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Crystallization of Spheres[1]

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Simplified computer models are used to gain insight into more complex real systems. In a reversion of this protocol, a colloidal suspension of submicron spherical particles, approximately hard and uniform, was recently crystallized in space and analyzed for crystal type. The objective was to establish how, and to what structure, hard spheres crystallize without gravity. Computational statistical thermodynamics predicts an equilibrium constant between fcc and hcp of order unity. The microgravity experiments, however, resulted in a random hybrid close-packed structure (rhcp) such that long-range order is two-dimensional. Here we report the mechanism from idealized computer "experiments" for crystallization of spheres from the metastable fluid. Model systems of up to $N = 64{,}000$ spheres with infinite spatial periodicity have been crystallized in runs of up to 10 billion collisions. When the fluid, initially in a metastable supercooled state at 58% packing, is allowed to nucleate and freeze, a variety of structures emerges. There are three identifiable stages of structural growth: (i) initial nucleation of fcc, rhcp, and also bcc-like (body-centered cubic) local structures; (ii) rapid growth of all incipient nucleites to random stacked two-dimensional hexagonal (rhcp) grains, plus some fcc, to fill the volume; and (iii) relatively slow dissolution of unstable rhcp faces at grain boundaries. Eventually, stable nucleites emerge comprising hexagonal layers, arranged so as to contain predominantly either fcc arrangements of spheres or rhcp, in roughly 50% proportions.

KEY WORDS: computer simulation; crystallization; hard spheres.

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1. INTRODUCTION

The phase diagram of the thermodynamic hard-sphere model is now well known from computer simulation. Until recently, however, it was not known which of the close packed structures, fcc, hcp, or perhaps a hybrid or random hybrid structure, is the most stable. Five methods of computational statistical mechanics have recently been applied to this task. All find the fcc structure to be more stable at the freezing point than the hcp structure by a free energy difference of the order $RT/1000$, where R is the molar gas constant and T is the absolute temperature. The question then arises, Can a fluid system of hard spheres, metastable with respect to crystallization, on time scales accessible either in nature or perhaps in computer "experiments" achieve this most stable structure and by what mechanism?

If there were only two possibilities, the answer would be simple. The free energy difference is so small that the equilibrium constant (K_p) for the transformation of hard spheres (HS)

$$\mathrm{HS}_{\mathrm{fcc}} \rightarrow \mathrm{HS}_{\mathrm{hcp}}$$

is equal to $\exp(-0.001) \simeq 1$; therefore, at equilibrium one expects to find a 50/50 mixture. The situation is complicated, however, because there is an infinite number of hybrid lattices and random hybrids. The completely random stacked phase has been designated rhcp. It seems likely that rhcp will be present to about 50% at equilibrium because nature cannot distinguish between hcp and rhcp. However, the fcc structure is distinct due to the different lattice symmetry. The sixfold symmetry of fcc is unique.

There are two alternative empirical approaches to this problem presently available, real experiments on suspended quasi-"hard-sphere" colloids and idealized computer experiments on mathematically precise spheres. Both approaches have advantages and limitations.

In the last 15 years a number of experimental studies have demonstrated that polymer-coated colloidal particles in organic solvents bear a close resemblance to the ideal hard-sphere system. By matching the refractive indices of solvent and particle as closely as possible, the attractive van der Waals forces between particles can be quelled. Grafting of polymer chains to the particle surfaces ensures that the particles experience a steep repulsive interaction on close approach, never experiencing any residual van der Waals attractions. These "quasi"-hard-sphere systems can serve as larger scale mimics of simpler atom-like hard-sphere systems; the appeal for colloid scientists is that time scales in these systems are slow enough for experimental observation. By employing colloidal PMMA particles of diameter ~0.5 μm, sample sizes of 10^{14} cm^3 (boundary effects are likely to be negligible with such large systems) are accessible and Brownian diffusion has characteristic relaxation times typically of days. Such time scales in the colloid dimension enable the use of real-time optical techniques, such as microscopy and light scattering in the study of crystal nucleation, for example.

