Diffusive redistribution of small spheres in crystallization of highly asymmetric binary hard-sphere mixtures

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Abstract – We report a molecular-dynamics study of crystallization in highly size-asymmetric binary hard-sphere mixtures, in which the large spheres can form a crystal phase while the small ones remain disordered during the crystallization process of the large spheres. By taking advantage of assisting crystal nucleation with a patterned substrate, we find that adding a second, much smaller component will not alter the crystal structure formed by the large spheres. Instead of having fully random distributions, the small spheres are found to diffusively redistribute during the crystal formation of the large spheres and their density profile exhibits a strong coupling with that of the large spheres. We discuss the corresponding changes of the density profile for the small spheres at different crystallization stages.

Crystallization of hard-sphere colloids has been the subject of intense research since assemblies of hard spheres constitute a very simple model but have potential important applications and exhibit complex behavior. Pioneering work by Alder and Wainwright in 1957 [1] demonstrated that the monodisperse hard-sphere system crystallizes at high enough volume fractions, driven by purely entropic effects. Over the last few decades, the understanding of crystallization of hard-sphere colloids has been greatly improved due to the development of new experimental techniques [2–4] and novel numerical methods [5,6]. The binary hard-sphere mixtures with moderate size disparity also attract considerable interest for both practical and fundamental reasons, e.g., various types of binary crystals can be formed in such systems [7–10] and a nonstandard nucleation and growth scenario has been proposed by studying binary hard-sphere mixtures with a small-to-large–sphere diameter ratio \( q = \sigma_s / \sigma_l = 0.9 \) (\( \sigma_s \) and \( \sigma_l \) denote small- and large-sphere diameters) at a total volume fraction of 0.58 [11]. In contrast, much less attention was paid to the crystallization of highly asymmetric binary hard-sphere mixtures [12,13], in which the large spheres can form a crystal phase while the small ones remain disordered. The main reason resides in the fact that the addition of a second much smaller component will intuitively not affect the crystal structure and hence the properties of the resulting material. However, it is unknown whether the small spheres play any role during the crystallization process or not.

In this work, we focus on the crystallization of binary hard spheres with large size disparity. In such system, the presence of the small spheres can induce attractive forces between the large spheres, called the depletion effect [14], which is most clearly present in colloid-polymer mixtures. By taking this effect into account (through either the effective one-component model treatment or a direct study of true binary mixtures), extremely rich-phase behavior, including a stable isostructural solid-solid transition, a metastable fluid-fluid transition and two types of glassy states, has been revealed in the highly asymmetric binary hard-sphere system [15]. However, less is known about the role played by the smaller component in nonequilibrium processes such as crystallization process. In particular, it remains unclear whether the small-sphere distribution is fully random and whether some properties of the small spheres display corresponding changes during the crystallization process. It should be noted that anomalous crystallization kinetics, such as a \( t^{1/3} \) (with \( t \) being the time) growth law of the crystallite size during both the conversion and coarsening stage and Furukawa’s dynamic scaling of the small angle light scattering data, was observed in crystallization of colloid-polymer mixtures, and the authors of [16] pointed out that a key aspect in explaining these anomalous phenomena is to account for

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the role of the polymer during the crystal formation of the colloids.

In principle, one can study these questions from the homogeneous crystallization of binary mixtures. However, because the nuclei are formed randomly throughout the system, it is impossible to control the orientation of the growing crystal and the shape of the forming crystallite is often irregular. This makes it difficult to characterize the properties of the small spheres during the crystal formation. To alleviate this, a patterned substrate can be introduced into the system as the seed of crystallization, then the direction of the growing crystal can be controlled by the substrate and the crystal grows almost layer-by-layer. Although this also introduces a degree of complexity compared to the homogeneous crystallization, we expect that the generic features for the small spheres can be generalized to the case of homogeneous crystallization. We find that adding a second much smaller component will not alter the crystal structure formed by the large spheres. However, instead of having fully random distributions, we observe that the small spheres diffusively redistribute during the crystal formation of the large spheres and that their density profile displays corresponding changes during the crystal formation of the large spheres and that their density profile displays corresponding changes at different crystallization stages and exhibits a strong coupling with that of the large spheres.

