Growing Binary Hard Sphere Crystals

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Computer simulations of the fluid-to-solid phase transition in the hard sphere system were instrumental for our understanding of the crystallization process. While colloids experiments and theory have been predicting the stability of several binary crystals for many years, simulations were not successful to confirm this phenomenon. Mixtures, such as the binary hard sphere fluid, are also common model systems for research in glass physics, and it is crucial to know about the presence of any crystallization transition. Here, we report the growth of binary crystals isostructural to Laves phases, AlB$_2$, and NaZn$_{13}$ in simulation directly from the fluid. We analyze particle kinetics during Laves phase growth by comparing event-driven molecular dynamics simulations with and without swap moves that speed up diffusion. Finally, we present packing fraction–size ratio state diagrams in the vicinity of the stability regions of these three binary hard sphere crystals.

Introduction.—Hard spheres are arguably one of the simplest particle model. Their crystallization is a classic example of a phase transition discovered by computer simulation [1][3]. A prediction of the model is the spontaneous ordering of concentrated suspensions of nearly-hard colloidal spheres [4]. Generalizations are mixtures of spheres with different sizes such that small spheres fit between large spheres to stabilize binary crystals. Early experimental realizations are binary crystals isostructural to AlB$_2$ and NaZn$_{13}$ found in natural opal gems [5][7]. More recent experiments [8][12] and theory [13][20] predicted additional ones. By now four binary crystals have been proposed in the hard sphere phase diagram near the solidus line: NaCl (0.30 ≤ α ≤ 0.41), AlB$_2$ (0.45 ≤ α ≤ 0.62), NaZn$_{13}$ (0.54 ≤ α ≤ 0.61), and Laves MgCu$_2$ and MgZn$_2$ (0.76 ≤ α ≤ 0.84). This list identifies binary crystals by their atomic prototype and contains the reported ranges for size ratio α = σ$_S$/σ$_L$, where σ$_S$ and σ$_L$ are the diameters of small and large spheres, respectively. Additional binary crystals, such as CsCl [11], are believed to be metastable or appear only at high packing fraction φ as predicted by dense packing studies [21][23].

Equal-sized hard spheres crystallize rapidly into the face-centered cubic (fcc) crystal or stack variations thereof. They have been an ideal testing ground for studying fundamental aspects of crystal nucleation and growth [24][26]. It was thus expected that simulations produce binary crystals in a similar manner. This has not been the case. To date, the only hard sphere binary crystal growth reported in simulation from the fluid is NaCl [18]. That report is more than 20 years old and the crystals grown are highly defective with many vacancies of the small spheres [27][28]. AlB$_2$ so far required a seeding procedure to grow [29]. Laves phases and NaZn$_{13}$ formed from size-disperse sphere fluids only with the assistance of Monte Carlo swap or resize moves [30][31]. Laves phases also grew in soft sphere simulations where particle softness enhances crystallization [32]. The absence of binary hard sphere crystallization in simulation has been puzzling. Here, we resolve this puzzle by reporting the spontaneous formation of AlB$_2$, NaZn$_{13}$, and Laves phases directly from the fluid in simulation. Our results demonstrate that binary hard sphere crystals grow robustly and reproducibly in standard event-driven molecular dynamics (EDMD) given only sufficient simulation time and large enough system sizes. Crystallization into the Laves phase proceeds at weak supersaturation in the coexistence regime via spinodal decomposition. We observe that the bottleneck for binary crystal growth is diffusion in the dense fluid.

Growth of Laves phase.—Laves phases are of relevance for materials scientists because they are the most common binary intermetallic compounds [33] and have interesting photonic properties when self-assembled from colloids [34]. For this reason, we focus on their growth first. We speed up crystallization in an initial test by combining EDMD simulations with swap moves [30][31][35][38]. Particle pairs are attempted to be swapped as a Monte Carlo move at every collision (Appendix A). Gibbs free energy calculations [19] guide us to the parameter set (α, φ) = (0.57, 0.80), which lies in the fluid-Laves coexistence regime slightly below the solidus line. We initialize a simulation at composition LS$_2$ in the fluid state and run it at isochoric (constant volume) conditions with periodic boundaries. The ordering process of our system is monitored by recording reduced pressure $P^*$ = $P/\Pi$ over reduced simulation time $t^*$ = $t/\tau$. Here, $\Pi = k_B T/V_L$ with volume of the large sphere $V_L = \pi \sigma_L^3/6$ is a unit of pressure and $\tau = \sigma_L \sqrt{m/k_B T}$ is a unit of time.

