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J. Chem. Phys. 148, 191101 (2018)

<https://doi.org/10.1063/1.5028279>

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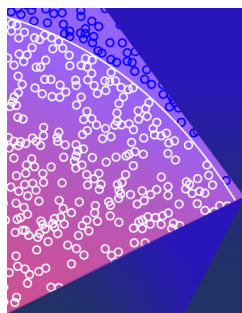


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Communication: From close-packed to topologically close-packed: Formation of Laves phases in moderately polydisperse hard-sphere mixtures

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(Received 8 March 2018; accepted 23 April 2018; published online 15 May 2018)

Particle size polydispersity can help to inhibit crystallization of the hard-sphere fluid into close-packed structures at high packing fractions and thus is often employed to create model glass-forming systems. Nonetheless, it is known that hard-sphere mixtures with modest polydispersity still have ordered ground states. Here, we demonstrate by computer simulation that hard-sphere mixtures with increased polydispersity fractionate on the basis of particle size and a bimodal subpopulation favors the formation of topologically close-packed C14 and C15 Laves phases in coexistence with a disordered phase. The generality of this result is supported by simulations of hard-sphere mixtures with particle-size distributions of four different forms. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5028279>

Size-polydisperse hard-sphere (HS) fluids are popular models for computational studies of glass formers. Polydispersity in such systems is well known to inhibit the formation of close-packed lattice structures that otherwise readily assemble from the monodisperse fluid upon densification prior to reaching glassy states.^{1–6} While polydispersity slows the kinetics of crystallization, fractionation into particle-size-selective close-packed crystalline phases is thermodynamically favored over the fluid in modestly polydisperse mixtures of HS-like particles.^{1–4}

Crystallization of fluid mixtures with higher polydispersity, on the other hand, is a largely uncharted territory. By analogy to binary HS mixtures, it has been postulated that more complex, non-close-packed crystalline phases could be favored in such systems where the close-packed crystals are penalized.^{1–4} Analogous behavior is well established for the Dzugutov pair potential, which features a single energetic barrier at distance characteristic of close-packed order, instead favoring the self-assembly of dodecagonal quasicrystals.⁷ Similarly, in a simulation study of a monodisperse HS model with a many-body energy term that favors non-close-packed crystal structure formation, an icosahedra-rich phase is observed—postulated to be either a quasicrystal or of the Frank-Kasper family of crystals (i.e., a quasicrystal approximant).⁸

Motivated by the above, we study the possibility of crystalline assembly in a moderately size disperse HS mixture with particle diameters distributed according to a third-order power law with lower and upper size cutoffs chosen to realize a 12% polydispersity (i.e., the standard deviation relative to the mean, or the coefficient of variation, $c_v = 0.12$).^{5,9} Because polydisperse fluids are normally slow to crystallize at high density, we leverage particle-swap Monte Carlo

simulations to explore their behavior.^{5,9} This method, while powerful, is simple to implement. In addition to standard particle translations, a pair of particles is randomly selected and an attempt is made to swap their diameters. Of the attempted Monte Carlo moves, 20% are swaps and 80% are translations. For additional simulation details, see the [supplementary material](#).

Upon densification, the pressure of the aforementioned HS mixture noticeably deviates from the theoretical prediction;¹⁰ see Fig. 1(a). Visualization of configuration data after the abrupt drop in pressure reveals the presence of large ordered domains; see Figs. 1(b) and 1(c) for two snapshots from independent simulations, where particle diameters are scaled by 0.5 in all snapshots for visual clarity. The crystalline domains are reminiscent of Laves phases—a class of topologically close-packed structures that are known to be thermodynamically stable for certain binary mixtures of hard spheres.¹¹ Specifically, comparison of the structures outlined in yellow in Figs. 1(b) and 1(c) to ideal repeating units of the C14 and C15 lattices in Figs. 1(d) and 1(e) reveals that the former are consistent with the latter, with some substitutional disorder present due to the polydispersity.

To confirm the presence of Laves phases, we applied a template-matching scheme for the C14 and C15 lattices using the lattice constants extracted from the simulation box above, computing the root-mean-square deviation (RMSD) from an idealized lattice; see the [supplementary material](#) for details. Using the C14 template, the lattice shown in Fig. 1(b) is color-coded according to the RMSD in Figs. 2(a) and 2(b), where the co-existence of fluid and crystalline regions on the basis of color is clear. The distribution of RMSDs, shown in Fig. 2(c), is weakly bimodal, functioning as an order metric to segregate the particles into crystalline and fluid regions—though the interface between the fluid and crystal regimes weakens the bimodality. We chose a value of 0.25 as the maximum RMSD for a crystalline particle