The packing of nearly hard spherical particles was first examined in detail by Pusey et al. [1], who used light scattering studies to observe the packings of crystals produced at a range of values of the packing fraction (ϕ). They were able to produce crystals with a strong preference for fcc stacking using slow sedimentation of a fairly low packing fraction, i.e., $\phi = 0.25$. At a slightly higher packing fraction in the coexistence region, the preference for fcc stacking was less marked (with a stacking probability [2] of 0.58), which is characteristic of a faster time scale for crystallization. It was pointed out by Pusey et al. that none of the close-packed simple atomic systems display such complete randomness in packing, choosing, instead, to be either fully fcc or hcp. This indicates, perhaps, that such systems of colloidal hard spheres have not reached their equilibrium configuration or that the influence of gravitational effects requires consideration.

A number of subsequent studies have reported a slow growth in the stacking probability with time: Elliot et al. [3] observed a structure which became more fcc-like with time looking at crystallization from a random structure with a packing fraction of 0.529. Details of the change and its time scale were not provided. Dux and Versmold [4] reported the slow structural transition of a system of charge stabilized polystyrene hard-sphere-like particles: a nearly rhcp structure (stacking probability, 0.55) was produced, which was converted over a period of 40 h to a more fcc-like structure (stacking probability, 0.75).

A very detailed study by Heymann et al. [5] looked at the crystallization kinetics of shear-melted samples of polymer-coated PMMA (polymethylmethacrylate) spheres, with packing fractions of between 0.51 and 0.57, using a light scattering method. Peaks in the scattering intensity-versus-wavelength plot corresponding to fcc and hcp lattices were monitored with time; they report stacking probabilities of the order of 0.9 after a long ripening stage. They also report an observation, in line with the simulation findings of Courtemanche and van Swol [6], of heterogeneous nucleation at the walls of the suspension container on short time scales. At higher packing fractions above melting, Heymann et al. [5] note that the induction time for homogeneous nucleation from the bulk decreases rapidly with increasing volume fraction, eventually inhibiting the effects of heterogeneous nucleation. At packing fractions above the melting transition, homogenous nucleation should be the primary mechanism for creating order in the system. Experimental evidence appears to point toward fcc-oriented growth of colloidal hard spheres. However, all these studies include the effects of sedimentation under gravity.

More recently, in an attempt to get closer to ideal hard-sphere colloidal systems by excluding the effects of gravity, similar light scattering experiments on shear-melted hard-sphere suspensions were performed onboard the Space Shuttle Columbia under microgravity [7]. The hard spheres used in this case were the familiar ~500-nm-diameter PMMA particles with a short (~10-nm) grafted organic layer. Packing fractions in the range between $\phi = 0.5$ and $\phi = 0.619$ were examined over a number of days. One of the interesting results of these experiments was that a sample with $\phi = 0.537$, that showed a strong tendency to pack toward the fcc structure under gravity, showed no such tendency under microgravity. The authors report finding almost-pure rhcp crystals and suggest that gravity is instrumental in converting a predominantly rhcp arrangement to fcc. They also report that microgravity enhances crystallization: a system of particles with $\phi = 0.619$ crystallized in 3.6 days; the same system, shear melted when returned to gravity, failed to crystallize over a 2-month period.

Zero gravity, along with the ability to achieve perfect hard spheres, is a natural feature of computer simulations. Given the surprising results from the crystallization under microgravity, the work we present here aims to use the advantages offered by computer simulation to examine the freezing kinetics of the perfect hard-sphere system without the influence of gravity. In a simulation all particle coordinates can be determined for any particular moment in time; one can employ sophisticated techniques that allow the detection of structural features. One disadvantage of simulation is that the number of particles and the time scale of the simulation are limited by present-day computing power. Recent algorithmic developments [8, 9] have enabled inroads to be made into the study of large-scale systems over longer time scales, thereby following the crystallization path over many billions of hard-sphere collisions.

2. SIMULATION METHOD

Four systems of 12,000 spheres were used in our initial attempts to study hard-sphere crystallization. These spheres were set up in a cubic box with periodic boundary conditions, at a packing fraction of 0.3, initially in a lattice arrangement, which was then allowed to melt to produce a fluid configuration. This configuration was slowly compressed isotropically to the reduced density $\rho^* = 1.1$ (packing fraction $\phi = 0.576$). At this density the pressure of the metastable pure hard-sphere fluid is about 23.5 in reduced units of $\beta\sigma^3$, where σ is the hard-sphere diameter and

$\beta = 1/(k_B T)$. On completion of the densification at $\rho\sigma^3 = 1.1$, the pressure can exceed the metastable fluid branch value.

