the 3D diamond and simple cubic lattice obtained via quenching systems interacting with 2D-optimized φ_{hc} and φ_{squ} interactions are shown in Figs. 4(e) and 4(f), respectively. The structures obtained are inspected visually, and their configurational energies and pair distribution functions $g(r)$ are compared to equilibrated lattice structures at the corresponding densities and temperatures (see Table S1 in the Supplemental Material [58]). In Fig. 4(g), the complete overlap of the pair distribution functions of the quenched fluid (red circles) and the equilibrated simple cubic structure (black dashed lines) demonstrates the assembly of a defect-free simple cubic crystal. The φ_{hc} model similarly assembles into a (slightly defective) diamond structure as illustrated by the comparison of the pair distribution functions in Fig. 4(h). The energy of the quenched configuration is only 0.09% higher than the perfectly equilibrated diamond lattice. Nonetheless, in all cases, the structures obtained by the Monte Carlo quench procedure match the expectations of the ground-state calculations.

In summary, we investigate the cross-dimensional phase behavior of specifically designed isotropic interactions with low coordination. In particular, we determine the 3D-ordered lattices favored by isotropic potentials φ_{hc} (φ_{squ}) optimized to exhibit stable 2D honeycomb (square) lattice structures, as well as the 2D periodic structures favored by isotropic potentials φ_{dia} (φ_{sc}) optimized to assemble into 3D diamond (simple cubic) morphologies.

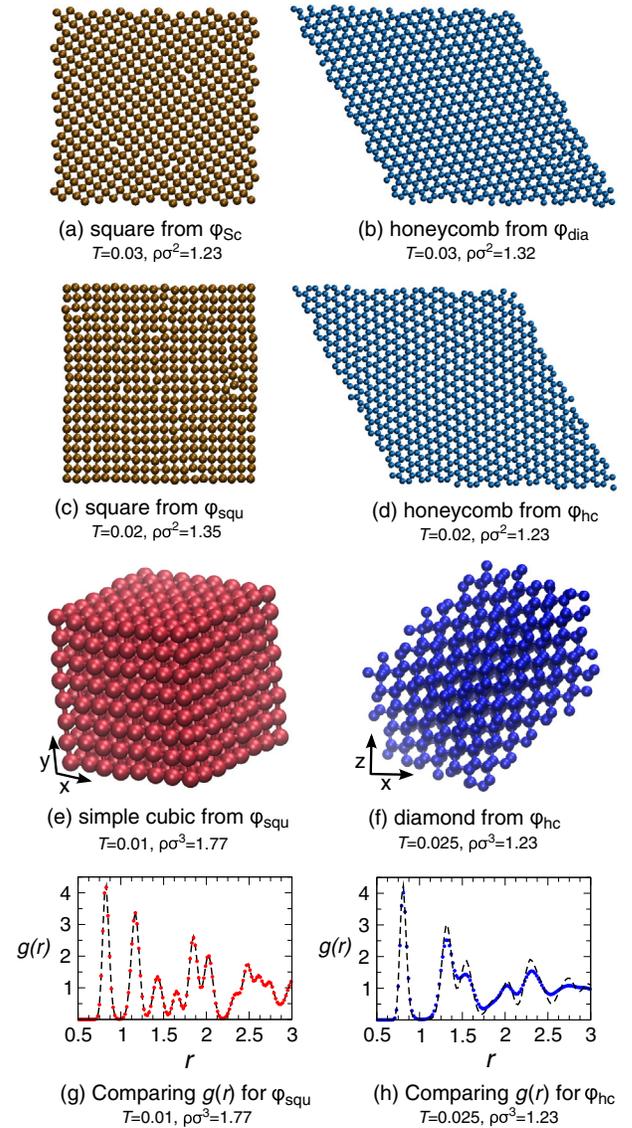


FIG. 4. Snapshots of 2D configurations obtained from Monte Carlo quenches of (a) φ_{sc} , (b) φ_{dia} , (c) φ_{squ} , (d) φ_{hc} and 3D configurations obtained from quenches of (e) φ_{squ} and (f) φ_{hc} . For the 3D structures, we plot the corresponding pair distribution functions $g(r)$ of the quenched configurations (dots) and the perfectly equilibrated lattice structures (dashed lines) in (g) and (h), at the specific temperature (T) and density (ρ), to demonstrate the structural similarities. The comparison between the pair distribution functions of the annealed and perfectly equilibrated diamond lattice in (h) shows that the annealed structure is not quite defect free, but the configuration energy is only 0.09% higher than that of the perfect lattice. For more details, see Table S1 in the Supplemental Material [58].

We find surprising transferability of interactions designed to stabilize analogous structures in 2D and 3D, and we gain insight into this behavior by studying the different ways in which information in the analogous target structures encodes itself in the optimal isotropic potentials through coordination-shell geometry.

One practical implication of the observed physics in this study is that the design of certain 3D lattices can greatly benefit from knowledge of potentials derived to maximize the stability of analogous 2D structures, information that can be obtained at relatively modest computational expense. The computational efficiency gained from this approach might be most valuable in multistep optimization processes, where the goal to search for an interaction potential favoring a target structure is only one of several objectives within the design calculation. It will also be interesting in future studies to explore the effects of the interaction range on the cross-dimensional behavior of isotropic interactions obtained through inverse design, especially where one limits the potential range to encompass only two coordination shells. While we focus here on the dimensionality dependence of design rules pertaining to target structures formed by isotropic interactions, it will also be informative to study the effect of spatial dimension on other classes of interactions, e.g., short-ranged anisotropic interactions of patchy particles relevant to 2D and 3D assembly scenarios.

Finally, in the context of cross-dimensional freezing behavior, we note the differences between the soft repulsive interactions studied here—which enthalpically stabilize low-coordinated periodic structures—and hard-sphere systems where entropy drives the particles to adopt close-packed periodic structures at high density. For the latter, crystallization from the fluid becomes increasingly more challenging in higher spatial dimensions due to correspondingly stronger geometric frustration [64,65]. The role that frustration plays in the dimensionality dependence of crystallization for particles with considerably softer repulsions remains a potentially rich area for future study.

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($b/a = 1.7$), and snub-hexagonal lattices. For the square lattice, the final pool comprised triangular, oblique ($b/a = 1.514$, $\theta = 1.234$), kagome, honeycomb, elongated-triangular, snub-hexagonal, and snub-square lattices. For diamond, the pool [30] consisted of fcc, WUR, SH ($c/a = 1.5$), β Sn ($c/a = 1.39$), β Sn ($c/a = 1.25$), A7 ($b/a = 3.79$, $u = 0.1385$), and A20 ($b/a = 1.728$, $c/a = 0.626$, $y = 0.167$) lattices. For simple cubic, the pool [30] comprised fcc, bcc, diamond, Hexagonal (SH) ($c/a = 1$), SH ($c/a = 1.08$), SH ($c/a = 1.172$), A20 ($b/a = 1.72$, $c/a = 0.66$, $y = 0.67$), β Sn ($c/a = 0.873$), β Sn ($c/a = 0.78$), and β Sn ($c/a = 1.75$) lattices. Here, b/a and c/a denote the aspect ratio of the sides of the unit cell, and θ is the angle between the two sides. The other symbols u and y , we adopt here, are the same as those used in a previous study [56].

- [58] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevX.4.031049> for details on the Monte Carlo isochoric quenching simulations, 2D ground-state phase diagrams for all the four optimal potentials, and coordination shell analysis corresponding to the honeycomb-forming potential for honeycomb, diamond and graphite structures.
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