

Formation of binary cluster crystals by ultrasoft particles

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We provide, to our knowledge, first and unambiguous evidence of the existence of cluster crystals formed by a binary mixture of ultrasoft, cluster-forming particles. In an effort to reduce the high dimensionality of the parameter space of binary mixtures, we have restricted ourselves to a symmetric, equimolar system, introducing as the pivotal parameter the scaling factor ζ that characterizes the cross interaction. Our investigations are based on a commonly used model for ultrasoft particles and on classical density functional theory, which, within a mean-field framework, allows for mixed clusters composed of particles of both species. Minimizing the free energy functional predicts three competing cluster crystal structures, namely, a bcc and a tetragonal lattice that reduces under certain conditions to an fcc lattice. The emerging phase diagram is rather intricate, but is well understood in terms of an energetic competition between the two sublattices. Complementary molecular dynamics simulations confirm the stability of the predicted structures and allow to trace the particles in their migration processes through the crystal.

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I. INTRODUCTION

Ever since their discovery [1], cluster crystals have attracted a remarkable amount of interest within the soft matter community (see, e.g., Refs. [2–6]). In this exotic phase, which is formed by a certain class of so-called ultrasoft particles (i.e., particles that can partially or fully overlap at a moderate energy penalty comparable to thermal energies), clusters of overlapping particles are formed, which, in turn, populate the lattice positions of regular (bcc and fcc) lattices. These ultrasoft particles can be viewed as coarse-grained models of soft matter particles that are characterized by complex internal structures (such as polymers, dendrimers, etc.). After tracing out the internal degrees of freedom of their monomeric constituents, these entities interact via effective potentials [7] that assume a finite value at vanishing separation and thus allow for partial or even full overlap. In most of the investigations dedicated to cluster-forming systems, a simplified, analytic model has been used [1,8,9], termed “general exponential model of index n ” (GEM- n and $n > 2$ [10]), given by

$$\Phi(r) = \epsilon \exp[-(r/\sigma)^n], \quad (1)$$

with parameters specified below.

Throughout the past years, cluster-forming systems have been thoroughly studied. For the novel phase of cluster crystals, several surprising features have been identified that stand in striking contrast to those observed in strongly repulsive

systems (such as Lennard-Jones systems): (1) An increase in the density ρ , for instance, by adding particles to the system, leaves the lattice constant of the cluster crystal unchanged, while the cluster occupation number increases linearly with ρ ; (2) the emergence of two types of density fluctuations, giving rise to two distinct sound modes [2]; (3) a highly complex phase diagram at low temperatures, including isostructural solid-solid transitions [3]; and (4) a striking self-assembly behavior when such systems are exposed to external shear forces [4], to name a few.

We note in passing that a different class of ultrasoft particles, namely particles interacting via a Gaussian potential (obtained from the above potential for $n = 2$), exhibits an entirely different phase behavior with ordered phases characterized by singly occupied lattice sites (see, in particular, the pioneering work of Stillinger [11,12]).

Pushing forward the investigations on the formation of cluster crystals by *binary* mixtures of these ultrasoft particles represents a formidable challenge: First, it is *a priori* not evident that such a binary cluster phase will emerge as a stable phase at all; second, the rather large number of parameters that characterize a binary system represents formidable conceptual and numerical challenges, which were presumably the reason why binary cluster crystals have been studied so far only very rarely (see, e.g., Ref. [5]).

In an effort to provide an answer to the first issue raised above and to cope concomitantly with the high dimensionality of the parameter space, we have considered in our investigations an equimolar, size-symmetric mixture of cluster-forming particles (specified below), reducing thereby the parameter space substantially: While like particles interact via the same GEM- n potential, unlike particles feel a scaled repulsion of the same functional form, quantified by the parameter $\zeta > 1$. Even though conceptually and numerically still challenging, our proposed approach, which is based on classical density functional theory (DFT), allows us to provide an unambiguous

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answer on the existence of binary cluster crystals; we note that the concept presented in this contribution (for details, see Appendix A) is formulated in a general manner such that it will help us to treat the general binary case readily in the future and to provide a comprehensive insight into the formation of binary cluster crystals.

Similar to the one-component case, our investigations are based on classical DFT [13–15], where the mean-field (MF) functional is generalized to the binary case. We critically assess these DFT predictions against extensive molecular dynamics (MD) simulations, which allow us to trace the trajectories of the individual particles in detail.

Based on these two complementary approaches, we can confirm the emergence of binary cluster crystals. For moderate values of ζ , both a bcc and an fcc/tetragonal phase emerge, where the tetragonal structure can be considered as a distorted fcc phase with the distortion induced by the parameter ζ and the cluster composition; the bcc and the fcc/tetragonal phases are separated by a well-defined first-order transition. As the repulsion becomes stronger with growing ζ , the bcc crystal is gradually suppressed, leaving an increasingly distorted tetragonal phase as the only stable ordered cluster crystal phase of the binary system.

II. MODEL

In our binary mixture (with components A and B), particles interact via the ultrasoft GEM- n potential specified in Eq. (1) which is generalized in a straightforward manner to the binary case (introducing energy and length parameters ϵ_{ij} and σ_{ij} , respectively). Henceforward, the indices i and j will assume the values A and B. As in previous contributions [1,8,9], we choose $n = 4$. Due to the aforementioned symmetry, we have $\epsilon_{AA} = \epsilon_{BB} \equiv \epsilon$ and $\epsilon_{AB} = \zeta\epsilon$ (with $\zeta > 1$) and $\sigma_{ij} \equiv \sigma$ (for $i, j = A$ or B); for $\zeta = 1$, we recover the one-component case. The concentrations for the two species fulfill $x_A = x_B = 0.5$ with $x_i = N_i/N$, N being the total number of particles (confined in volume V) and $N_A = N_B$. ϵ and σ represent henceforward the energy and the length scales of our system. $\rho = N/V$ is the bulk density and T denotes the temperature.

III. DFT

For the DFT calculations, we have throughout employed an MF format for the free energy functional $\mathcal{F} = \mathcal{F}[\rho_A, \rho_B]$, which is obtained in a straightforward extension of the one-component case (see, for instance, Refs. [16–19]); $\mathcal{F}[\rho_A, \rho_B]$ is now a functional of the two partial density profiles $\rho_i(\mathbf{r})$. The related, rather lengthy expression of the functional is presented in Appendix A along with further references about the conceptual steps that lead to this functional. We model the cluster crystal via two interlaced, commensurate sublattices (for details of the parametrization, cf. [20–23]). In the first and straightforward version (termed “standard format,” superscript “std”), we assume in an idealized manner that only *pure* clusters of particles of either species populate the respective sublattices; results based on this model were presented as a first contribution in Ref. [24]. In a more refined version of the functional (“extended format,” superscript “ext”), we introduce the parameter $m \in [0, 1]$ which quantifies the degree of mixing of the clusters (as observed in computer simulations

and as discussed below). To be more specific, m and $(1 - m)$ are the fractions of A and B particles, respectively, in the clusters populating one sublattice; conversely, $(1 - m)$ and m specify the respective fractions of A and B particles in the other sublattice. Obviously, for $m = 0$ the “standard format” is recovered. Within this “extended” framework, it is guaranteed that $N_A = N_B = N/2$, as imposed from the beginning [25]. The related expression for the functional is presented in Appendix A 2. m will enter the DFT formalism as an additional parameter to be optimized. The validity of the two formats for the functional will be discussed below, notably within the context of complementary simulation results. We note that a related step from pure to “mixed” sublattices was also previously considered for singly occupied ordered structures, populated by particles of a Gaussian mixture (see Ref. [18]).