Figure 1 shows the relaxation of two of these systems over several million collisions. It appears that there is no barrier to spontaneous homogeneous nucleation, as initial nucleation events appear throughout each system. This is evidenced by the immediate and continuous drop in pressure in both systems down to a plateau region at a pressure of about 18 $k_B T/\sigma^3$. The early stages of crystallization are independent of the starting configuration, as the pressure in both systems falls in a very similar manner initially. In the intermediate regions where the pressure settles at about 18 $k_B T/\sigma^3$, the evolution of each system follows a more spasmodic path. The number of collisions required to produce a substantial pressure drop varies in each system, although eventually it can be seen that they both approach the same pressure, just above 15 $k_B T/\sigma^3$. The pressure of a pure fcc crystal at this packing fraction is 14.6 $k_B T/\sigma^3$.

More detailed information on the nucleation process and the evolution of crystal structures has been obtained from continual analysis of the

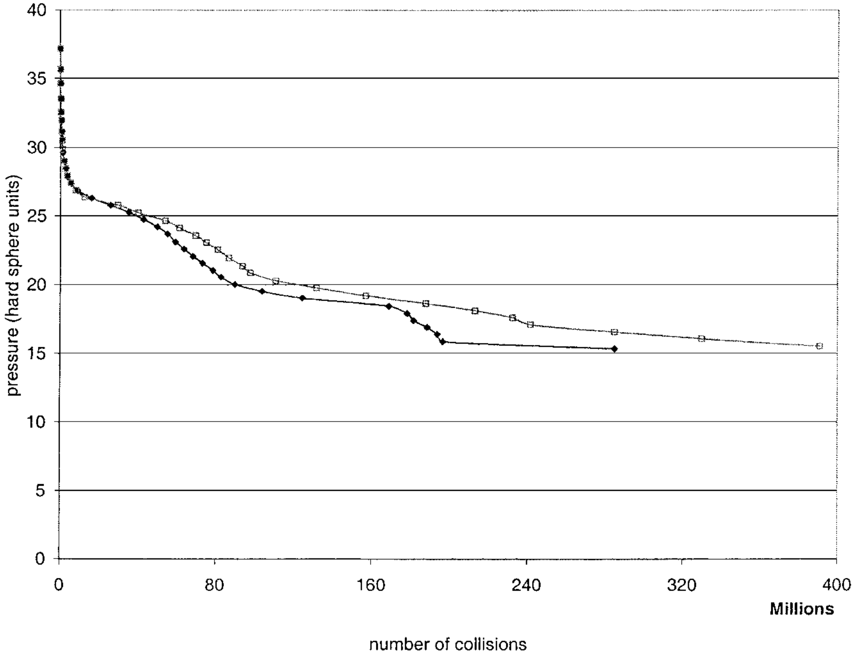

Fig. 1. Evolution of pressure with number of collisions for two systems of 12,000 hard spheres (initially densified to a fluid state at a packing fraction of 0.576) as they crystallize.

transient and final configurations using angular order parameters [10] and modified Voronoi polyhedra [11]. We have calculated the bond-order parameter distributions, wherein every atom in the system can first be distinguished as either crystalline or fluid, using the method of ten Wolde et al. [12]. Subsequently, local fcc ordering can be distinguished using the heuristic method established by Mitus et al. First, they calculated the local order parameter w_{446} for each particle in the system. The distribution of this parameter for a pure fcc crystal showed a distinct separation from other crystalline ordering. Using this approach we identified only those particles with a local order parameter lying within the pure hard-sphere fcc crystal local order parameter distribution as fcc. Verification of crystal type identification was made by examining the modified Voronoi polyhedron surrounding each particle. Local hexagonal ordering and body-centered cubic order could also be identified accurately using the Voronoi construction.

