Clustering in nondemixing mixtures of repulsive particles

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Using classical density functional theory (DFT), we investigate the phase behavior of binary mixtures, in which the interactions between all particles are described by ultrasoft, repulsive potentials. In the pure case, one of the species, species 2, forms clusters, and freezes into a cluster crystal at sufficiently high density, while the other, species 1, does not cluster and remains liquid at all densities of interest. For some mixtures, DFT predicts two instabilities in the liquid with respect to modulations of differing periodicities. One instability results from the cluster-crystal forming tendency of species 2. In concentrated species 2 mixtures, we find species 1 clusters in response to species 2 cluster formation, eventually freezing either on, or between the species 2 lattice sites. The second instability arises when the interaction between unlike species is either more favorable, or less favorable, than the interaction between like species; when less favorable, the particles form a highly delocalized cluster crystal. We examine the structure of the liquid and crystal phases. In addition, we explore the effect of the cross-interaction potential on the structure of the cluster crystal.

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I. INTRODUCTION

Ultrasoft potentials provide a coarse-grained description of the interaction between large, polymeric aggregates whose centers of mass can completely overlap. Because ultrasoft potentials allow particles to fully overlap, clustering is possible, even when the potentials are purely repulsive. In a pure system, the Fourier transform (FT) of the potential exclusively determines whether or not clustering occurs. When the FT oscillates around zero, the potential belongs to the \(-4\)-class and clustering does not occur at any temperature.

Some polymers and dendrimers are known to interact with each other through \(Q^+\) potentials. Simulation results suggest such potentials are relatively independent of density, and remain accurate well above the overlap density. Recent computer simulations suggest the interaction potential between dendrimers having amphiphilic end groups can be described by a \(Q^\pm\) potential. Coarse-grained potentials are state-dependent and the validity of ultrasoft potentials must break down at some density. However, the volume fraction occupied by a large polymer can greatly exceed that occupied by the sum of its constituent monomers. Since ultrasoft potentials can describe the interaction between very large polymeric entities, it is conceivable that, for some systems, as was shown for polymer chains and athermal dendrimers, they remain valid for densities well above the overlap density. Cluster-crystal formation by particles interacting through \(Q^\pm\) potentials is an example of the interesting and novel phase behavior possible in systems able to achieve such high densities. Although \(Q^+\) potentials do not give rise to clustering in a pure system, particles interacting through \(Q^+\) potentials can cluster in dense mixtures. When the interspecies interaction is more favorable than the intraspecies interactions, clustering maximizes contact between unlike species; a new microphase separation results and Archer et al. predicted the formation of a highly delocalized cluster crystal, with Lindemann ratios that can exceed 90%. When the interspecies interaction is less favorable than the intraspecies interactions, clustering minimizes contact between unlike species; microphase separation results and can precede macrophase separation.

Particles interacting through \(Q^+\)-potentials can also cluster when mixed with particles interacting through \(Q^\pm\)-potentials. In previous work, we found that the \(Q^+\)-component can be incorporated into the clusters formed by the \(Q^\pm\)-component; however, greater delocalization of the \(Q^+\)-species, suggests the two crystal components would have markedly different mobilities. In that work, a nearby demixing transition inhibits mixed cluster stability beyond very low concentrations of the \(Q^+\)-species.

In this work, we explore the phase behavior of \(Q^+/Q^\pm\) mixtures that do not undergo demixing at any density. We examine two systems in detail and consider the effect of the cross-interaction length and energy parameters on the stable crystal structure. In Sec. II we describe our model and method and in Sec. III we present and discuss our results. We provide a summary of our results with concluding remarks in Sec. IV.