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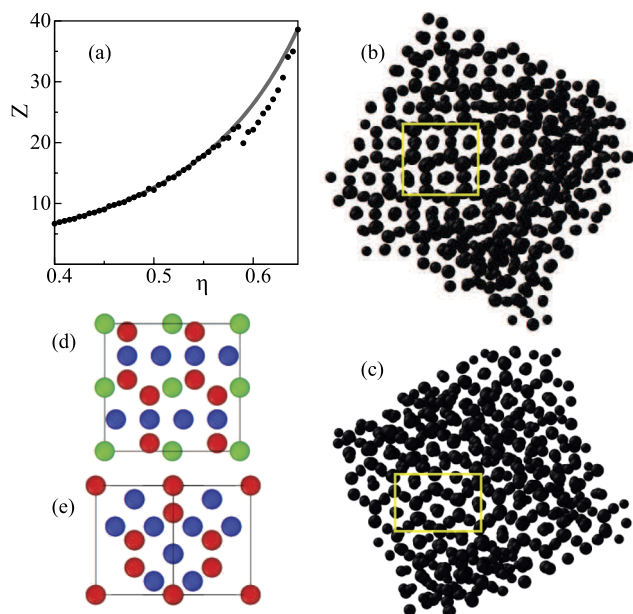


FIG. 1. (a) Compressibility factor, $Z \equiv P/\rho k_B T$, as a function of packing fraction, $\eta \equiv 4\pi\langle r^3 \rangle \rho / 3$, where P is the pressure, ρ is the number density, $\langle r^3 \rangle$ is the third moment of the particle radius distribution, k_B is the Boltzmann constant, and T is the temperature, for hard spheres with 12% polydispersity from simulation (symbols) compared to the theoretical prediction (line).¹⁰ [(b) and (c)] Two representative configurations compressed from $\eta = 0.595$ to $\eta = 0.66$ from two independent simulations. [(d) and (e)] Visualizations of a repeating unit for the C14 and C15 lattices, respectively. The C14 repeating unit shown is an orthogonalization of the hexagonal C14 unit cell, and the cubic C15 unit cell has been rotated by 45° . Throughout the manuscript, particles are depicted with diameters that are 50% of their true diameter for clarity.

in the analysis that follows. A parallel analysis for the configuration shown in Fig. 1(c) is given in the [supplementary material](#).

As shown in Figs. 1(d) and 1(e), the C14 and C15 lattices have three and two distinct lattice positions, respectively; the template-matching scheme above allows us to label the crystalline particles by the lattice site; see Figs. 3(a) and 3(b). Because (1) the C14 and C15 lattices are closely related structurally¹² and (2) the system possesses significant substitutional disorder, the template-matching scheme cannot always distinguish between the two lattices; however, labeling the lattice sites can be helpful to visualize C14 and C15 motifs. For instance, the few C15 domains co-existing with the larger C14 domain can be visualized where the green particles are vertically offset, as shown in Fig. 3(a). The co-existence of C14 and C15 structures is not surprising; it is known that the Laves phases have very similar free energies for certain bidisperse mixtures.¹²

Similar to prior work for systems with lower polydispersity,^{1–4} we observe fractionation on the basis of particle diameter. Figure 3(c) shows a histogram of the distributions of diameters associated with distinct lattice sites in comparison with the complete distribution of diameters in the mixture (black line). The subset of smaller diameters nearly exclusively occupy the A (blue) and B (green) lattice sites, whereas the larger particles occupy the C (red) lattice sites. (The A and B lattice sites have a highly similar coordination shell structure in the C14 lattice.)