3. RESULTS AND DISCUSSION

With these techniques we observed (Fig. 2) that initially bcc, fcc, and hcp nucleites can all appear spontaneously out of local density fluctuations throughout the system simultaneously. The amount of sample that can be characterized as "fluid" drops to about a quarter of the system after 500 hsu (hard sphere units of time). At this stage nucleites are beginning to fill

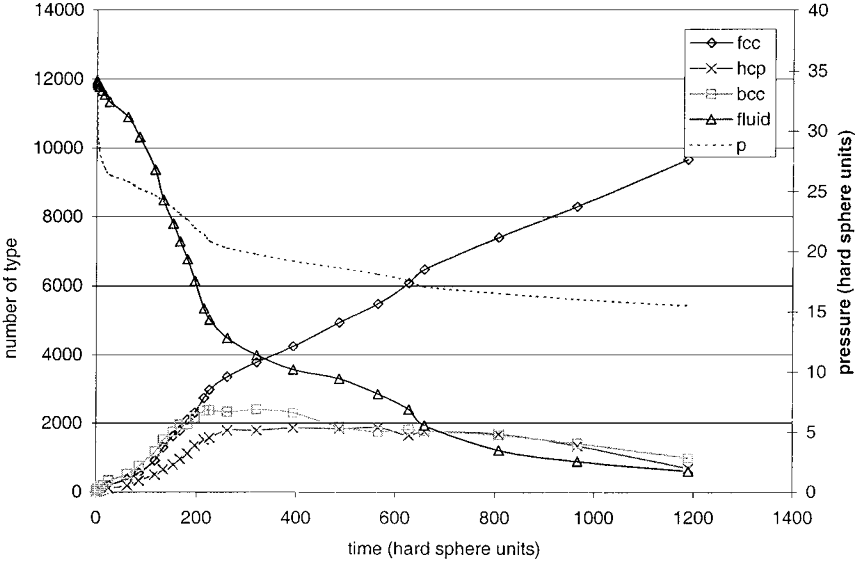

Fig. 2. Evolution of structural content in a crystallizing system of 12,000 spheres.

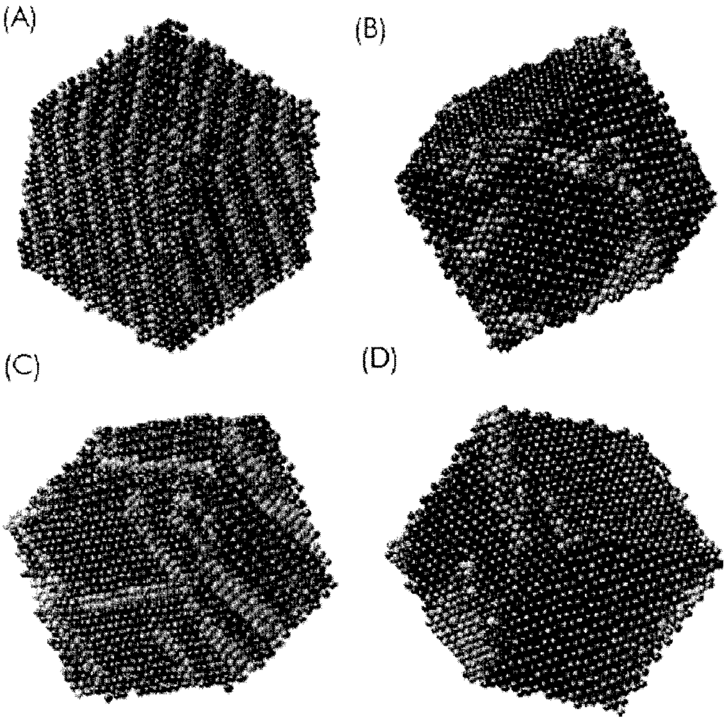

Fig. 3. Kinetically stable structures that emerged in independently crystallized 12,000-particle systems. Blue coloring of a sphere denotes local fcc order; green, hcp order; red, bcc; and yellow, "fluid" content. (A) A 65 % fcc content, (B) 81 % fcc, (C) 70 % fcc, and (D) an 82 % local fcc content.

the system and the "fluid" is found at boundaries between nucleites. At this early stage the predominant structure is fcc. For the next 1000 hsu, in a long annealing phase, the fcc fraction grows, and the bcc decays slowly, along with the rhcp content. The final structures in four independently prepared $N = 12{,}000$ systems were characterized by these methods to reveal the orderings shown in Fig. 3.