As usual, we have introduced Gaussian profiles for the partial densities for each species, i.e.,

$$\rho_i(\mathbf{r}) = \sum_{\{\mathbf{R}_i\}} n_{c,i} \left(\frac{\alpha_i}{\pi} \right)^{\frac{3}{2}} e^{-\alpha_i(\mathbf{r}-\mathbf{R}_i)^2}, \quad i = A, B; \quad (2)$$

the $\{\mathbf{R}_i\}$ are the positions of the clusters in the two interpenetrating sublattices. We further introduce the parameters α_i (the width of profile i) and $n_{c,i}$ (the cluster occupation number for species i in the related sublattice). According to the principles of DFT [13,14], the equilibrium cluster crystal is obtained at a given temperature T and density ρ by minimizing $\mathcal{F}[\rho_1, \rho_2]$ in the space spanned by the following set of parameters: It comprises α_i , $n_{c,i}$, and those parameters that specify “all possible” lattices (cf. [20–23]); for the “extended format,” the parameter m represents an additional parameter to be optimized. This optimization is realized for every state point by an unconstrained minimization of the functional in the high-dimensional parameter space, spanned by all the aforementioned quantities; for the case of simple sublattices, this space has at least 21 dimensions. The minimization is carried out in the first step with the help of sophisticated numerical tools based on evolutionary algorithms (EAs) [20,21,26,27] (see Refs. [20–23]) and is refined in the second step by a hill climbing algorithm (for details, cf. Refs. [20–23]). The reliability of this approach has been tested thoroughly.

For completeness, the expression of the free energy of the liquid phase with the MF concept at hand is given in Appendix B.

IV. SIMULATIONS

MD simulations were carried out in the NVT ensemble with typically ~ 300 particles, confined in a orthorhombic box and assuming periodic boundary conditions. We have taken benefit of the advantageous features of the LAMMPS code [28]; the heat bath was realized via a DPD thermostat (for details, see Ref. [29]). The time increment of the simulation runs was assumed to be $\Delta t = 0.005$, measured in time units $t_0 = \sigma \sqrt{m/\epsilon}$. Each system was equilibrated for 3×10^6 time steps; subsequent production runs extended the total simulation time over 1×10^7 time steps, from which eight statistically independent ensembles were extracted. Further details of the simulation protocol are provided in Appendix D.

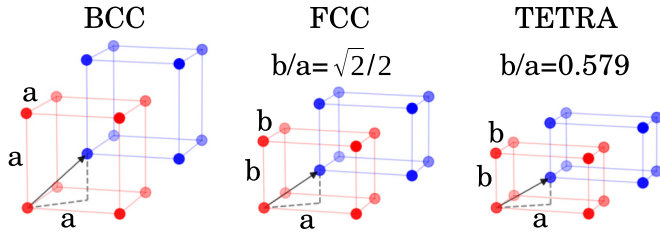


FIG. 1. Schematic representation of the bcc (left), fcc (center), and tetragonal (right) structures, identified as the energetically most favorable binary cluster crystals (see text); for the latter structure, the ratio b/a of the edge lengths is specified. The black vector connects the origins of the two interlaced sublattices (with its projections shown as black dashed lines). Red and blue points represent pure A or B clusters, located at the lattice positions of each sublattice, as imposed by the “standard format” of the functional (see text). The edges of the respective unit cells are labeled by a and b ; for the tetragonal lattice, the value of b/a is specified (occurring for $T = 1.0$, $\rho = 6.0$, and $\zeta = 1.5$).

In an effort to quantify the composition of the clusters, we have introduced the purity parameter π of a cluster, being defined as the fraction of the dominant species in this cluster, irrespective of A and B particles; π obviously ranges within the interval $[0.5, 1.0]$. We have intentionally introduced the symbol π for this quantity as it is calculated from simulations, while the above introduced variable m is obtained within the DFT concept. For further details related to the simulations, we refer to Appendix D.

V. RESULTS

Despite the fact that we consider the simplest system among all possible binary mixtures, the emerging phase diagram for the binary cluster crystal is rather involved and offers several unexpected features. The EA-based search proposes in total three interlaced structures of A and B sublattices, which are built up by the following structural units: (1) two cubic substructures where the origin of one sublattice is located in the center of the other sublattice (featuring a bcc-type structure); (2) two tetragonal sublattices (with an edge length ratio of $b/a = \sqrt{2}/2$), where the origin of one sublattice is located in the center of the other sublattice (featuring an fcc-type structure); and (3) two tetragonal sublattices where the origin of one sublattice is located in the center of the other substructure. For simplicity, we will term the remaining three structures as bcc (characterized by a cube of edge length a), fcc (characterized by the edge lengths a and b , with $b/a \equiv \sqrt{2}/2$), and tetragonal (characterized by edge lengths a , b , and b); for a schematic representation, see Fig. 1. The tetragonal structure reduces for $b/a \rightarrow \sqrt{2}/2$ to the fcc structure, as encountered in the phase diagram of the one-component case (i.e., for $\zeta \rightarrow 1$) [1,8].

Before proceeding to a detailed discussion of the emerging phase diagrams, the following notes are in order: (1) In the entirety of this contribution, we have set aside the disordered (liquid and gas) phases of the system. Due to the repulsion between unlike particles, the disordered system has a rich phase behavior itself, characterized—below a related critical

point—by a first-order phase transition between A- and B-rich disordered phases (see, e.g., Refs. [30,31] for the particular values $\rho\sigma^3 = 2$ and $\zeta = 1.5$). The interplay between these phase transitions (and the related critical lines and coexistence lines) and the phase diagrams of the ordered phases (as identified in this contribution) will eventually lead—depending on the parameter ζ —to a rather broad variety of intricate phase transition scenarios, whose identification and discussion would clearly pass the limits and intentions of this contribution. Thus, we will focus in the following exclusively on the emerging ordered cluster phases and the related phase diagrams. In an effort to “delimit” the ordered phases toward lower densities, we display in the phase diagram the “no solution line,” i.e., the line beyond which the optimization of the functional is incompatible with the assumption of a nonuniform phase; this line should give a qualitative indication of the limit of metastability of the respective ordered phase. (2) The ordered cluster phases transform via first-order phase transitions across very narrow coexistence regions which are not visible within line thickness. We have shifted the numerical details related to the identification of the coexistence densities to Appendix C; in the figures discussed below, the coexistence regions are represented by a single line.

The pivotal parameter of the system, ζ , has been varied over a representative range, i.e., $\zeta \in [1, 1.5]$. Depending on its value, different scenarios are encountered: (1) for $\zeta = 1$, we exactly reproduce the phase diagram presented in Ref. [32]; this applies not only to the coexistence lines of the bcc and the fcc cluster phases but also to the coexistence lines between the bcc and the well-defined disordered, liquid phase, using the free energy function for the latter phase as presented in Appendix B; for obvious reasons, this phase diagram is not fully reproduced here. (2) Between $\zeta = 1$ and a threshold value ζ_{th} (quantified and discussed below), a bcc and an fcc/tetragonal cluster crystal emerge in wedge-shaped regions of the (T, ρ) plane. (3) Eventually, for $\zeta \gtrsim \zeta_{\text{th}}$ the bcc lattice is energetically throughout less favorable and thus only—and now exclusively—tetragonal cluster crystals emerge as the ordered phase of the system.