Pressure evolution is shown as blue curve in Fig. 1(a). After a rapid initial relaxation of the fluid over time 3·10$^{-3}\tau$, pressure decreases slowly while the system starts ordering, then gradually faster, until it reaches a constant slope. Crystalline order in the system is well characterized by the $q_0$ local bond-orientational order parameter (Appendix B). The distribution of $q_0$ values in the system shows pronounced peaks (Fig. 1(b)), which can be
FIG. 1. Crystallization of the Laves phase from a binary hard sphere fluid using a hybrid EDMD simulation with swap moves. The system contains 9999 particles at composition LS2 and is simulated at \((\phi, \alpha) = (0.57, 0.80)\). (a) Evolution of pressure (blue) and solid fraction (red) with simulation time. (b) Distribution of local bond-orientational order parameters \(q_6\) at fluid-solid coexistence. Solid fraction is computed by fitting the distribution with three Gaussians as indicated by dashed curves. (c) Final snapshot of the simulation showing the coexistence of Laves phase and fluid. Large spheres are represented by yellow color, small spheres by blue color. Particles are drawn at 50% of their size for better visibility. Red line indicates stacking sequence.

assigned to the fluid (broad central peak) and the two particle species in the solid (narrow outer peaks). We fit the peaks to compute solid fraction. Evolution of solid fraction (red curve in Fig. 1(a)) essentially mirrors the evolution of pressure and increases in sync with the pressure drop. The slopes of both curves come to an abrupt halt at \(t = 30 \cdot 10^3 \tau\), indicating the end of the crystallization process. After this time, the system reached an equilibrium of 60% solid and 40% fluid in coexistence.

A snapshot of the equilibrated system viewed along a two-fold symmetry axis (Fig. 1(c)) confirms the coexistence. In projection, particles are arranged into columns in the crystal (top part) and are disordered in the fluid (bottom part). The pattern of the crystal in this projection consists of straight rows of small spheres separated by zigzag rows of pairs of large spheres alternating with single small spheres. Such a pattern is characteristic of Laves phases. We extract the stacking sequence of the Laves phase as indicated by the red line in Fig. 1(c). Hexagonal Laves MgZn2 (C14) has AB stacking, which gives a zigzag line. Cubic Laves MgCu2 (C15) on the other hand has ABC stacking, which results in a straight line. We observe both straight and zigzag segments along the red line, demonstrating that our Laves phase is a mixture of C14 slabs and C15 slabs. In this sense, Laves phase crystallization in our binary system resembles crystallization of identical spheres, which forms random stacking variants of fcc.

Well-ordered Laves phases form in all 20 simulations. Both simulation methods lead to similar pressure–time pathways (Fig. 2), even though the speed in which these pathways are traversed is different. As expected, swap simulations are significantly faster in crystallizing the binary fluid. But the speedup is not constant. If we rescale simulation times such that the initial pressure evolution matches (Fig. 2(a)), then the tails of the pathway do not match. Likewise, if we rescale and shift simulation times to match the pressure evolution in the tails (Fig. 2(b)), then the initial parts do not match.

We compare the average pathway of swap simulations to the average pathway of non-swap simulations in Fig. 2(c). The slope of the curve corresponds to the momentary speedup of crystal growth in swap simulations over crystal growth in non-swap simulations. Speedup increases from initially 20x up to 120x towards the end, demonstrating that the efficiency of swap moves increases over time as crystal growth advances. Indeed, the acceptance probability of swap moves increases over the same time window (Fig. S1). This indicates an increase in available free volume in the fluid and explains the higher speedup towards the end of the simulation. Swap moves primarily enhance diffusion. We conclude that spheres are integrated faster into the crystal than they diffuse through the fluid. Therefore, diffusion in the fluid is the bottleneck process for Laves phase growth.