Clearly the annealing phase can lead to wildly varying final structures, although it can be noted that in all the crystal structures the fcc content dominates at the end of this phase. An interesting observation was made from these crystallizations that may be a useful and fundamental generality. The structural identification as a function of time appears to vary widely from one run to the next because the crystallization process is dependent on infrequent random events (perhaps extreme density fluctuations); the proportion of crystal type and the ratio of fluid to crystal at any point

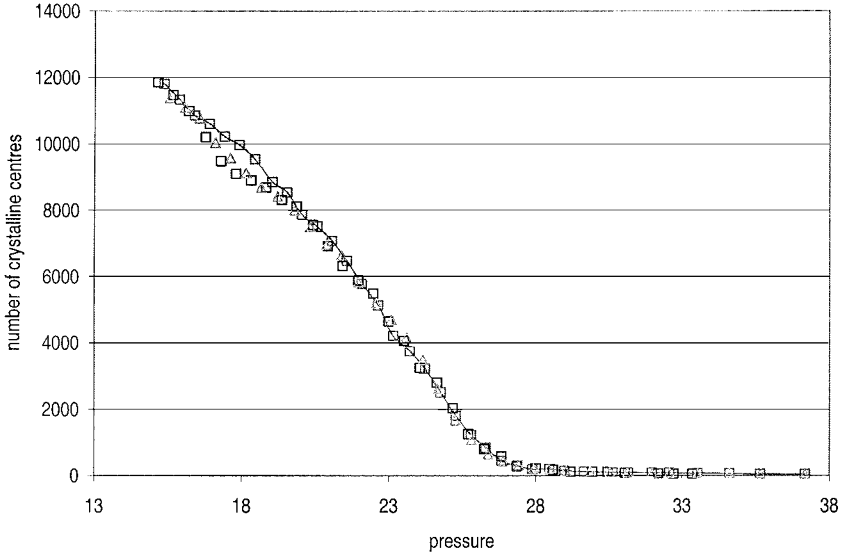

Fig. 4. Crystalline content plotted against pressure (in hard-sphere units) for independently prepared systems of $N = 12{,}000$ hard spheres with $\phi = 0.576$.

along the crystallization path appears to depend only on the transient pressure of the system, as shown in Fig. 4. Rather than discuss the system evolution with time, it makes more sense to discuss the process of crystallization as the pressure of the system decreases since this eliminates the differences between systems imposed by rare-event statistics.

Whether or not this is a useful generality will depend upon whether the same observations can be made for crystallization at differing packing fractions and differing system sizes. If the observation that the relative concentration of crystalline content is a function only of pressure, it is tempting to project the crystallization mechanism to larger systems such as those encountered in colloidal hard-sphere experiments, where the number density of particles can be about 10^{14} cm^{-3}. With the aim of looking at the system size dependence, a set of 64,000 hard spheres in a disordered arrangement was created with a packing fraction of 0.576 and allowed to crystallize. Here a picture slightly different from to that seen in the smaller system emerges. At early stages we observe the same hand-in-hand growth of the fcc and bcc content, followed by a depletion of the bcc content alongside the steady growth of the fcc and hcp content. However, the behavior of the larger system in the final stages of crystallization differs substantially. At no point in this state does the hcp content become depleted. Figure 5 shows the variation in structural content with time. We