The phase diagrams that are obtained for different ζ values in the (T, ρ) plane are shown in Fig. 2; for reference, the bcc-fcc transition line for the pure case ($\zeta = 1$) is also indicated. In the left panel we show results based on the “extended format” of the functional (as defined above): The bcc phase exists in a wedge-shaped region whose extent (denoted by the horizontal arrows) shrinks continuously as ζ increases and eventually vanishes. Concomitantly, the region of stability of the competing fcc/tetragonal structure (which is found along the isotherms for densities higher than the density at the transition) extends; more detailed calculations provide evidence that the bcc phase is entirely suppressed for $\zeta = \zeta_{\text{th}}^{\text{ext}} \simeq 1.23$. Furthermore, within the region denoted by “fcc/tetragonal,” the two lattices coexist over a limited range of ζ values, separated by a second-order transition. Detailed investigations about the location of this transition line in a phase diagram spanned by ρ , T , and ζ are currently carried out, notably supported by extensive and detailed computer simulations; related results are postponed to a forthcoming contribution [24]. In the right panel of Fig. 2, the related phase diagrams obtained within the “standard format” of the functional are

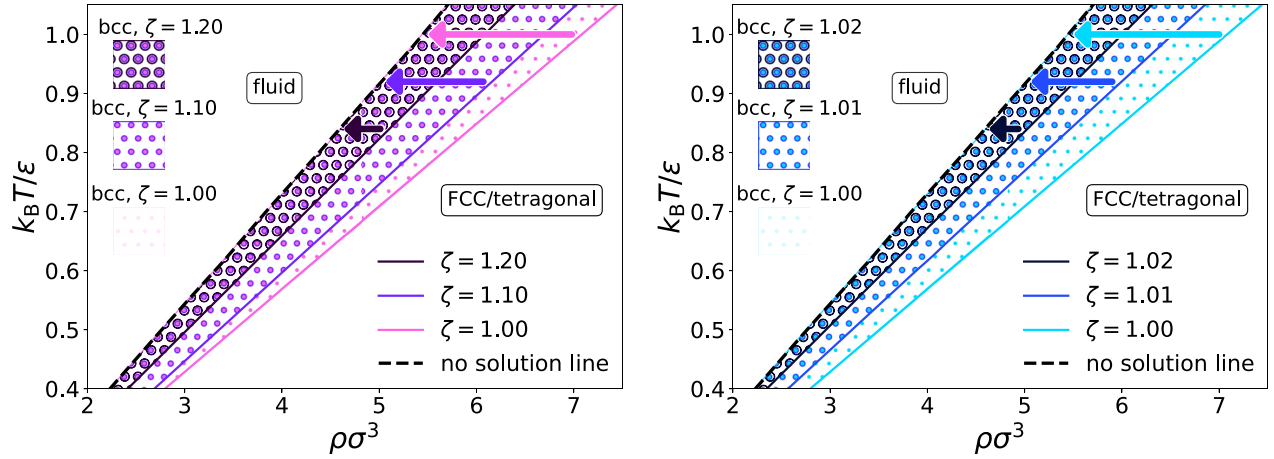


FIG. 2. Phase diagram in the (T, ρ) plane for the binary cluster system at hand evaluated for different values of ζ (as labeled); for reference, the bcc-fcc transition line of the one-component case is included (labeled with $\zeta = 1$) [1,8,9]. Results are based on DFT calculations: left—“extended format;” right—“standard format” (see text for details). The dashed black line (“no solution line”) indicates the line beyond which the optimization of the functional is incompatible with the assumption of a nonuniform phase. The colored, hatched regions represent the regions of stability of the bcc cluster phase with the horizontal arrows (colored according to the respective ζ values) indicating the “spatial extent” of the respective stable bcc phase (see insets for the color code). The region to the right of the respectively colored wedge is the region of stability of the fcc or tetragonal phases, whose limits tend with growing ζ toward the “no solution line” (see text).

shown: Note that within this framework the chosen ζ values are now considerably closer to unity and we find that already beyond $\zeta = \zeta_{\text{th}}^{\text{std}} \simeq 1.03$ the bcc phase eventually vanishes [22,23].

The competition between the emerging phases is discussed below on the basis of the data shown in Fig. 3. For ζ values close to unity (here, $\zeta = 1.02$), our results indicate that the clusters are essentially mixed, i.e., $m = 0.5$, irrespective of the underlying structure (see the right panel of Fig. 3). In

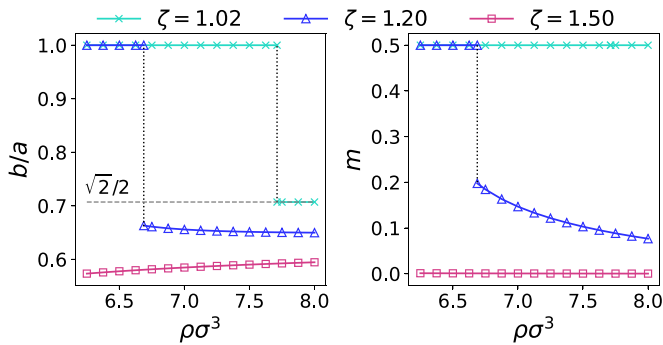


FIG. 3. Left: Ratio of lattice constants, b/a , as obtained via the “extended” version of the DFT concept (see text) for the emerging cluster crystal structures as a function of the density $\rho\sigma^3$ for different values of ζ (as labeled) at fixed temperature $k_B T/\epsilon = 1.1$. Dotted vertical lines indicate the first-order phase transitions from the bcc structure ($b/a \equiv 1$) to an fcc structure ($b/a \equiv \sqrt{2}/2$; dotted horizontal line) or a tetragonal structure (all other b/a values). For $\zeta_{\text{th}}^{\text{ext}} \gtrsim 1.24$, only the tetragonal structure is stable (see text). Right: m (as defined in the text) as a function of the density $\rho\sigma^3$ for different values of ζ (as labeled). $m = 0.5$ corresponds to mixed clusters, while $m = 0$ corresponds to pure clusters. The dotted vertical line indicates the transition bcc $\leftrightarrow$ tetragonal; see left panel.

this sense, the system resembles the one-component case, since *all* clusters are essentially identical, apart from local compositional fluctuations that a mean-field concept is not able to capture. Compared to the one-component case, however, the internal energy of the clusters is now higher due to the mutual repulsion between A and B particles within a cluster. It therefore does not take wonder that for the case of mixed clusters the bcc and the fcc lattices are again competing structures; note for $\zeta = 1.02$ the first-order transition, marked by the discontinuities in the quantities displayed in both panels at $\rho\sigma^3 \simeq 7.7$ (see the vertical dotted line) along the selected isotherm of $k_B T/\epsilon = 1.1$. However, with a furthermore increasing ζ (visualized in this figure for $\zeta = 1.2$), the repulsion between A and B particles leads to an—at least partial—purification process of the clusters (which is documented in more detail via the simulation data; see below): In this process, one of the two species in a given cluster dominates and eventually excludes particles of the other species from these clusters; within our “extended” formalism, pure clusters occupy the positions of the respective sublattices. Now, a competition between the sublattices sets in based on energetic reasons: While in the bcc structure (characterized by $b/a \equiv 1$; see left panel of Fig. 3) the clusters still remain mixed ($m = 0.5$), a substantial purification process leads in the competing fcc/tetragonal structure to a significant drop in m (right panel of Fig. 3); notably, m tends with increasing ρ to $m = 0$, corresponding to pure clusters. Concomitantly, the former fcc structure (with $b/a \equiv \sqrt{2}/2$) becomes distorted leading to b/a values that now lie considerably below $\sqrt{2}/2$ for the emerging tetragonal structure; the related transition bcc $\leftrightarrow$ tetragonal occurs at $\rho\sigma^3 \simeq 6.7$ (see dotted vertical lines). Eventually, at $\zeta = 1.5$ all clusters are pure ($m \equiv 0$; see right panel of Fig. 3), the bcc cluster crystal is energetically no longer favoured and has vanished at the cost of a tetragonal lattice with $b/a \simeq 0.6$.