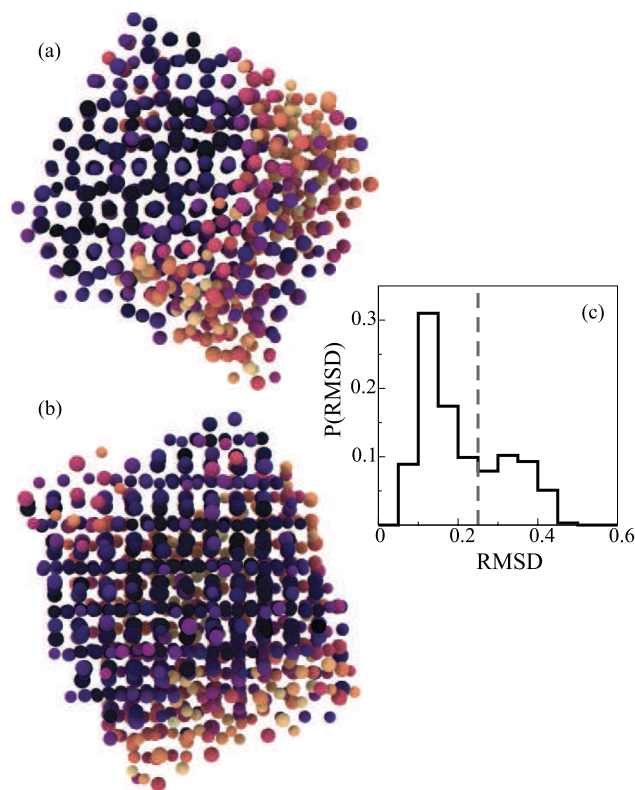


FIG. 2. [(a) and (b)] Two views of the configuration from Fig. 1(b), color-coded by the RMSD metric described in the main text and in the [supplementary material](#). Darker regions indicate C14 crystalline domains and lighter regions appear disordered. (c) Probability distribution as a function of RMSD for the snapshot in panels (a) and (b).

While the preceding self-assembled structures do not prove that the Laves phases are thermodynamically stable for the above polydisperse mixture, the characteristics of the crystalline phase are consistent with the known phase behavior of binary HS systems. Based on free energy calculations, Laves phases are expected if the diameter ratio of large to small particles (d_L/d_S) falls within the range 1.19–1.35.¹² This range is in direct accord with the approximate size ratio we find in the solid phase: $d_L/d_S \approx 1.24$ (where d_L and d_S are the averages of the C site and A + B site distributions, respectively). The existence of Laves phases for similar size ratios has also been confirmed experimentally.¹³ In essence, the larger range of particle diameters characteristic of higher polydispersity allows for thermodynamically driven size-segregation resulting in domains that can form complex lattices.

To evaluate the generality of Laves phase formation, we explore other particle size distributions with the same mean diameter and coefficient of variation (c_v). Specifically, we repeated the above simulation analysis for uniform, sixth-order power law, and Gaussian size distribution forms—each of which are shown in Figs. 4(a)–4(d) in conjunction with the third-order distribution studied above. The first two distributions are effectively flattened and stretched versions, respectively, of the third-order distribution. The Gaussian distribution in Fig. 4(d) provides a qualitatively distinct scenario, where particle diameters are concentrated around the mean of the distribution. Nonetheless, in all mixtures, we find the presence of Laves phases, driven by size-selective

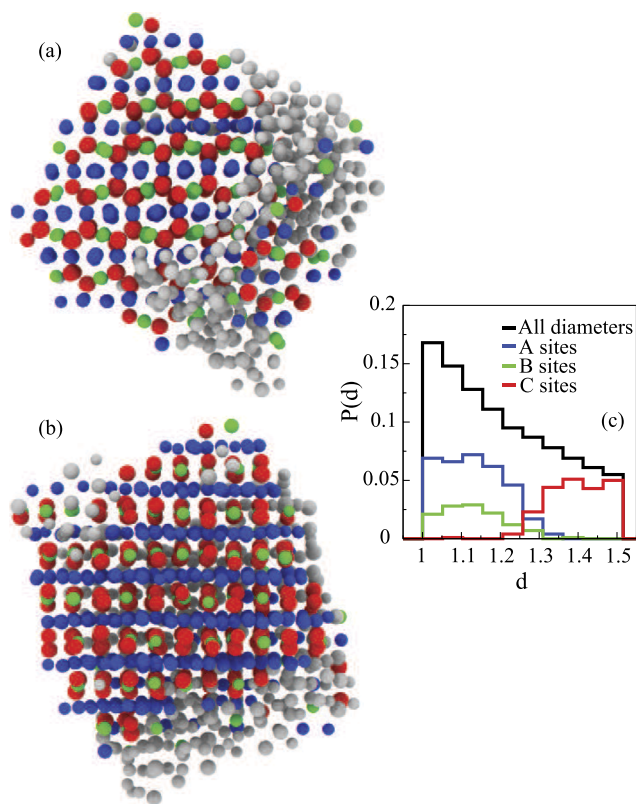


FIG. 3. [(a) and (b)] The same configuration shown in Figs. 2(a) and 2(b) color-coded by particle type. A sites are blue, B sites are green, and C sites are red. (c) The overall probability distribution for the diameters (black), and the probability distributions for the A, B, and C sites; all distributions are normalized by the total number of particles in the simulation box.

fractionation into solid and fluid phases. The template-matching scheme finds that bimodal distributions with respect to diameter accommodate the formation of the Laves phases, where the smaller particles occupy the A (or A + B) sites and the larger particles occupy the C sites. While the shapes