II. MODEL AND METHOD

As in previous work, we consider two systems, each being a mixture of particles interacting through the generalized exponential model of index \(m\) (GEM-\(m\)).
when to minimize the potential energy and length parameters, respectively, of species \( i \) and \( j \). The GEM-\( m \) potential belongs to the \( Q^m \) class of potentials when \( m \leq 2 \) and the \( Q^m \) class when \( m > 2 \). In physical terms, the decay of the potential when \( m > 2 \) is sufficiently steep that the energetic cost of two particles completely overlapping is nearly the same as the cost of two particles partially overlapping, driving the system to minimize the total number of overlapping particles. In a pure \( Q^m \) system, minimizing the number of overlapping particles is achieved by the formation of a cluster crystal with a lattice constant that is nearly independent of density.13,15 For both systems, we choose \( m_{11} = 2 \), \( m_{12} = 3 \), and \( m_{22} = 4 \). Our choice for the other potential parameters are described in Sec. III. The parameters are chosen to demonstrate typical phase behavior; we expect the behavior we predict to be relevant for a range of parameters, as discussed in Sec. III.

The equilibrium one-body density profile of species \( i \) \( \rho_i(r) \), for chemical potentials \( \mu_i \), are obtained via the test-particle route.20 We consider a system with a test particle of species \( j \) held fixed at the origin and minimize the grand potential functional

\[
\Omega[\rho_j] = \mathcal{F}_{\text{id}}[\rho_j] + \mathcal{F}_{\text{ex}}[\rho_j] - \sum_{i=1}^{2} \int dr (\mu_i - u_{ij}(r)) \rho_i(r),
\]

with respect to density. The ideal part of the Helmholtz free energy functional is given by

\[
F_{\text{id}}[\rho] = k_B T \sum_{i=1}^{2} \int d^3 r \rho_i(r) \left[ \ln(\rho_i(r) \Lambda_i^3) - 1 \right],
\]

where \( k_B \) is Boltzmann’s constant, \( T \) is the temperature and \( \Lambda_i \) are the de Broglie wavelengths. The excess part of the Helmholtz free energy functional,

\[
F_{\text{ex}}[\rho_i, \rho_j] = \frac{1}{2} \sum_{i,j=1}^{2} \int d^3 r d^3 r' \rho_i(r) \rho_j(r') u_{ij}(|r - r'|),
\]

generates the random phase approximation (RPA) \( c_{ij}(r) = -\beta u_{ij}(r) \), the RPA is highly accurate for ultrasonic fluids at sufficiently high density and/or temperature.15,17,22,23

To calculate the pair structure of the homogeneous liquid phase, we introduce the total correlation functions \( h_{ij}(r) = \rho_i(r)/\rho_j - 1 \), where \( \rho_i \) is the bulk density of species \( i \) and, taking the functional derivative of Eq. (2), we obtain the coupled set of equations,

\[
h_{ij}(r) = -1 + \exp \left[ -\beta u_{ij}(r) - \sum_{k=1}^{2} \rho_k \int dr' h_{ik}(r') \times \beta u_{kj}(|r - r'|) \right].
\]

The correlation functions can also be obtained by using the RPA as a closure to the Ornstein–Zernike (OZ) relation.20,23 Likos et al.15 provided a thorough analysis of the validity of the RPA, and discuss differences between the OZ and test-particle DFT routes. Here we use the test-particle route because it generally produces more accurate results, although for many systems the results from the two routes are nearly indistinguishable.

Simulation results show the cluster density profiles in the solid state have a Gaussian shape in a pure GEM-4 system.14 We assume the cluster density profiles in a solid mixture also have a Gaussian shape. The one-particle density profiles of each species can then be written as a sum of Gaussians centered around the lattice sites \( \{R_i\} \),

\[
\rho_i(r) = n_i \left( \frac{\alpha_i}{\pi} \right)^{3/2} \sum_{R_i} \exp\left[-\alpha_i(r - R_i)^2\right],
\]

where \( n_i \) is the number of particles of species \( i \) at each lattice site and \( \alpha_i \) is the delocalization parameter. The total Helmholtz free energy functional [Eqs. (3) and (4)] is minimized with respect to the density parameters \( \alpha_i \) and the lattice spacing \( d = \xi n_i/\rho_i \) (for a cubic lattice), where \( \xi \) is the number of lattice sites per unit cell.