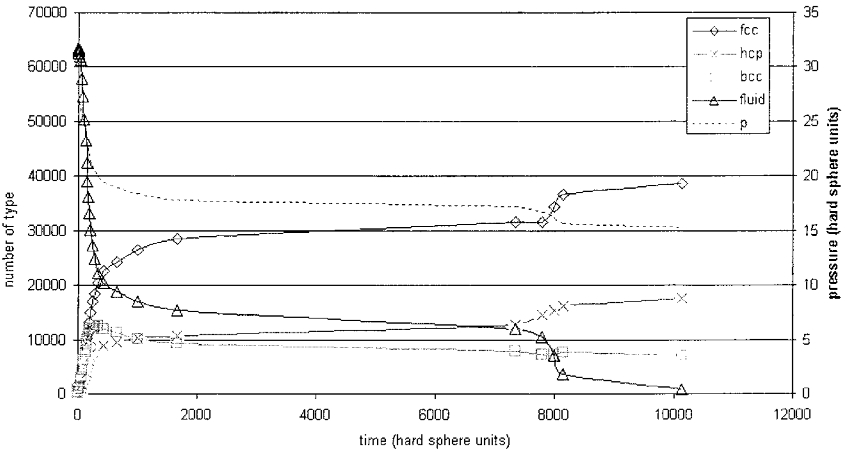

Fig. 5. The emergence of fcc, bcc, and hcp crystal structures from the metastable fluid with time (in hard-sphere units) in an $N = 64{,}000$-particle systems; the evolution of the system pressure with time is also plotted, with the pressure scale on the right-hand axis.

note that there is apparently a system-size dependence to the time taken in the annealing phase.

The pressure drops rapidly to about 18 $k_{\mathrm{B}}T/\sigma^3$ in about 400 hsu, along the same time scale as for the smaller $N = 12{,}000$ system. This is followed by an immensely longer annealing time scale that is suggestive of a more complex distribution of crystalline orientations in the system—an alignment and subsequent growth may require an improbable density fluctuation; if there are several alignments required to stimulate crystal growth, then a substantially longer time will elapse before the larger system of particles becomes almost fully crystalline. After this long annealing process in the larger system, taking the pressure down to about 17.2 $k_{\mathrm{B}}T/\sigma^3$, a sharp drop in pressure occurs, taking the system down to a pressure of 15.2 $k_{\mathrm{B}}T/\sigma^3$, in the same manner as observed in the smaller system. We present a series of snapshot images of the system as it undergoes this transition (Fig. 6). They show, very clearly, that the system initally forms faulted fcc/hcp crystalline mixtures or “grains” (Fig. 6A) surrounded by disordered boundaries that are eventually eradicated (Figs. 6B–E), until, finally, a faulted and defective set of close packed layers (Fig. 6F) is produced as the pressure reaches a plateau.

4. CONCLUSIONS

In conclusion, we observe that, in the initial stages of freezing, the metastable fluid generates small nuclei. From a thermodynamic viewpoint