We use a (100) patterned substrate and the lattice spacing is $a = 1.576\sigma_l$. The patterned substrate is set in the $xy$ plane and located in the middle of $z$-direction of the simulation box and the spheres in the substrate are fixed. Periodic boundary conditions are applied in all three directions. To model binary mixtures with considerably large size disparities, the size ratio $q$ ranges from 0.1 to 0.2. The volume fraction of the small spheres $\phi_s = \pi N_s \sigma_s^3 / 6V$ ($N_s$ and $V$ denote the small-sphere number and the volume of the simulation box), covers the range from 0.001 to 0.009. The starting supercooled liquid with desired $\phi_s$ is obtained by compressing a low-density binary liquid to a large-sphere volume fraction $\phi_l = \pi N_l \sigma_l^3 / 6V = 0.535$ ($N_l$ stands for the large-sphere number) by using the Lubachevsky-Stillinger (LS) algorithm [17] with a compression rate of 0.02. The crystallization process is then simulated using a collision-driven molecular-dynamics simulation technique [18]. Since supersaturation depends on the composition of binary mixtures, usage of the same compression rate will result in different supercoolings of the initial liquids. This may affect the speed of crystallization and further discussion will be given later. The large and small spheres have the same mass $m$. The temperature $T$ is set to be 1. Length and time are given in units of $\sigma_t$ and $\sigma_t \sqrt{m/k_BT}$ with $k_B$ the Boltzmann constant. The number of large spheres is fixed at $N_l = N_{bulk} + N_{sub} = 1000$ with $N_{sub} = 100$, where $N_{sub}$ and $N_{bulk}$ are the sphere numbers in the substrate and in the bulk. The corresponding dimensions of the simulation box are $L_x = L_y = 7.88\sigma_l$ and $L_z = 15.76\sigma_l$. Although $N_l = 1000$ may seem too small a number to perform simulations of hard-sphere crystallization, we note that i) the maximum value of $N_s$ is 16822 due to the small size ratio; ii) our aim is to identify the possible changes for some properties of the small spheres during crystallization process, rather than to focus on the forming crystal by the large spheres; iii) the basic results remain unchanged with $N_l = 2000$ performed for several $\phi_s$ values; and iv) results on the large spheres are qualitatively consistent with the previous work [19], in which a much larger $N_l$ was used for the same patterned substrate. We use a spherical harmonic method [20,21] to identify the large spheres in a crystalline environment with the criterion of $d_c = 0.5$ and $N_c = 10$ (see refs. [19,21] for the definition of $d_c$ and $N_c$).

We first present the distribution of the local bond-orientation order parameter for the large spheres$^1$ at $q = 0.1$ and $\phi_s = 0.005$ in fig. 1. The local bond-orientation order parameter is defined as

$$Q_{b,local} = \left( \frac{4\pi}{15} \sum_{m=-6}^{6} |Y_{m \ell}^{(s)}|^2 \right)^{1/2}$$

where $Y_{m \ell}$ is the spherical harmonics with $\ell = 6$ in this case and $N_s^b$ the number of neighbors for the $j$-th sphere. Here, the neighbors are defined as those within a cutoff distance of $1.4\sigma_l$ from the target sphere. The values of $Q_{b,local}$ for perfect structures of face-centered cubic (fcc), hexagonal closed packed (hcp), and body-centered cubic (bcc) crystals are 0.575, 0.485, 0.511, respectively. It is clearly seen in fig. 1 that a peak at around 0.57, which indicates the formation of the fcc structure, emerges and its height increases as crystallization proceeds. No apparent peaks appear at other positions, thus the forming crystal structure under the influence of (100) patterned substrate is purely fcc, which is consistent with the result in the monodisperse system [19,22]. We note that the formation of the hcp crystal phase is fully suppressed due to the presence of the (100) patterned substrate. This indicates that the crystal structure formed by the large spheres is

$^1$See supplementary material Video-S1.mov for a full time evolution of the crystallization process for $q = 0.1$ and $\phi_s = 0.005$. 

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Fig. 2: (Color online) Sample-averaged mean squared displacements (MSD) of both species at varying $\phi_s$ with $q = 0.1$ (a) and varying $q$ with $\phi_s = 0.005$ (b). $N_s$ denotes the small-sphere number or the large-sphere number in the bulk. The red dashed lines with slopes 1 and 2 have been included to stress the fact that the small spheres undergo typical diffusion of simple liquids. The results are averaged over 50 independent runs. $t_0$ stands for the time when the compression process finishes. Insets: extracted slopes of MSD for both species.

not altered by adding very small spheres. On the other hand, the appearance of the peak can also roughly show the onset of crystallization. It should be noted that the method proposed by Klumov and coworkers [23] has been proven to be powerful on quantifying crystallization of the hard-sphere system, in particular on identifying the onset of crystallization.