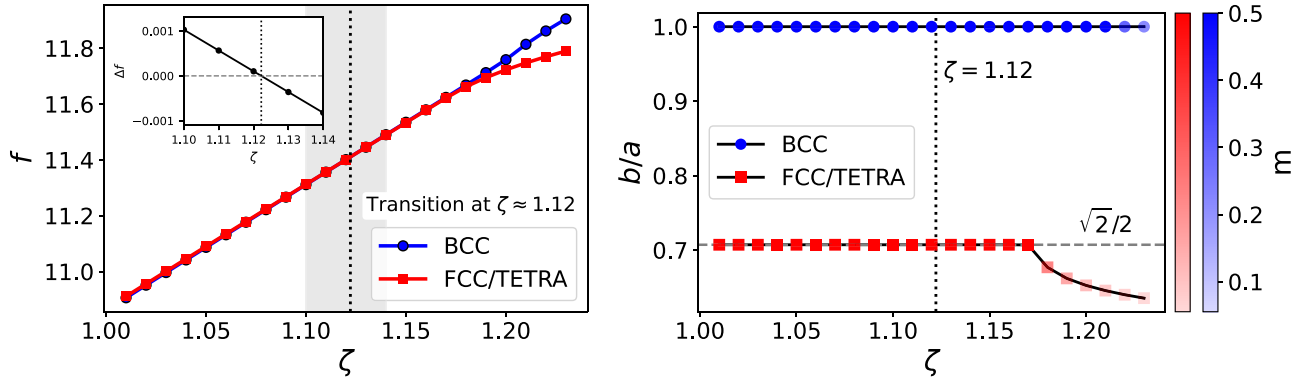


FIG. 4. Left: $f = \mathcal{F}/N$ as a function of ζ for the emerging bcc (blue line with circular markers) and the fcc/tetragonal (red line with square markers) structure at a state point, defined by $\rho\sigma^3 = 6$ and $k_B T/\epsilon = 0.9$. The inset of this panel provides for better visibility an enlarged view of the region where the two energy curves cross; to be more specific, we display in the inset $\Delta f = f_{\text{fcc/tetragonal}} - f_{\text{bcc}}$ and have highlighted the horizontal extent of this inset via the gray-shaded region in the main panel. Right: Ratio of the lattice parameters, b/a , as a function of ζ for the same state point: bcc lattice (with $b/a \equiv 1$)—blue line with circular markers, tetragonal lattice—red line with square markers; the dotted horizontal line quantifies the b/a value for an ideal fcc lattice. The red and blue symbols are furthermore shade coded for the respective m value; see scale at the right-hand side of the panels. The vertical dotted line indicates in both panels the location of the transition bcc $\rightarrow$ fcc/tetragonal.

In an alternative perspective, we present in Fig. 4 the free energy $f = \mathcal{F}/N$ and the ratio of the lattice constants, b/a , of the competing phases as functions of ζ for a given state point (i.e., fixing both ρ and T); temperature and density are chosen such that—depending on the value of ζ —the bcc as well as the fcc/tetragonal structures emerge as stable cluster crystals. The crossing of the two $f(\zeta)$ curves at $\zeta \simeq 1.12$ (vertical dotted line)—see left panel of Fig. 4—marks the transition between the competing lattices (for a detailed discussion of the common tangent construction of the coexisting phases, we refer the reader to Appendix C): Even though hardly visible on this scale, the bcc has a lower free energy for $\zeta \lesssim 1.12$, whereas the fcc/tetragonal phase is energetically more favorable for $\zeta \gtrsim 1.12$. The right panel of this figure, displaying the ratio b/a , provides evidence that the bcc structure (which is rigorously maintained, i.e., $b/a \equiv 1$ up to the ζ value of transition) transforms into an fcc lattice. The data for b/a visualize that the now stable fcc lattice furthermore transforms with increasing ζ continuously into a tetragonal structure (with $b/a < \sqrt{2}/2$), with a sizable distortion of the unit cell: An impression of this distortion can be obtained

from an exemplary simulation snapshot presented in the right panel of Fig. 5. With the symbols in the right panel of Fig. 4 being shade coded with respect to their m value, one can read off that in the bcc and in the fcc phase the clusters are mixed ($m = 0.5$), while the transition from fcc to tetragonal is accompanied (or possibly induced) by a purification process, visualized by a rapid decay from $m = 0.5$ to $m = 0$ as ζ increases.

Complementary MD runs have been carried out for numerous state points and confirm the stability of the DFT-predicted structures; exemplary snapshots, representing a bcc (left) and a tetragonal (right) cluster crystal, are shown in Fig. 5 with parameters T , ρ , and ζ specified in the caption. From both panels—notably the left panel—it is obvious that in the simulations the clusters are not pure. To clarify this issue, we have tracked the purity, π , of the emerging clusters (with π defined above). To this end, we have decorated in the initial configuration of the simulations the lattice positions of the cluster crystals randomly with A and B particles or we have created “pure” sublattices: for the equilibrated structures, we have calculated π once the system has been simulated

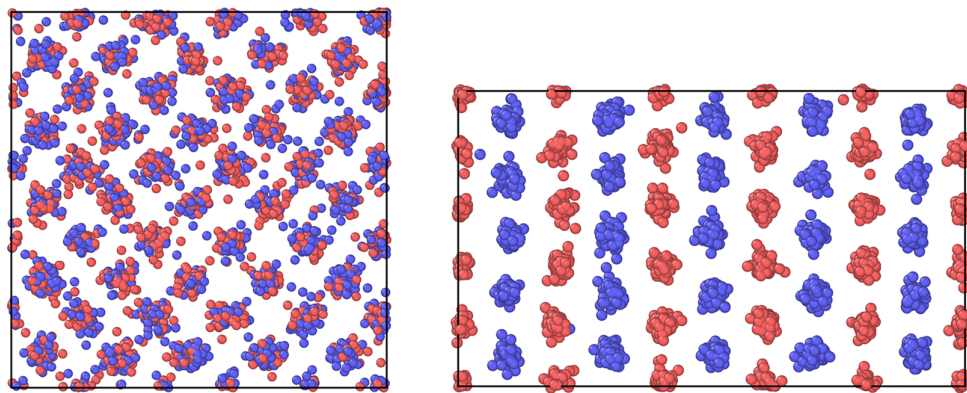


FIG. 5. MD simulation snapshots of two cluster crystals, both for $k_B T/\epsilon = 1.0$ and for $\rho\sigma^3 = 6.0$. Left: bcc lattice ($\zeta = 1.02$); right: tetragonal lattice ($\zeta = 1.5$). Particles of species A and B are colored in red and blue, respectively.