We use genetic algorithms (GAs) to determine the optimum cluster-crystal lattice structures at \( T = 0 \). Details of the implementation of GA for stable crystal structure determination can be found elsewhere.8,9,24,25 Briefly, we initially randomly generate a set of lattice structures and assign a fitness value to each: A lattice structure with a lower free energy is given a higher fitness value. Parent lattice structures are chosen, with more fit structures having a higher probability of becoming parents, and combined to create new structures (offspring). The offspring of the first generation become the second generation, and we repeat the mating process until the algorithm converges to an equilibrium structure. The optimum structure is the lattice structure with the highest fitness value.

At \( T = 0 \) the free energy is given by the internal energy. We assume that particles in a cluster are positioned perfectly on top of each other and that all clusters are populated by an equal number of particles. In addition, we assume that the GEM-4 and GEM-2 clusters form two identical lattices that are shifted from each other; the vector describing the shift between the two lattices is also a variational parameter of the GA. Optimum structures identified by the GA are used as candidate structures for our DFT calculations at finite \( T \).

III. RESULTS

In this section we consider two systems, labeled system I and system II, which do not undergo demixing at any density. The potential parameters, \( e_{ij} \) and \( \sigma_{ij} \), distinguish the two systems and are given in what follows; the energy and length parameters of system I are equivalent for all interactions, while those of system II are chosen to make the interaction between unlike species more favorable than the interaction between like species.

Divergence of the partial structure factors,

\[
S_{ij}(k) = \delta_{ij} + \rho \rho \tilde{h}_{ij}(k); \tag{7}
\]

where
\[ \vec{n}_{ij}(k) = \frac{\vec{N}_{ij}(k)}{D(k)}, \]

\[ \vec{N}_{ij}(k) = -\beta \vec{u}^2_{ij}(k) + \delta_{ij} \rho \beta^2 [\vec{u}^2_{11}(k) - \vec{u}_{11}(k)\vec{u}_{22}(k)], \]

and

\[ D(k) = 1 + \beta \rho[(1 - x)\vec{u}_{11}(k) + x\vec{u}_{22}(k)] \]

\[ -\beta^2 \rho^2 x(1 - x)[\vec{u}^2_{11}(k) - \vec{u}_{11}(k)\vec{u}_{22}(k)], \]

at nonzero wavelength signals an instability in the fluid with respect to periodic modulation, referred to as a \( \lambda \)-transition. In Eq. (10), \( x \) is the mole fraction of species 2. In Eq. (9), we provide the expression obtained from the OZ route; an analytic expression for \( \vec{N}_{ij}(k) \) cannot be obtained from the test-particle DFT route. Both the test-particle DFT and the OZ routes yield the same expression for \( D(k) \) Eq. (10). The structure factors diverge when \( D(k)=0 \) and can occur when either of the following two conditions is satisfied: \( \vec{u}_{ij}(k)<0 \) or \( \vec{U}(k)=-\vec{u}^2_{12}(k)+\vec{u}_{11}(k)\vec{u}_{22}(k)<0 \). In both systems we examine, the first condition is satisfied since \( \vec{u}_{22}(k) \), belongs to the \( Q^2 \) class of potentials, i.e., \( \vec{u}_{22}(k)<0 \) for some nonzero value of \( k \). \( \vec{u}_{22}(k) \) obtains its negative minimum at \( k_F \). The second condition is also satisfied in both systems, inevitably when \( k=k_F \), but also over a distinctly different range of nonzero wavelengths; \( \vec{U}(k) \) obtains its negative minimum when \( k=k_M \).

In Fig. 1, we plot \( \vec{u}_{22}(k), \vec{U}(k) \) and the corresponding \( \lambda \)-lines, defined as the locus of points where \( D(k=k_F)=0 \), for both systems. The absence of a minimum in \( \vec{U}(k) \) at \( k=0 \) demonstrates that macrophase separation cannot occur in either system at any density, i.e., \( D(k=0) \neq 0 \) for all \( \rho \) and \( x \). Although both systems do have two \( \lambda \)-lines, in system I, the \( \lambda \)-line associated with a divergence at \( k\approx k_M \) (the \( \lambda_M \)-line), lies nearly entirely within the \( \lambda_P \)-line, and occurs at very high density. We therefore expect the presence of the \( \lambda_P \)-line to dominate the phase behavior, and limit our study of system I to densities well below the \( \lambda_M \)-line. In contrast, the \( \lambda_M \)-line in system II occurs at lower densities, allowing us to study a system where both \( \lambda \)-instabilities contribute to the phase behavior.