**Bottleneck process for Laves phase growth.**—Our simulation in Fig. 1 established Laves phase growth from the binary hard sphere fluid using swap moves rather easily. To show reproducibility and generality, ten swap simulations and ten non-swap simulations are performed at the same parameters and similar initial conditions.

**Laves phase crystallization pathway.**—We analyze one exemplary non-swap simulation pathway in more detail by tracking crystalline clusters. Fig. 3(a) shows the evolution of the number of clusters and the size of the three largest clusters. A particle is identified as solid-like using a \(q_6\) cut-off (Fig. S2). A solid-like particle belongs to a cluster if it has more than five solid-like particles.
of the three largest clusters (‘cluster 1’ to ‘cluster 3’). Simulation snapshots at times (b) \( t = 2 \times 10^5 \tau \), (c) \( t = 10^5 \tau \), (d) \( 5 \times 10^5 \tau \), and (e) \( 2 \times 10^6 \tau \). Particles are colored according to their local environment. Blue particles have high \( q_6 \), yellow particles low \( q_6 \). Green particles have intermediate \( q_6 \) corresponding to a fluid-like environment. Non-clustered particles are drawn with reduced size for better visibility.

FIG. 2. Comparison of Laves phase growth pathways from swap simulations and non-swap simulations. Simulation parameters and conditions as in Fig. 1. (a) Initial pressure evolution is matched by rescaling simulation times by \( t_1 = 10^4 \tau = 2.3 \) CPU hours for swap simulations and \( t_1 = 20 \times 10^4 \tau = 45 \) CPU hours for non-swap simulations. (b) Tails of pressure evolution are matched by rescaling simulation times by \( t_2 = 3 \times 10^4 \tau \) for swap simulations and \( t_2 = 250 \times 10^4 \tau \) for non-swap simulations. (c) Simulation times necessary to reach certain pressure values in swap and non-swap simulations are compared on the two axes of the plot. The speedups for the matches in (a,b) are indicated by dashed lines. Data in this plot is averaged over ten runs each.

within distance \( 1.1 \sigma_L \). Already right at the start of the simulation ten clusters are detected, indicating there is a very small or negligible free energy barrier for the Laves phase to form. The clusters grow independently, and their number decreases when they merge, which is also directly apparent in simulation snapshots at increasing times (Fig. 3(b-e)). A movie of the growth process is contained as Supplementary Information. Overall, Laves phase growth in this simulation proceeds not as predicted by classical nucleation theory but as expected from spinodal decomposition. This is surprising given that our simulation parameters are chosen in the coexistence regime slightly below the solidus line but does not exclude a nucleation and growth regime at lower packing fraction closer to the liquidus line.

**Binary crystal state diagrams.**—So far, we investigated binary crystal growth for a specific set of parameters in detail. Now, we systematically vary packing fraction \( \phi \) and size ratio \( \alpha \) to obtain full state diagrams. We focus on the compositions LS\(_2\) and LS\(_{13}\), for which binary crystals have been predicted. Simulations run for a total time of \( 2 \times 10^6 \tau \). Simulations that crystallize undergo their phase transition completely and fully grow into well-ordered crystals.

We start with composition LS\(_2\). Fig. 4(a) shows the state diagram in the vicinity of Laves phases and Fig. 4(b) the state diagram in the vicinity of AlB\(_2\). Both binary crystals form over extended parameter regions. The size ratio range for the Laves phases, \( 0.76 \leq \alpha \leq 0.86 \), and the lower limit of size ratio for AlB\(_2\), \( \alpha = 0.46 \), agree with predicted values [13, 19]. For \( 0.57 \leq \alpha \leq 0.75 \), the system remains amorphous. For \( \alpha \leq 0.45 \), the binary fluid phase separates into coexisting NaCl and AlB\(_2\) solids. For \( \alpha \geq 0.87 \), the fluid forms the substitutionally disordered fcc solid.