We show the diffusion behavior of both species in fig. 2 by calculating the mean squared displacements (MSD). We observe that the ballistic motion ($\langle \Delta r^2/N_s \rangle \sim t^2$) at short times crosses over into the diffusive behavior ($\langle \Delta r^2/N_s \rangle \sim t$) at long times for the small spheres. For the large spheres, the diffusive region cannot be reached since crystallization occurs. When crystallization completes, a typical large sphere has diffused only about 1 large-sphere diameter. This is about 10 times smaller than that in the homogeneous crystallization [24], indicating the high efficiency of the substrate in directing crystal growth. To better characterize the diffusion behavior of both species at different $q$ and $\phi_s$, we also present the extracted long-time slopes of MSD in the insets. For the large spheres, the slopes are obtained by extracting long-time data before the cessation of diffusion. At fixed $q$, the slopes for both species decrease as $\phi_s$ increases (fig. 2(a)). Surprisingly, the slope for the large spheres increases as $q$ increases at fixed $\phi_s$ (fig. 2(b)), which indicates that the speed of crystallization is fast for large size disparity at fixed volume fraction of the small spheres. This is also confirmed by the growth speed of crystal fraction (data not shown). We speculate that this is because of a change in the driving force since the supersaturation of the initial supercooled binary liquids is different for various mixtures in our study. As the small spheres diffuse as typical simple liquids, one may think that the density profile of the small spheres during the crystallization process is fully random. However, we will show below that the distribution of the small spheres has a strong coupling with the density profile of the large spheres.

Fig. 3: (Color online) Sample-averaged density profiles of the large (upper panel) and small (lower panel) spheres for $q = 0.1$ and $\phi_s = 0.005$ at $t = 100$ (a) and $t = 1000$ (b). The yellow dashed lines indicate the substrate position. $H(t)$ denotes the thickness of the crystalline film (see text for its definition) and $z_s(t)$ the position relative to the substrate where the maximum local density for small spheres appears. The density profiles are averaged over 200 independent runs. Insets: representative corresponding snapshots. The spheres in the substrate are colored with yellow, crystalline with violet, and liquid with cyan. The smaller red spheres denote the small particles.
will distribute uniformly in the voids of the resulting crystal after crystallization completes ($t = 1000$). The corresponding snapshots in the insets of fig. 3 also confirm the above results.

The clearer support for connections between the small-sphere distribution and the large-sphere crystal formation is provided by calculating the maximum local density of the small spheres $\rho_{s}^{\text{max}} (t)$ and the thickness of the crystalline film $H(t)$ for the large spheres at time $t$. $\rho_{s}^{\text{max}} (t)$ is determined by searching for the maximum local density of the small spheres, which can be readily identified before the completion of crystallization, and the corresponding position relative to the substrate is denoted as $z_{s}(t)$. We determine $H(t)$ as the last peak position relative to the substrate in the large-sphere density profile, where the peaks are defined as local densities larger than $\rho_{l} + \rho_{l}$, where $\rho_{l}$ indicates the average density of the large spheres along the $z$-axis and $\rho_{l}$ is a threshold. We use $\rho_{l} = 1.0$ and the qualitative result is independent of the choice of $\rho_{l}$. The resulting $H(t)$ and $z_{s}(t)$ are shown in fig. 4(a).

As can be seen, they have similar behavior with $t$, i.e., the growth of the crystalline film is accompanied by a shift of $z_{s}(t)$ to larger distances relative to the substrate before crystallization completes. $H(t)$ saturates at $7.05 \sigma_{l}$ and $z_{s}(t)$ varies randomly when crystallization completes. Thus, the results unambiguously demonstrate a coupling between the distribution of the small spheres and the crystal growth of the large-spheres during the crystallization process. In fig. 4(b), we also show the maximum local density for the small spheres $\rho_{s}^{\text{max}}$ and its connection to the growth of the large-sphere crystal fraction during the crystallization process. We observe that $i)$ $\rho_{s}^{\text{max}}$ has large values in the initial supercooled liquid and the corresponding position is near the substrate (see fig. 4), which is due to the presence of the substrate during the compression; $ii)$ when entering into the stage of crystal growth ($t > 1$), $\rho_{s}^{\text{max}}$ at first drops from $\sim 12.2$ to $\sim 11.4$ and then remains nearly constant at $\sim 11.4$ for $t < 100$. The latter observation suggests that there is first an expulsion of the small spheres followed by a diffusion back-in during the crystallization of the large spheres. In other words, the small spheres diffusively redistribute during the crystallization process; $iii)$ on the approach to the completion of crystallization, $\rho_{s}^{\text{max}}$ dramatically increases to $\sim 12.0$ followed by a fast decrease, indicating the non-balance between the expulsion and diffusion back-in of the small spheres at this stage; $iv)$ after the completion of crystallization, the small spheres uniformly distribute in the voids of the crystal left by the large spheres, thus $\rho_{s}^{\text{max}}$ remains unchanged at about 10.5. The result again clearly shows that the distribution of the small spheres exhibits corresponding changes at different crystallization stages. And the observation for the small spheres may also help to better understand and distinguish the different crystallization stages.