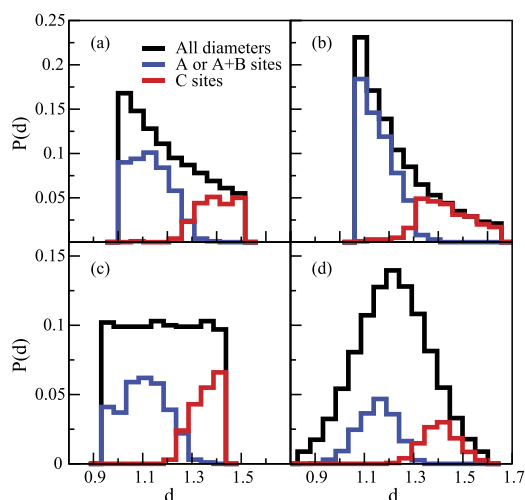


FIG. 4. [(a)–(d)] For the third-order, sixth-order, uniform, and Gaussian distributions, respectively, the A (or A + B) distribution (blue, smaller diameters), the C distribution (red, larger diameters), and the total distribution (black). Where the C14 template was used, the A and B particles have been combined into the blue distribution. All distributions are normalized by the total number of particles in the simulation box.

of the sub-distributions are sensitive to the form of the total distribution, d_L/d_S is between 1.22 and 1.24 for all four cases. In binary mixtures, $d_L/d_S = 1.225$ is the size ratio, where the Laves phases have a maximum packing fraction.¹²

A 2(A + B):1C stoichiometric ratio is needed to form the C14 lattice; similarly, the required ratio is 2A:1C for the C15 lattice. Therefore, the distributions that are shifted toward greater numbers of smaller particles are particularly well suited to form Laves phases. Indeed, the Laves phase domains present in the sixth-order power law distribution comprise 85% of the total particles in the simulation. By contrast, for the case of the flat-top distribution, the Laves phase regime identified by template-matching only accounts for 51% of the total particles in the simulation.

One limitation of our simulation protocol can be gleaned from the size distributions shown in Fig. 4, where there are cases for which all (or almost all) of the particles of a given size have been incorporated into the crystal structure. As a result, it is possible that the crystalline phase has incorporated particles with a non-ideal diameter compared to a system connected to an infinite reservoir of particles. For this reason, it is known that finite-size effects are particularly relevant to mixtures.¹⁴ On the other hand, the relative insensitivity of d_L/d_S with respect to the form of the distribution and the consistency of Laves phase formation is suggestive that these two findings are not especially sensitive to finite-size effects. Furthermore, we have performed an identical analysis to that shown in Figs. 2 and 3 for $N = 10\,000$ and found near quantitative agreement between the two system sizes; see the [supplementary material](#). Ultimately though, simulations in the isobaric-semi-grand canonical ensemble could be useful to confirm the reported properties of the crystalline phase.¹⁴

The results reported in this work may be useful in the interpretation of several prior studies. One such study employing polydisperse soft spheres with a $c_V \approx 0.24$ found a high-density inhomogeneous state comprised of coexisting ordered and fluid phases with strong particle size segregation.^{15,16} The ordered phase was not identified; however, the published snapshots are consistent with a Laves phase, and $d_L/d_S \approx 1.26$ for the ordered phase.¹⁶ In another study, a soft sphere ternary mixture yielded a structurally similar solid phase dominated by two of the three particle types with $d_L/d_S = 1.25$.⁹ Taken together, it appears that the formation of Laves phases in HS systems may be a far more common and general phenomenon than previously recognized. Therefore, studies of moderately polydisperse HS fluids should explicitly consider the possibility of Laves phase formation.

Furthermore, the binary HS phase diagram may provide a generally useful reference to anticipate and interpret the crystalline phases that emerge in polydisperse mixtures. A recent study of a polydisperse HS system with $c_V \approx 0.23$ observed partial crystallization of the aluminum diboride (AlB₂) lattice with $d_L/d_S \approx 2$, a value within the AlB₂ stability window for the binary HS system.¹⁷ Finally, we note that the disordered phase that exists in coexistence with the Laves phases may have interesting properties (e.g., it may be a particularly good glass former)—an interesting avenue for future studies.

See [supplementary material](#) for additional details regarding the simulation protocol, template-matching scheme, analysis for the structure given in Fig. 1(c), configurations corresponding to the data in Figs. 4(b)–4(d), and data corresponding to a simulation with 10 000 particles.

This research was partially supported by the Welch Foundation (No. F-1696) and by the National Science Foundation through the Center for Dynamics and Control of Materials: an NSF MRSEC under Cooperative Agreement No. DMR-1720595. We acknowledge the Texas Advanced Computing Center (TACC) at The University of Texas at Austin for providing HPC resources.

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