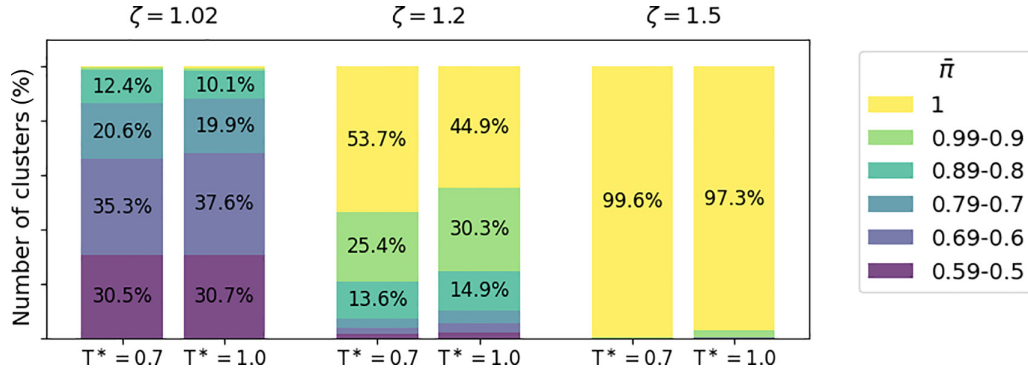


FIG. 6. Averaged purity parameter $\bar{\pi}$ obtained for different ζ values and different temperatures T (as labeled). The bar plot quantifies the percentage of clusters in the system that have attained after 3×10^6 simulation steps Δt a certain degree of average purity $\bar{\pi}$, according to the color code. For convenience, the values of $\bar{\pi}$ have been grouped into suitable intervals (see color code).

over $3 \times 10^6 \Delta t$; the values of π were averaged over 8000 independent configurations, leading to $\bar{\pi}$. This quantity is shown in Fig. 6 for three different values of ζ assuming in all cases the same two temperatures (as labeled); the results are independent of the two scenarios assumed for the initial configurations.

While a (rather small) value of $\zeta = 1.02$ leaves the clusters in a profoundly mixed state, the situation is found to be completely different as ζ increases from $\zeta = 1.2$ to eventually $\zeta = 1.5$. In the former case, nearly half of the clusters are pure ($\bar{\pi} \simeq 1$), while in the latter case essentially all clusters are pure. Thus, it is obviously a strong repulsion (via ζ) between unlike particles that pushes the particles back into “their” cluster, leading thereby to a purification process of the lattice. An additional temperature dependence becomes evident in the case $\zeta = 1.2$, where for the higher temperature the clusters are characterized by a lesser degree of purity due to the higher kinetic energy of the particles, which migrate via hopping processes from one cluster to a neighboring one. The simulation data fully confirm the necessity to introduce for ζ values closer to unity the use of the “extended format” of the functional, while for intermediate and large ζ values the “standard format” is fully sufficient.

VI. CONCLUSIONS

DFT-based calculations have provided first and convincing evidence of the existence of cluster crystals formed by binary mixtures of ultrasoft, cluster-forming particles, using the well-established GEM-4 interparticle potential. Considering a symmetric, equimolar binary mixture, we have optimized the functional and have identified three types of stable cluster crystals, formed either by two interlaced cubic or by two interlaced tetragonal sublattices, respectively: The first one is a generalized bcc lattice, the second one is a generalized fcc lattice, while the third one is a tetragonal lattice, which emerges from an fcc lattice via distortion. Depending on the pivotal parameter ζ , which quantifies the repulsion between unlike particles, we obtain a rather complex phase diagram in the (T, ρ) plane. The regions of stability of the three types of cluster crystals are found to emerge from a complex competition between the two sublattices and the composition of the clusters: The parameters that trigger the repulsion are ζ

and the density. Remarkably, the bcc structure can withstand this competition up to certain limiting values of $\zeta_{\text{th}}^{\text{ext}} \simeq 1.24$ and ρ but eventually has to give in, leaving either the fcc with mixed clusters (i.e., $m = 0.5$) or—eventually—the tetragonal structure with (essentially) pure clusters (i.e., $m = 0$) as the only remaining stable cluster crystal phases. The emerging first-order phase transitions are discussed with the help of characteristic quantities (such as the ratio of the lattice constants of the partial cluster occupancy parameter) that specify the two competing lattices. Complementary MD simulations confirm the stability of the predicted structures and document the emergence of mixed and pure clusters depending on the value of ζ . The investigations at hand open the gate into a so far unexplored field of research in soft matter physics. Even though the generalization of the DFT calculations to a *general* binary mixture of ultrasoft, cluster-forming particles (possibly mixing GEM particles with different exponents; see Ref. [33]) will definitely be very challenging, it will be highly rewarding, as it has a high potential to reveal surprising, so far unexplored and unexpected properties of this exotic phase.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX A: CLASSICAL DENSITY FUNCTIONAL THEORY

The formalism of classical density functional theory (DFT) [13–15] can be readily generalized to the binary case, where the free energy functional $\mathcal{F}$ is now a functional of the two partial density profiles $\rho_i = \rho_i(\mathbf{r})$, with $i = A$ or B denoting the two species. Choosing a mean-field format for the functional (as appropriate for a wide class of ultrasoft interactions [1,8,9,34]), $\mathcal{F}[\rho_A, \rho_B]$ is given by

$$\mathcal{F}[\rho_A, \rho_B] = \mathcal{F}^{\text{id}}[\rho_A, \rho_B] + \mathcal{F}^{\text{exc}}[\rho_A, \rho_B], \quad (\text{A1})$$

$$\mathcal{F}^{\text{id}}[\rho_A, \rho_B] = k_B T \sum_{i=A, B} \int d\mathbf{r} \rho_i(\mathbf{r}) \{ \ln[\Lambda_i^3 \rho_i(\mathbf{r})] - 1 \}, \quad (\text{A2})$$

$$\mathcal{F}^{\text{exc}}[\rho_A, \rho_B] = \sum_{i,j=A, B} \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') \Phi_{ij}(|\mathbf{r} - \mathbf{r}'|), \quad (\text{A3})$$

where $\Phi_{ij}(r)$ is the GEM-4 potential introduced in Eq. (1). Henceforward, T is the temperature, ρ is the bulk density, k_B is the Boltzmann constant, and the Λ_i are the de Broglie wavelengths whose role can be ignored.