Results for composition LS\(_{13}\) are shown in Fig. 4(c).
The binary crystal found at this composition, NaZn$_{13}$, is a complex arrangement of large spheres on a simple cubic lattice and icosahedra made from 13 small spheres at body-centered positions. NaZn$_{13}$ forms in the range $0.54 \leq \alpha \leq 0.61$ as predicted by free energy calculation [14][15]. The range of packing fractions, for which crystallization is observed, is for all three binary crystals about 3%. Growth of AlB$_2$ is more difficult and leads to more defects than growth of Laves phases and NaZn$_{13}$, possibly because it occurs at higher packing fractions.

Discussion.—Our findings demonstrate that binary crystal growth from the binary hard sphere fluid is robust and reproducible. Why then have similar binary hard sphere crystals not been seen in simulation before? We are not sure. But we can list a few arguments that indicate doing so is not necessarily trivial. In simulations, growth without swap moves requires more than two weeks of continuous simulation with today’s fastest processors at the right parameters to obtain well-defined crystals that are easy to identify. EDMD simulations cannot be parallelized. Furthermore, many simulations in the past used Monte Carlo simulation instead of EDM, which slows down the growth process further by about one order of magnitude [10].

We map our simulations on two experimental conditions: magnesium atoms and polystyrene colloids. The unit of time for magnesium atoms at a temperature slightly below the liquidus line for hexagonal Laves MgZn$_2$, $T = 850$ K, correspond to about $\tau = 0.6$ ps (Appendix C). A magnesium atom takes on average about the time $\tau$ to move over its diameter. We estimate that Laves phase crystallization requires an experimental time of $10^7 \tau = 10$ ps to form nanocrystalline grains. Such times are easily reachable. This explains why Laves phases are ubiquitous in alloys. Colloids, on the other hand, are much larger and slowed down by drag in solution. We use the Stokes-Einstein equation to estimate $\tau = 0.2$ s for colloids with diameter 1 $\mu$m suspended in water (Appendix C). Only crystallization of identical colloids into fcc has been achieved with such large colloids as it is about $10^3$ times faster, even though the softness of charged spheres seems to help to obtain a variety of structures [11][14]. Crystallization speeds up proportional to $\sigma^{-3}$ with shrinking colloid diameter $\sigma$. Experiments with 170 nm colloids need to rest for months at the optimal condition to form Laves phases [12], which corresponds to an equilibration time of $10^9 \tau$ to $10^{10} \tau$ to grow macroscale crystals. Even smaller $\leq 10$ nm nanoparticles crystallize rather easily into binary superlattices [15][48].

Our results confirm once again the power of swap simulations for speeding up structure formation in particle mixtures [30][31][35][38]. There have been concerns that swaps alter phase transformation pathways because they preferentially accelerate specific aspects of kinetics. At least for the processes investigated here, crystallization of binary hard sphere Laves phases, trajectories with and without swap are indistinguishable. If these observations are confirmed in more systems, then swaps can become a standard tool for simulating mixtures, in particular those with small size difference. Swap methods have the potential to speed up such simulations by orders of magnitude.

Finally, our findings add to the growing list of recent observations of crystallization processes in model systems that were once believed to be good glass formers [31][34][36][43][50]. Knowledge of crystal structures competing with the amorphous state, as reported here for the binary hard sphere fluid, is important to ensure that the analysis of local order and particle dynamics in such model systems intended for glasses is not affected by hidden crystallization transitions.
FIG. S1. Evolution of particle swap acceptance probability for the trajectory shown in Fig. 1. Particle swap acceptance probability is defined as the number of accepted particle swaps to the number of attempted particle swaps. Acceptance probability gradually increases from $5 \times 10^{-5}$ to $20 \times 10^{-5}$ while the system crystallizes.

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APPENDIX A: SIMULATION METHOD.