A. System I

The potential parameters [Eq. (1)] we choose for this system are \( \sigma_{11}=\sigma_{12}=\sigma_{22}=\sigma \) and \( \epsilon_{11}=\epsilon_{12}=\epsilon_{22}=\epsilon \). These parameters are similar to those chosen in previous work of demixing systems, except that here we have \( \sigma_{12}=\sigma \), rather than \( \sigma_2=\sigma_1 \). In the demixing systems studied previously, we found that both species occupy all sites of either a face-centered-cubic (fcc) or body-centered-cubic (bcc) lattice. However, the cluster-crystal phase in these systems is only stable when the concentration of GEM-2 particles is extremely low (\( x<0.99 \)). Here we demonstrate that clusters containing both species can be stabilized over an increased concentration range by removing the tendency of the system to demix.

Before discussing the phase behavior of system I, we look at the pair correlation functions \( g_{ij}(r) = \rho_{ij}(r) / \rho \). Fig. 2. We see that, as in the demixing systems studied previously, there are peaks in all \( g_{ij}(r) \) at \( r=0 \), suggesting the GEM-4 clustering tendency induces GEM-2 particles to cluster within the GEM-4 clusters. Our choice of \( m_{12}=3 \) means that the cross-interaction potential decay is sufficiently steep that the energetic cost of partial 1-2 overlaps is nearly as unfavorable as full 1-2 overlaps. Being too large to fit in either the tetrahedral, or octahedral holes of the fcc lattice formed by the GEM-4 species, the GEM-2 particles clusters on the
GEM-4 lattice sites; by fully overlapping with the GEM-4 particles in a single cluster, the GEM-2 particles avoid partially overlapping with GEM-4 particles occupying neighboring clusters.

The pair correlation results shown in Fig. 2 suggest the stable cluster-crystal phase consists of clusters containing both species. The stable structure at $T=0$ obtained using our GA consists of both species sharing each site of an fcc lattice (disordered fcc). For the temperature of interest, we perform density functional calculations for a variety of test lattice structures: Disordered fcc, disordered bcc, intercalated fcc, where the fcc lattice sites of one of the species occupy either the octahedral (NaCl-type) or tetrahedral (ZnS-type) holes of the fcc lattice formed by the other species, and intercalated simple cubic (CsCl-type). We find that only the disordered bcc and fcc lattices are stable, consistent with both the presence of a peak in $g_{12}(r)$ at $r=0$, and with the phase behavior of a pure GEM-4 system; in a pure GEM-4 system the bcc lattice is favored at lower densities before the fcc lattice becomes the most stable configuration. We find the coexisting solid and liquid, or solid and solid densities by performing the common tangent construction on the Gibbs free energy per particle $g=(F_{id}+F_{ex})/N+P/\rho$ of the two phases along an isobar. As found previously for demixing systems, the GEM-2 particles are much less localized than the GEM-4 particles, with $\alpha_4 \sim \alpha_2/2$. The lattice constant increases with decreasing $x$, but changes by less than 1%.

We plot the phase diagram in Fig. 3, showing the regions of bcc and fcc stability. In contrast to the demixing systems examined in previous work, the cluster crystals in this case are stable over a broader GEM-2 concentration range. However, the concentration gap between coexisting liquid and solid phases is still rather large. Although $\sigma_{ij}=\sigma$ in this system, the values of $m_{ij}$ differ; the 1-2 interaction is more energetically favorable than the 1-1 interaction, but less favorable than the 2-2 interaction. Thus, the GEM-4 particles “prefer” to cluster solely with other GEM-4 particles, and the mixed clusters, while more stable than those formed in demixing systems, are still not particularly stable. This interaction asymmetry is also the physical basis for the presence of the $\lambda_M$-instability at high density.