1. The standard format

Starting from the above relation, the “standard format” of the functional is based on the following (simplifying) assumptions, which are discussed in the article in the context of MD simulations. These assumptions are as follows: (1) The structure of the cluster crystal is composed of two interlaced, commensurate sublattices with lattice vectors $\{\mathbf{R}_A\}$ and $\{\mathbf{R}_B\}$; (2) each sublattice is occupied by one particle species only; (3) the density profiles $\rho_i(\mathbf{r})$ are of Gaussian shape—see Eq. (2)—introducing thereby the width of the profiles α_i and the cluster occupation numbers $n_{c,i}$. With all this in mind, one arrives after some straightforward, albeit tedious manipulations at the following expression for $\mathcal{F}[\rho_A, \rho_B]$:

$$\frac{\mathcal{F}^{\text{id}}[\rho_A, \rho_B]}{N} = k_B T \sum_{i=A, B} x_i \left\{ \ln(n_{c,i}) + \frac{3}{2} \ln\left(\frac{\alpha_i}{\pi}\right) + 3 \ln(\Lambda_i) - \frac{5}{2} \right\}, \quad (\text{A4})$$

$$\begin{aligned} \frac{\mathcal{F}^{\text{exc}}[\rho_A, \rho_B]}{N} = & \sum_{i=A, B} x_i (n_{c,i} - 1) \sqrt{\frac{\alpha_i^3}{2\pi}} \int_0^\infty dr r^2 e^{-\frac{1}{2}\alpha_i r^2} \Phi_{ii}(r) \\ & + \sum_{i=A, B} x_i n_{c,i} \sqrt{\frac{\alpha_i}{8\pi}} \sum_{\{\mathbf{R}_i \neq 0\}} \int_0^\infty dr \frac{r}{R_i} [e^{-\frac{1}{2}\alpha_i(r-R_i)^2} - e^{-\frac{1}{2}\alpha_i(r+R_i)^2}] \Phi_{ii}(r) \\ & + \frac{n_{c,A} n_{c,B}}{N} \sum_{\{\mathbf{R}_A\}} \sum_{\{\mathbf{R}_B\}} \left\{ \delta_{\mathbf{R}_A, \mathbf{R}_B} \sqrt{\frac{\alpha_{AB}^3}{2\pi}} \int_0^\infty dr r^2 e^{-\frac{1}{2}\alpha_{AB} r^2} \Phi_{AB}(r) \right. \\ & + (1 - \delta_{\mathbf{R}_A, \mathbf{R}_B}) \sqrt{\frac{\alpha_{AB}}{8\pi}} \int_0^\infty dr \frac{r}{R_{AB}} [e^{-\frac{1}{2}\alpha_{AB}(r-R_{AB})^2} - e^{-\frac{1}{2}\alpha_{AB}(r+R_{AB})^2}] \Phi_{AB}(r) \Big\} \\ & + \frac{n_{c,A} n_{c,B}}{N} \sum_{\{\mathbf{R}_B\}} \sum_{\{\mathbf{R}_A\}} \left\{ \delta_{\mathbf{R}_A, \mathbf{R}_B} \sqrt{\frac{\alpha_{AB}^3}{2\pi}} \int_0^\infty dr r^2 e^{-\frac{1}{2}\alpha_{AB} r^2} \Phi_{AB}(r) \right. \\ & + (1 - \delta_{\mathbf{R}_A, \mathbf{R}_B}) \sqrt{\frac{\alpha_{AB}}{8\pi}} \int_0^\infty dr \frac{r}{R_{AB}} [e^{-\frac{1}{2}\alpha_{AB}(r-R_{AB})^2} - e^{-\frac{1}{2}\alpha_{AB}(r+R_{AB})^2}] \Phi_{AB}(r) \Big\}. \end{aligned} \quad (\text{A5})$$

In the above relation, $\alpha_{AB} = 2 \frac{\alpha_A \alpha_B}{\alpha_A + \alpha_B}$. For details, we refer the reader to the Supplemental Material of Ref. [23] and to Ref. [22].

2. The extended format

Data obtained from simulations indicate that for weak cross interactions (notably for $\zeta \lesssim 1.2$)—after a sufficient long equilibration, leading to the equilibrated cluster phases—mixed clusters (containing both A and B particles) populate the sublattices. Furthermore, it is found that irrespective of the sublattice and irrespective of the position in the respective sublattice the distribution of A and B particles within a given cluster is essentially identical.

The “standard format” of the functional as given in the preceding subsection, which assumes that each sublattice is populated by pure A or B clusters, is not able to take into account this feature in an adequate manner. Thus an “extended format” for the functional is required, which appropriately takes into account these findings of the simulations. In this version of the functional, we allow—again within an MF framework—both particle species to occupy both sublattices. To this end, we now label the sublattices with the index $\nu = \text{I or II}$, where I and II are no longer assigned to the particle species A and B (as this was assumed in the “standard format”). Further, we define a mixing parameter m and assume that a cluster of occupation number n_I on sublattice I contains mn_I particles of species A and $(1-m)n_I$ particles of

species B, while on sublattice II the compositions are given by $(1 - m)n_{\text{II}}$ and mn_{II} for A and B particles, respectively. In the limiting cases $m = 0$ and $m = 1$, we recover the ansatz of pure sublattices of the “standard format”; in contrast, $m = 1/2$ corresponds to completely mixed clusters located on the lattice positions of both sublattices (as observed in the simulations). The parameter m is incorporated into the formalism as an additional variational parameter and is determined by minimizing the free energy.

In the “extended” formulation, we keep the assumption of two interlaced, commensurate sublattices. The density profile of species i ($i = \text{A, B}$) is then written as

$$\rho_i(\mathbf{r}) = \sum_{\mathbf{R}_\text{I}} n_{\text{I},i} \left(\frac{\alpha_\text{I}}{\pi} \right)^{3/2} \exp[-\alpha_\text{I}(\mathbf{r} - \mathbf{R}_\text{I})^2] + \sum_{\mathbf{R}_\text{II}} n_{\text{II},i} \left(\frac{\alpha_\text{II}}{\pi} \right)^{3/2} \exp[-\alpha_\text{II}(\mathbf{r} - \mathbf{R}_\text{II})^2]. \quad (\text{A6})$$

Here, n_{vi} denotes the mean occupation number of species i on a cluster located on sublattice v and α_v is the localization parameter associated with sublattice v . Hence, all particles occupying sublattice v share the same Gaussian width, irrespective of their species. The Gaussian density peaks are defined as for the “standard format”—see Eq. (2)—except that the localization parameter α_v is now associated with sublattice v , rather than with the particle species. Therefore, all particles occupying sublattice v share the same localization parameter α_v . The total number of particles of species i is then given by

$$N_i = \int d\mathbf{r} \rho_i(\mathbf{r}) = \sum_{v=\text{I,II}} n_{\text{latt},v} n_{vi}, \quad i = \text{A or B}, \quad (\text{A7})$$

where $n_{\text{latt},v}$ is the number of lattice sites belonging to sublattice v . The total number of particles is thus

$$N = \sum_{i=\text{A,B}} N_i = \sum_{v=\text{I,II}} \sum_{i=\text{A,B}} n_{\text{latt},v} n_{vi}. \quad (\text{A8})$$

Proceeding as in the “standard format” and neglecting the overlap between Gaussian peaks centered on different lattice sites, the ideal contribution to the free energy functional (per particle) can be written as

$$\frac{\mathcal{F}^{\text{id}}[\rho_\text{A}, \rho_\text{B}]}{N} = k_\text{B} T \sum_{v=\text{I,II}} \sum_{i=\text{A,B}} x_{vi} \left[\ln(n_{vi}) + \frac{3}{2} \ln\left(\frac{\alpha_v}{\pi}\right) + 3 \ln(\Lambda_i) - \frac{5}{2} \right], \quad (\text{A9})$$

where

$$x_{vi} = \frac{N_{vi}}{N}, \quad N_{vi} := n_{\text{latt},v} n_{vi}. \quad (\text{A10})$$