Binary hard spheres are simulated in event-driven molecular dynamics (EDMD) with and without swap as described in recent work [31]. Setting the mass equal for all particles simplifies momentum conservation and has no effect on the phase behavior of the system. Dimensionless pressure $P^*$ is computed as

$$P^* = \frac{P \sigma_1^3}{6 k_B T} = \phi \left( 1 + \frac{\sqrt{\pi}}{3} \frac{\tau N_c}{N} \right), \quad (1)$$

from the number of particle collisions $N_c$ during a simulation time window $t_{tot}$.

APPENDIX B: DETECTION OF CRYSTALLINE CLUSTERS.

Crystalline clusters growing from the binary hard sphere fluid are tracked with local bond-orientational order parameters $q_l$ [53]. We compute the $(2l+1)$-dimensional complex vectors

$$q_l^m(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_l^m(\vec{r}_{ij}). \quad (2)$$

Here, $N_b(i)$ is the number of neighbors of particle $i$, $Y_l^m(\vec{r}_{ij})$ are spherical harmonics coefficients for neighboring particles $j$, and $\vec{r}_{ij}$ is the separation vector. Nearest neighbor particles are identified using the parameter free solid-angle based nearest-neighbor (SANN) algorithm [54]. Local order parameters are defined as

$$q_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_l^m(i)|^2}. \quad (3)$$

Fig. S2 shows the scatter plot of $q_4$ and $q_6$ for all particles in a fluid and in a fluid-solid coexistence of Fig. 1. $q_6$ alone is sufficient to detect whether a small or large particle is in a fluid-like environment or a solid-like envi-
In other words, the atom takes on average about the time $\tau$ to move over its diameter under the assumption of ballistic motion.

For polystyrene colloids with diameter $\sigma_L = 1\,\mu m$ in water, we use room temperature $T = 293\,K$ to calculate as before

$$ \Pi = \frac{6k_BT}{\pi \sigma_L^3} = 8\,mPa. $$

The assumption of ballistic motion is clearly not valid for colloids in solution. To compensate for diffusion of colloids in solution, we use the relation for the mean squared displacement and the Stokes-Einstein equation for the diffusion coefficient,

$$ \langle x^2 \rangle = D = \frac{k_BT}{6\pi \eta \sigma_L}. $$

We assume that particles move diffusively between collisions and average the slowdown from diffusion over all collisions $c$. This means time is replaced by the average time between two successive collisions, $t = \langle \Delta t_c \rangle_c$, and mean squared displacement is replaced by the average squared distance the particle moves between two successive collisions, $\langle x^2 \rangle = \langle \Delta x^2_c \rangle_c$. We then obtain an estimate for the effective unit of time as

$$ \tau_{\text{diffusive}} = \frac{3\pi \eta \sigma_L^2 \langle \Delta x^2_c \rangle_c / \sigma_L^2}{k_BT} \frac{\langle \Delta t_c \rangle_c / \tau}{\langle \Delta t_c \rangle_c / \tau}, $$

where we used the viscosity of water $\eta = 0.94\,mPa\cdot s$.

From the analysis of collisions in the EDMD simulation shown in Fig. 3, we obtain in the fluid $\langle \Delta x^2_c \rangle_c = 10^{-3}\sigma_L^2$, $\langle \Delta t_c \rangle_c = 0.01\tau$ and in the fluid-solid coexistence $\langle \Delta x^2_c \rangle_c = 2 \times 10^{-3}\sigma_L^2$, $\langle \Delta t_c \rangle_c = 0.02\tau$. The unit of time is thus estimated in both cases to be

$$ \tau_{\text{diffusive}} = 200\,ms. $$

For comparison, the (much more incorrect) assumption of ballistic motion applied to polystyrene colloids gives a significantly smaller unit of time,

$$ \tau_{\text{ballistic}} = \frac{\sqrt{\rho \pi \sigma_L^2}}{6k_BT} = 0.4\,ms. $$

Here, we used the density of polystyrene $\rho = 1060\,kg/m^3$.

The crude estimate outlined above suggests that diffusion of the colloids in solution slows down crystallization kinetics by up to three orders of magnitude.

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