In summary, by taking advantage of assisting crystal nucleation with a patterned substrate, we have demonstrated very directly a coupling between density profiles of both species in the highly size-asymmetric binary hard-sphere mixtures. Although we cannot show in what way the small spheres will affect the crystallization of the large spheres, our study makes a first step in understanding crystallization of highly asymmetric binary hard spheres. We hope that our findings will trigger further relevant study on crystallization of highly asymmetric binary hard spheres.

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REFERENCES

[1] ALDER B. J. and WAINWRIGHT T. E., J. Chem. Phys., 27 (1957) 1208.
[2] PUSEY P. N. and VAN MEGE W., Nature (London), 320 (1986) 340.
[3] VAN BLAADEREN A. and WILTZIUS P., Science, 270 (1995) 1177.
[4] ZHU J., LI M., ROGERS R., MEYER W., OTTEWILL R. H., STS-73 SPACE SHUTTLE CREW, RUSSEL W. B. and CHAIRIN P. M., Nature (London), 387 (1997) 883.
[5] AUER S. and FRENKEL D., Nature (London), 409 (2001) 1020; 413 (2001) 711.
[6] O’MALLEY B. and SNOOK I., Phys. Rev. Lett., 90 (2003) 085702.
[7] FILON L. and Dijkstra M., Phys. Rev. E, 79 (2009) 046714.

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[8] Velikov K. P., Christova C. G., Dullens R. P. A. and van Blaaderen A., Science, 296 (2002) 106.
[9] Hynninen A.-P., Thijssen J. H. J., Vermolen E. C. M., Dijkstra M. and van Blaaderen A., Nat. Mater., 6 (2007) 202.
[10] Schofield A. B., Phys. Rev. E, 64 (2001) 051403; Schofield A. B., Pusey P. N. and Radcliffe P., Phys. Rev. E, 72 (2005) 031407.
[11] Williams S. R., Royall C. P. and Bryant G., Phys. Rev. Lett., 100 (2008) 225502.
[12] Ferreira W. P., Farias G. A. and Peeters F. M., J. Phys.: Condens. Matter, 22 (2010) 285103.
[13] Ni R., Smallegenburg F., Filion L. and Dijkstra M., Mol. Phys., 109 (2011) 1213.
[14] Asakura S. and Oosawa F., J. Chem. Phys., 22 (1954) 1255; Vrij A., Pure Appl. Chem., 48 (1976) 471.
[15] Dijkstra M., van Roij R. and Evans R., Phys. Rev. E, 59 (1999) 5744; Phys. Rev. Lett., 81 (1998) 2268; 82 (1999) 117; Imhof A. and Dhont J. K. G., Phys. Rev. Lett., 75 (1995) 1662.
[16] Palberg T., Stipp A. and Bartsch E., Phys. Rev. Lett., 102 (2009) 038302.
[17] Lubachevsky B. D. and Stillinger F. H., J. Stat. Phys., 60 (1990) 561.
[18] Doney A., Torquato S. and Stillinger F. H., J. Comput. Phys., 202 (2005) 737.
[19] Xu W. S., Sun Z. Y. and An L. J., J. Chem. Phys., 132 (2010) 144506.
[20] Steinhardt P. J., Nelson D. R. and Ronchetti M., Phys. Rev. B, 28 (1983) 784.
[21] ten Wolde P. R., Ruiz-Montero M. J. and Frenkel D., J. Chem. Phys., 104 (1996) 9932.
[22] Cacciuto A. and Frenkel D., Phys. Rev. E, 72 (2002) 041604.
[23] Klumov B. A., Phys. Usp., 53 (2010) 1053; Klumov B. A., Khrapak S. A. and Morfill G. E., Phys. Rev. B, 83 (2011) 184105.
[24] Pusey P. N., Zaccarelli E., Valeriani C., Sanz E., Poon W. C. K. and Cates M. E., Philos. Trans. R. Soc. A, 367 (2009) 4993.