The excess contribution to the functional, $\mathcal{F}^{\text{exc}}[\rho_\text{A}, \rho_\text{B}]$, preserves the MF structure of Eq. (A3). In particular, the Gaussian convolution kernels (defined below) are identical to those appearing in the pure cluster, “standard format”; only the occupancy-dependent prefactors have to be generalized; this generalization enters only through the sublattice- and species-resolved occupation numbers that weight the corresponding like- and unlike-pair contributions. For latter use,

we define

$$\alpha_{\text{I,II}} = \frac{2\alpha_\text{I}\alpha_\text{II}}{\alpha_\text{I} + \alpha_\text{II}}. \quad (\text{A11})$$

For pairs of particles whose Gaussian peaks belong to the same sublattice v , the relevant kernels are

$$u_{ij}^{\text{intra}}(\alpha_v) = \sqrt{\frac{\alpha_v^3}{2\pi}} \int_0^\infty dr r^2 e^{-\frac{1}{2}\alpha_v r^2} \Phi_{ij}(r), \quad (\text{A12})$$

$$u_{ij}^{\text{inter}}(\alpha_v; \mathbf{R}_v) = \sqrt{\frac{\alpha_v}{8\pi}} \int_0^\infty dr \frac{r}{R_v} [e^{-\frac{1}{2}\alpha_v(r-R_v)^2} - e^{-\frac{1}{2}\alpha_v(r+R_v)^2}] \Phi_{ij}(r), \quad (\text{A13})$$

where $R_v = |\mathbf{R}_v|$. For pairs connecting the two different sublattices, one obtains

$$u_{ij}^{\text{I,II}}(\alpha_{\text{I,II}}; \mathbf{R}_{\text{I,II}}) = \delta_{\mathbf{R}_\text{I}, \mathbf{R}_{\text{II}}} \sqrt{\frac{\alpha_{\text{I,II}}^3}{2\pi}} \int_0^\infty dr r^2 e^{-\frac{\alpha_{\text{I,II}}}{2} r^2} \Phi_{ij}(r) + (1 - \delta_{\mathbf{R}_\text{I}, \mathbf{R}_{\text{II}}}) \sqrt{\frac{\alpha_{\text{I,II}}}{8\pi}} \int_0^\infty dr \frac{r}{R_{\text{I,II}}} \times [e^{-\frac{\alpha_{\text{I,II}}}{2}(r-R_{\text{I,II}})^2} - e^{-\frac{\alpha_{\text{I,II}}}{2}(r+R_{\text{I,II}})^2}] \Phi_{ij}(r), \quad (\text{A14})$$

with $R_{\text{I,II}} = |\mathbf{R}_\text{I} - \mathbf{R}_{\text{II}}|$. As in the derivation of the “standard format,” the excess contribution to the free energy functional, $\mathcal{F}^{\text{exc}}[\rho_\text{A}, \rho_\text{B}]$, can be decomposed into intracluster, same-sublattice intercluster, and cross-sublattice contributions (with obvious superscripts) as follows:

$$\mathcal{F}^{\text{exc}}[\rho_\text{A}, \rho_\text{B}] = \mathcal{F}^{\text{intra}}[\rho_\text{A}, \rho_\text{B}] + \mathcal{F}^{\text{inter}}[\rho_\text{A}, \rho_\text{B}] + \mathcal{F}^{\text{cross}}[\rho_\text{A}, \rho_\text{B}]. \quad (\text{A15})$$

For a cluster on sublattice $v = \text{I or II}$, the intracluster contribution is weighted by the pair counts $n_{vi}(n_{vi} - 1)$ for like species pairs and by $n_{vi}n_{vj}$ for unlike species pairs ($i \neq j$). Hence,

$$\mathcal{F}^{\text{intra}}[\rho_\text{A}, \rho_\text{B}] = \sum_{v=\text{I,II}} n_{\text{latt},v} \left[\sum_{i=\text{A,B}} n_{vi}(n_{vi} - 1) u_{ii}^{\text{intra}}(\alpha_v) + \sum_{\substack{i,j=\text{A,B} \\ i \neq j}} n_{vi}n_{vj} u_{ij}^{\text{intra}}(\alpha_v) \right]. \quad (\text{A16})$$

For particles belonging to different clusters on the same sublattice, no self-exclusion has to be taken into account; one therefore obtains

$$\mathcal{F}^{\text{inter}}[\rho_\text{A}, \rho_\text{B}] = \sum_{v=\text{I,II}} n_{\text{latt},v} \sum_{\{\mathbf{R}_v \neq \mathbf{0}\}} \left[\sum_{i=\text{A,B}} n_{vi}^2 u_{ii}^{\text{inter}}(\alpha_v; \mathbf{R}_v) + \sum_{\substack{i,j=\text{A,B} \\ i \neq j}} n_{vi}n_{vj} u_{ij}^{\text{inter}}(\alpha_v; \mathbf{R}_v) \right]. \quad (\text{A17})$$

Finally, the cross-sublattice contribution takes the form

$$\mathcal{F}^{\text{cross}}[\rho_A, \rho_B] = \sum_{R_I} \sum_{R_{II}} \sum_{i,j=A,B} n_{Ii} n_{IIj} u_{ij}^{I,II}(\alpha_{I,II}; R_{I,II}), \quad (\text{A18})$$

As can easily be verified, the pure cluster case (i.e., the “standard format”) is recovered as a limit by setting

$$n_{IA} = n_{c,A}, \quad n_{IB} = 0, \quad n_{IIA} = 0, \quad n_{IIB} = n_{c,B}. \quad (\text{A19})$$

Hence, the “extended format” represents a direct generalization of the “standard format,” allowing for mixed clusters while preserving the underlying DFT structure.

APPENDIX B: FREE ENERGY OF THE LIQUID PHASE

Starting from the above Eqs. (1)–(3) for $\mathcal{F}[\rho_A, \rho_B] = \mathcal{F}^{\text{id}}[\rho_A, \rho_B] + \mathcal{F}^{\text{exc}}[\rho_A, \rho_B]$ and taking the homogeneous limit, i.e., $\rho_A(\mathbf{r}) \rightarrow \rho_A$ and $\rho_B(\mathbf{r}) \rightarrow \rho_B$, one obtains for the free energy of the homogeneous phase $F(\rho_A, \rho_B)$ the following expression:

$$\begin{aligned} \frac{F(\rho_A, \rho_B)}{V} &= k_B T \sum_{i=A,B} \rho_i [\ln(\Lambda_i^3 \rho_i) - 1] \\ &+ \frac{1}{2} \sum_{i,j=A,B} \rho_i \rho_j \hat{\Phi}_{ij}(0) \end{aligned} \quad (\text{B1})$$

or

$$\begin{aligned} \frac{F(\rho_A, \rho_B)}{N} &= \frac{k_B T}{\rho} \sum_{i=A,B} \rho_i [\ln(\Lambda_i^3 \rho_i) - 1] \\ &+ \frac{1}{2\rho} \sum_{i,j=A,B} \rho_i \rho_j \hat{\Phi}_{ij}(0), \end{aligned} \quad (\text{B2})$$

where $\hat{\Phi}_{ij}(q)$ denotes the Fourier transform of the potential.