![FIG. 3. Phase diagram for system I. The mole fraction of the GEM-4 species is denoted by $x$. The thick lines denote the boundaries of the coexistence regions. The thin lines join coexisting points. The three-phase coexistence area is denoted by the yellow triangle.](image)

![FIG. 4. The radial distribution functions $g_{ij}(r)$ for $\rho\sigma^3=8.0$. Note the absence of a peak in $g_{12}(r)$, and presence thereof in $g_{ij}(r)$, at $r=0$. The lines correspond to the points A ($x=0.15$), B ($x=0.65$), and C ($x=0.85$) plotted in Fig. 1.](image)

### B. System II

The parameters we choose for our second system are inspired by work done on Gaussian (GEM-2) mixtures: $\sigma_{11}=\sigma, \sigma_{12}=0.8\sigma, \sigma_{22}=0.6\sigma, \varepsilon_{11}=\varepsilon_{22}=2.0k_BT=\varepsilon$, and $\nu_{12}=1.8877k_BT$. Our parameters differ from the GEM-2 mixture case in the exponents, $m_{12}=3$ and $m_{22}=4$, and in our choice of a larger $\sigma_{12}$. A larger $\sigma_{12}$ moves the $\lambda_M$-line to lower densities, allowing us to study a system where the $\lambda_F$- and $\lambda_M$-instabilities “compete” with one another at similar densities. We expect our results to hold for other parameters, whenever $\sigma_{12}<\sigma_i$ and two $\lambda$-instabilities are present. In the GEM-2 mixtures, the formation of very delocalized cluster crystals occurs; the Lindemann ratios, which, in atomic fluids typically signal melting at 10%, exceed 90%. In contrast, the Lindemann ratios at freezing for the pure GEM-4 and pure GEM-2 systems are much lower, ~18.9% (Ref. 15) and ~10%, respectively. The formation of cluster crystals in the GEM-2 mixture is due to the preference for 1-2 ordering; a particle of either species “sees” particles of the other species as smaller and less repulsive than particles of its own species. Our choice of parameters allows us to examine cluster-crystal formation due both to the preference for 1-2 ordering, and to the tendency of $Q^\pm$ systems to minimize the number of overlapping particles.

We compare the $g_{ij}(r)$ for system II obtained near the $\lambda_F$-line (Fig. 4), with those obtained for system I (Fig. 2). In both cases there are peaks in $g_{11}(r)$ and $g_{22}(r)$ at $r=0$. However, in contrast to the System I case, there is no corresponding peak in $g_{12}(r)$, suggesting the GEM-2 particles form distinct clusters rather than being drawn into the GEM-4
clusters. Near the \( \lambda_P \)-line (point C in Fig. 1), the cluster-crystal forming tendency of the GEM-4 species dominates and, as expected, in Fig. 5 we see a strong peak in \( S_{12}(k) \) at \( k \sim k_P \). In contrast, a corresponding peak in \( S_{11}(k) \) is nearly absent, demonstrating that the behavior of the GEM-2 species is much less affected by the nearby \( \lambda_P \)-transition.

We consider the concentration-concentration

\[
h_{cc}(r) = (1-x)^2 h_{11}(r) + x^2 h_{22}(r) - 2x(1-x) h_{12}(r)
\]

and number-number

\[
h_{nn}(r) = (1-x)^2 h_{11}(r) + x^2 h_{22}(r) + 2x(1-x) h_{12}(r)
\]

correlation functions for further information about the fluid structure. When the GEM-4 concentration is low, near the \( \lambda_M \)-line (Fig. 1), the concentration-concentration correlations are much stronger than those of the number-number correlations (Fig. 6), suggesting the stable solid structure within the \( \lambda_M \)-line alternates in species but remains liquidlike, with nearly uniform number density. In contrast, as the concentration of GEM-4 particles increases, the density gaps become more pronounced; at \( x_P = 0.8 \), both correlations are pronounced suggesting greater localization of the particles within the clusters.