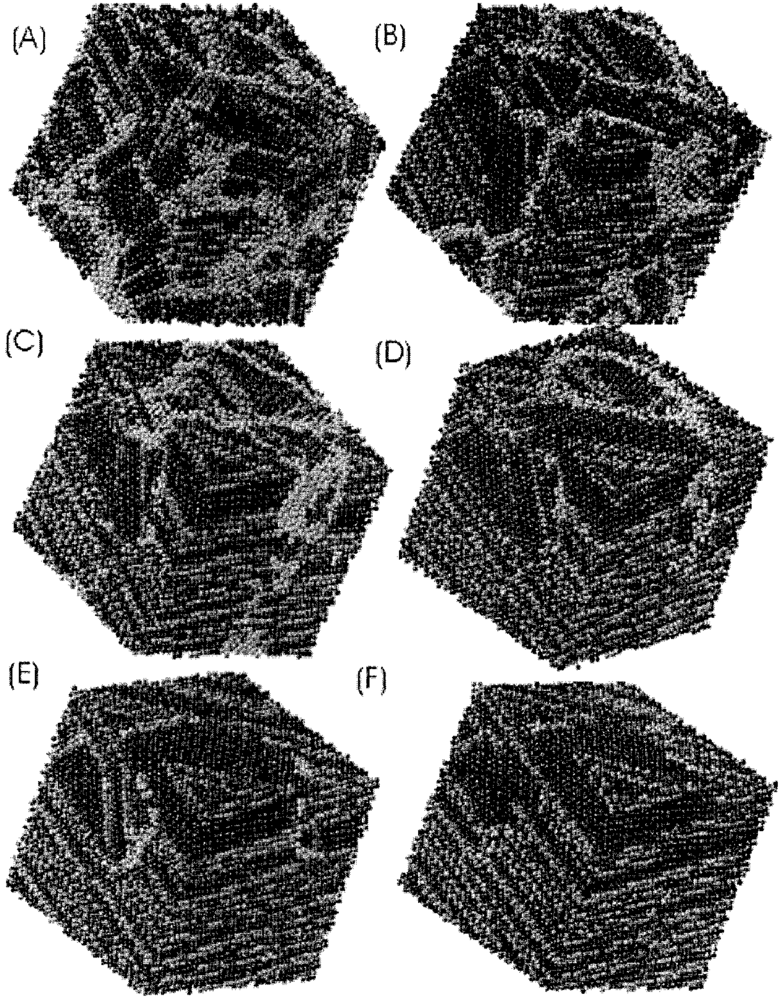

Fig. 6. A series of snapshots from the system of 64,000 spheres in the annealing phase as the pressure drops from (A) 17.8, (B) 17.2, (C) 16.7, (D) 16.2, and (E) 15.7 to (F) 15.2 k_BT/σ^3.

it is the chemical potential difference between the fluid and the crystal phases that is the essential driving force for this. With this perspective, we know from recent theory that the bulk fcc structure is only very marginally the most stable crystal structure. There is no thermodynamic reason, therefore, to expect the fcc crystal phase to dominate. However, nuclei growth kinetics are governed by surface free energy and other steric factors competing with the bulk free energy differences.

Our simulation evidence suggests that the emergence of crystal structures from the fluid follows Ostwald's step rule, which anticipates the influence of surface free energy factors. Ostwald formulated the rule that the crystal phase nucleated from the fluid could in fact be the one that is nearest in free energy to the fluid phase rather than the one farthest away (i.e., the most stable). In these simulations we see, initially, the growth of bcc and fcc structural components, with bcc leading fcc slightly. Woodcock [13] reported that the bcc lattice melts at a packing fraction of 0.548 and begins to freeze at a packing fraction of 0.528, with a coexistence pressure slightly higher than the fcc–fluid coexistence pressure. The operation of Ostwald's step rule, with the bcc phase predominating among the earliest nuclei, at a packing fraction of 0.576 is therefore to be expected.

At early stages, the appearance of fcc structural content is also rapid, traveling almost simultaneously with the bcc growth. Although this could be attributed to the thermodynamic drive to achieve the state with the lowest free energy, it may also be due to an inherent coupling of the unconstrained hard-sphere bcc crystal with the fcc crystal. We have observed that a bcc lattice of 16,000 hard spheres is unstable at a packing fraction of 0.576, rapidly losing its structural integrity to collapse to a faulted mixture of fcc and hcp structures. Local fluctuations and resulting stresses are capable of inducing slip in the bcc lattice. The mechanical instability of the bcc crystal thus presents a plausible mechanism for the coupling of fcc and bcc nuclei growth.

At intermediate stages the crystallization has a percolative character where crystalline regions containing many variations of local order become intermingled and span the whole system. A slow conversion and growth of nuclei occurs at this stage, with large regions gradually reducing the local bcc content to form predominantly fcc structures, albeit containing numerous stacking faults. At later stages, annealing of nuclei in the system can occur, provoking more stacking faults, and the crystallization follows an unpredictable path once seemingly kinetically stable structures are obtained. It is observed that from simulation to simulation these vary from having an almost entirely fcc content to being completely rhcp and, in some cases, mixtures. This result is entirely consistent with the stable crystal structure of hard spheres in the thermodynamic limit being essentially 50% fcc and 50% rhcp, in accord with the different symmetry and free energy difference of $0.001kT$.

This essentially random outcome seems to be independent of the size of the system that is studied. The present computations confirm complete crystallization to neither fcc nor rhcp. Experiments on colloids under the influence of gravity suggest a long time scale for crystallization toward a wholly fcc structuring. On the other hand, the experiment undertaken in microgravity describes stable rhcp structures appearing on a much shorter time scale. However, the claim for "rhcp" in this experiment requires closer examination. The existence of rhcp structuring was deduced from the absence of an fcc signature peak in the scattered intensity from the sample. In these simulation studies we also find an absence of the fcc signature peak at intermediate and annealing time scales. It may simply be that the microgravity experiments represent unstable hard-sphere systems which are in this slow grain growth conversion process. Very recent work by Pronk and Frenkel [14] also suggests that this is the case and go some way toward explaining the unpredictable latter stage of crystallization in our simulated systems. The evolution of the system in these latter stages is dominated by the random peculiarities of just a few grains.

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