APPENDIX C: COEXISTENCE REGIONS

Despite the glancing intersection of the free energy curves of the competing ordered cluster phases, we have calculated via a common tangent construction the coexistence densities of the two competing ordered structures, ρ_{bcc} and $\rho_{\text{fcc/tet}}$. To this end, we have used a considerably refined ρ -grid and have constructed numerically common tangents to the curves $f = \mathcal{F}/N$ versus $1/\rho$. The slope of these tangents is the pressure $P = -[\partial f / \partial (1/\rho)]_T$ (in units ϵ/σ^3) and their intercept is the chemical potential μ (in units ϵ) at coexistence. All the related data are compiled in the Table I along with the value ρ_{cr} , which represents the density-value where the two free energy curves of the competing phases intersect. As the difference $|\rho_{\text{bcc}} - \rho_{\text{fcc/tet}}|$ is throughout of the order of 1% (or even less) with respect to the absolute values of the densities, the coexistence region cannot be made visible on the ρ scale of Fig. 2. Hence, we have denoted, instead, the density-curve, where the free energy curves of the competing crystals intersect—labeled by ρ_{cr} —as a “coexistence line.”

APPENDIX D: COMPUTER SIMULATIONS AND CLUSTER ANALYSIS

In our MD simulations, the systems were initialized at some given temperature T —measured in $k_B T/\epsilon$ (see the main text)—and density $\rho\sigma^3$ via two different protocols: (1) particles of the two species (A and B) were located on the lattice

TABLE I. Coexistence densities ρ_{bcc} and $\rho_{\text{fcc/tet}}$ of the competing bcc and fcc/tetragonal phases as obtained in a common tangent construction for the three ζ values investigated in this study and for selected temperatures (as specified); for details see text. ρ_{cr} is the value where the $f = \mathcal{F}/N$ curves of the two coexisting phases intersect; the ρ_{cr} data have been plotted in Fig. 2 of the as “coexistence lines.” The pressure P (in units of ϵ/σ^3) and the chemical potential μ (in units of ϵ) at coexistence are collected in the respective columns. Data presented for $\zeta = 1$ (i.e., the one-component case) agree with the data presented in Ref. [2].

ζ	$k_B T$	ρ_{bcc}	$\rho_{\text{fcc/tet}}$	ρ_{cr}	P	μ
1.00	0.6	4.2091	4.2353	4.2222	29.1873	14.5307
	0.8	5.6342	5.6708	5.6524	51.6484	19.7222
	1.0	7.0610	7.1007	7.0808	81.7168	25.1425
1.01	0.6	4.1882	4.2155	4.2018	28.8277	14.0600
	0.8	5.6029	5.6450	5.6238	50.7871	19.0555
	1.0	7.0212	7.0690	7.0450	80.4888	24.3285
1.02	0.6	4.1618	4.2117	4.1863	28.0693	13.9109
	0.8	5.5809	5.6123	5.5966	51.7043	19.2610
	1.0	6.9851	7.0347	7.0097	79.8205	24.2854

positions of their respective sublattices (as predicted from the DFT calculation) or (2) the particles of the two species were assigned randomly to the lattice positions; the latter option allowed us to study the purifying process of the sublattices (see article). In both scenarios, particles are positioned in the initial configuration exactly on top of each other at the respective lattice sites.

Keeping for this contribution the density fixed to $\rho\sigma^3 = 6$, simulations have been carried out for four different temperature values (i.e., $k_B T/\epsilon = 0.7, 0.8, 0.9$, and 1.0) and assuming the following three values for the cross-interaction parameter: $\zeta = 1.02, 1.2$, and 1.5 . A considerably larger number of simulations (exploring thus a much finer grid in T , ρ , and ζ) have been carried out for the investigations in Ref. [24]; the related data are discussed in detail in this contribution.

The simulation protocol is as follows: First the system was equilibrated over 3×10^6 time steps Δt with $\Delta t = 0.005t_0$ and the time unit t_0 given by $t_0 = \sigma\sqrt{m/\epsilon}$. Subsequently, every $1 \times 10^6 \Delta t$ steps a configuration was stored, until a total simulation time of $1 \times 10^7 \Delta t$ had been reached, resulting in eight different and independent ensembles available for further production runs. Each of these ensembles was run for an additional 1×10^6 steps, during which configurations were stored every $1000\Delta t$, leading thus—in total—to 8000 configurations that could be used for the different statistical averaging procedures.

Based on the configurations of the particles, stored along the simulation run, a cluster analysis has been carried out. To this end, we have used the clustering algorithm DBSCAN “density-based spatial clustering of applications with noise” [35,36], available in the `scikit-learn` Python library [37]. This method is able to identify particle clusters of arbitrary shape without requiring the number of clusters to be specified in advance. The key parameter of this algorithm is the cutoff parameter r_c . We have used $r_c \approx \frac{2}{3}g_{\text{min}}$, where g_{min} denotes the position of the first minimum of the radial distribution

function $g(r)$ [38] (which, in turn, is extracted from the particle positions via standard routines); see Fig. 7. This particular choice for r_c is motivated by the fact that DBSCAN associates with each particle a neighborhood of spatial extent r_c : By imposing that r_c is smaller than the value $g_{\min}$, particles belonging to different clusters remain separated, while the prefactor $2/3$ ensures that intra-cluster nearest-neighbor distances are still captured; it is therefore an approximate measure for the intra-cluster connectivity. The second relevant parameter, `min_samples`, in this cluster analysis specifies the minimum number of particles required to form a cluster. DFT predicts occupancies of 12–13 particles per cluster for the states investigated in this study, suggesting thus to choose `min_samples` ≈ 10 ; in our investigations, we have used a more permissive value, namely `min_samples` = 3, which allows for rather large fluctuations in the occupancy of the clusters while still suppressing noise originating from hopping particles between neighboring clusters. For resolving particle trajectories, where the identity of hopping particles has to be captured, we use, instead, `min_samples` = 1 such that these particles are classified as clusters rather than being discarded as noise.

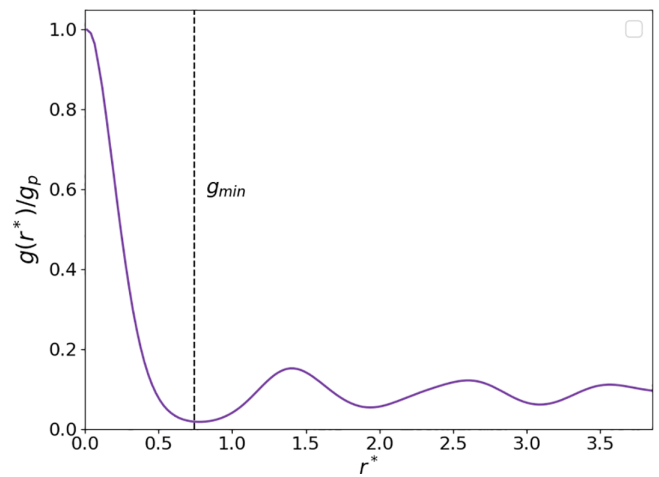


FIG. 7. Radial distribution function $g(r^*)$ of a BCC cluster crystal at density $\rho^* = \rho\sigma^3 = 6.5$ and temperature $T^* = \frac{k_B T}{\epsilon} = 1.0$ as a function of $r^* = r/\sigma$, r being the distance; the function is normalized with respect to its peak value at $g_p = g(0)$. The black dashed line indicates the first minimum $g_{\min}$.

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