Our GA predicts a NaCl-type structure to be stable when \( T = 0 \) for all \( x \) tested. For the temperature of interest, we perform density functional calculations and find the NaCl-type structure is stable at high GEM-4 concentration (near the \( \lambda_P \)-line). The GEM-4 particles form a fcc lattice as in system I, but in system II, the GEM-2 particles occupy the octahedral holes of the fcc lattice, rather than sharing the GEM-4 lattice sites. The cross-interaction length scale, \( \sigma_{12} \), allows GEM-2 clusters to “fit” between the GEM-4 lattice sites. Although the GEM-2 particles do form clusters, these are much more delocalized than the GEM-4 clusters; values of \( \sigma_1 \) are roughly three times smaller than the values of \( \sigma_2 \). Changes to the lattice constant with increasing GEM-2 concentration are \( \leq 5\% \), and are consistent with the increasing value of \( k \) at which \( S_0(k) \) diverges. The distance between nearest GEM-4 lattice sites approaches \( \sim 1.4 \sigma_{22} \) as \( x \to 1 \).

We find a CsCl-type structure to be stable within the \( \lambda_M \)-line, consistent with the predicted formation of a CsCl-type structure in the GEM-2 mixture discussed previously. The density gaps of the coexisting crystal and liquid phases are small, and we plot the locus \( g_{cl} \equiv g_{liq} \) in Fig. 7. As was found also for the GEM-2 mixture, the crystal-liquid phase boundary lies just inside the \( \lambda_M \)-line. Since the two are close, we echo Archer et al. and hypothesize that in a more accurate theory, the phase boundary would lie outside of the \( \lambda_M \)-line. We note however, that we have not considered the possibility of other ordered phases, such as micellarlike or lamellarlike phases, that may also be stable in some regions of the phase diagram.

The Lindemann ratios are shown in the inset of Fig. 7. The Lindemann ratios \( L_i \) of the CsCl-type structure are much greater than those of the NaCl-type structure for both species. The former attains Lindemann ratios of up to \( \sim 70\% \) at melting.

We note that our \( T = 0 \) GA does not predict a stable CsCl-type structure at any concentration considered. The GA also predict that a GEM-2 mixture \( (m_{11} = m_{12} = m_{22} = 2) \) with length parameters equivalent to those chosen for System II, forms a NaCl-type structure at \( T = 0 \), despite the absence of a \( \lambda_P \)-line; at finite temperature, we find the CsCl-type structure to be more stable than the NaCl-type structure for the GEM-2 mixture, consistent with the prediction of Archer.
Rather than exploring the full phase diagram for varying parameters, we consider a nearly pure GEM-4 liquid at a density $\rho^4=9$ and $x=0.999$. Black shading on the left indicates the region where the NaCl-type structure is stable, blue shading in the middle indicates the region where the disordered fcc structure is stable, and the white areas denote where the difference in free energy is small, within the error of our calculations. The solid red line denotes the spinodal. We expect the mixed cluster crystal to only be stable for very high $x$ near the demixing instability (see Ref. 19).

Thus, the formation of the CsCl-type structure appears to be an entropy driven effect. At finite temperature, particles within a cluster delocalize, and the CsCl-type structure becomes more favorable than the NaCl-type structure.

C. Crystal structure: The effect of cross-interaction parameters

Partial overlap of two particles interacting via a $Q^{\pm}$ potential of the GEM-$m$ type is nearly as energetically unfavorable as complete overlap of the particles. Minimization of the energetic contribution to the free energy is therefore achieved by minimizing the number of particles that overlap, either partially or fully, inevitably leading to clustering at high densities. In the two systems discussed above, the cross-interaction potential decays sharply; therefore, each system seeks to minimize the number of 1-2 overlaps, either partial or full. In system I, $\sigma_{12}=\sigma_{22}$: the GEM-2 particles are too large to fit between the GEM-4 clusters, resulting in the formation of a disordered fcc structure. In system II, $\sigma_{12}<\sigma_{22}$: the GEM-2 particles are small enough to fit between the GEM-4 cluster, resulting in the formation of a NaCl-type structure. Clearly, the cross-interaction length scale plays an important role in determining the mixed cluster-crystal structure.

In this section, we further examine the combined effect of $\sigma_{12}$ and $\varepsilon_{12}$ on the crystal structure within the $\lambda_f$ line. Rather than exploring the full phase diagram for varying $\varepsilon_{12}$ and $\sigma_{12}$ parameters, we consider a nearly pure GEM-4 ($x=0.999$) system at a density $\rho^4=9$, with system II-type parameters (i.e., $\sigma_{11}=\sigma$, $\sigma_{22}=0.8\sigma$, and $\varepsilon_{22}^{\text{CSCl}}=2k_B T=\varepsilon$). From previous work we know that, at this density, GEM-4 clusters organize to form a fcc lattice in the pure case. We assume the fcc arrangement of GEM-4 particles persists in the presence of a small amount of GEM-2 particles. Minimizing Eq. (2) with respect to $\alpha_i$ and $d$, we obtain the Helmholtz free energies of the disordered fcc and NaCl-type structures for varying $\sigma_{12}$ and $\varepsilon_{12}$.

The difference between the free energies of the two structures is shown in Fig. 8. As expected, $\sigma_{12}$ essentially determines where within the fcc GEM-4 lattice the GEM-2 particles cluster: If $\sigma_{12}$ is small enough, the GEM-2 particles cluster between the GEM-4 clusters; if $\sigma_{12} \approx \sigma_{22}$, the GEM-2 particles cluster on the GEM-4 lattice sites; and, if $\sigma_{12} \approx 2\sigma_{22}$, the GEM-2 particles again cluster between the GEM-4 lattice sites, preferring to overlap with the six clusters neighboring an octahedral hole rather than the twelve that neighbor the GEM-4 fcc lattice site. In the last case, the difference in the free energies of the two structures is small, suggesting that neither arrangement is particularly favorable.
In fact, based on our previous study of demixing systems, we expect such crystals are only stable for very small GEM-2 concentrations, preferring instead to phase separate into a nearly pure GEM-4 cluster crystal and a liquid mixture.

We turn our attention now to the dependence of the localization parameter $\alpha_1$, on $\sigma_{12}$ and $\varepsilon_{12}$, noting that $\sigma_2$ and $d$ remain nearly constant with changes to the cross-interaction parameters. The energetic cost of 1-2 overlaps increases with increasing $\varepsilon_{12}$: therefore we expect larger values of $\varepsilon_{12}$ to result in larger values of $\alpha_1$. This is indeed the case for both crystal structures, as shown in Fig. 9 (bottom). Less intuitive, is the effect of $\sigma_{12}$ on $\alpha_1$. In Fig. 9 (top) we plot $\alpha_1$ as a function of $\sigma_{12}$. Localization of the GEM-2 particles is greatest when the cost of forming 1-2 overlaps most outweighs the cost of forming GEM-2 clusters. This occurs in the NaCl-type structure when $\sigma_{12}$ is comparable to the space between GEM-4 clusters, and in the CsCl-type structure when $\sigma_{12}$ is comparable to the space occupied by a GEM-4 cluster.

### IV. SUMMARY AND CONCLUSIONS

Using an accurate density functional theory, we have investigated the phase behavior in nondemixing mixtures containing a clustering component (species 2) and a nonclustering component (species 1). In a species 2-rich system, species 1 clusters either on, or between the species 2 lattice sites, depending on the length scale of the cross-interaction potential. The localization of species 1 in the clusters is much less than that of species 2 and depends strongly on both energy and length cross-interaction parameters, suggesting the possibility to form mixed cluster crystals with tunable mobilities. In near equimolar mixtures, the presence of a second $\lambda$-line is associated with the formation of cluster crystals in which both species are delocalized.

Our results pertain to mixtures able to achieve very high densities. While there is evidence that both classes of ultrasoft potentials accurately model the interactions between real particles in dilute systems, the validity of these potentials in dense systems has yet to be verified. The results we present in this paper add to a growing body of work that suggests the search for dense systems where ultrasoft potentials remain valid, is a worthwhile pursuit.

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