Shear-induced crystallisation in binary colloidal suspensions investigated using confocal microscopy

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Abstract

Hard sphere colloids crystallise at large volume fractions. However, crystallisation is suppressed in the presence of large polydispersities. We investigate the effect of polydispersity on shear-induced crystallisation using binary suspensions of hard spheres. Depending on the size ratio, the samples fully crystallise, partially crystallise or remain amorphous. Using confocal microscopy, the structural changes are characterised on a single particle level. This allows us to determine the local bond order parameter, the number of nearest neighbours, the Voronoi volume, the local volume fraction and other quantities. Upon the application of shear, only minor changes of these quantities are detected in regions that remain amorphous whereas noticeable changes are observed in regions where shear-induced crystallisation occurs. These changes mainly reduce the effects of the different particle sizes on the particle arrangement. This allows substitutionally disordered crystals to form. However, with increasing size disparity the volume fraction in substitutionally disordered crystals decreases while the volume fraction in amorphous regions slightly increases. Beyond a size ratio of 1.18, the volume fraction of the crystals is smaller than the volume fraction of the amorphous regions. At the same size ratio shear-induced crystallisation ceases. The terminal size ratio of 1.18 is close to the value given by the empirical Hume-Rothery rule for metallic alloys and the corresponding polydispersity (about 0.1) is consistent with the polydispersity beyond which crystallisation is found to be suppressed.

1. Introduction

Crystallisation is probably the most prominent phase transition. It occurs in various systems, ranging from atomic and molecular systems to colloids and granular matter. A suspension of colloidal hard spheres is a widely applied model system that has very simple interactions and can easily be studied [1–3]. For this system, the only relevant parameter is the volume fraction \( \phi \). Upon increasing the volume fraction, fluid (\( \phi < 0.494 \)), partially crystalline (\( 0.494 < \phi < 0.545 \)) and fully crystalline (\( \phi > 0.545 \)) samples are observed. However, at volume fractions beyond \( \phi \approx 0.58 \), the particle dynamics is arrested, crystallisation ceases and a glass is formed, although this is not the thermodynamically most stable state [3].

In addition to the scientific interest, crystallisation is of considerable relevance for technological and industrial applications. For example, the mechanical properties of crystalline and amorphous materials differ significantly [4]. In many industrial systems, the particles have a finite size distribution; they are polydisperse. The effects of polydispersity on crystallisation have been investigated by experiments [1–3], computer simulations [5–9] and different theoretical approaches, such as density functional theory or geometrical models [9–16]. These studies have revealed that substitutionally disordered crystals form up to a terminal polydispersity, typically values between 5 % and 12 % are cited. Beyond the terminal polydispersity, crystallisation nevertheless occurs if size fractionation is possible. This involves particle movements over distances comparable to crystallite sizes. Fractionation leads to sub-populations that have at most the terminal polydispersity and different mean sizes. The sub-populations form crystallites with different lattice
sizes which coexist with a fluid of arbitrary polydispersity [8–11]. Moreover, sufficiently different particles can form crystals in which the smaller particles occupy the interstices of the larger particles [7, 17–19]. The formation of these substitutionally ordered crystals needs considerable rearrangements. Crystallisation in systems with large polydispersities thus requires rearrangements beyond the nearest neighbours to exchange particles with different sizes. This needs sufficiently fast dynamics and hence occurs only below the glass transition. In contrast, in systems with small polydispersities, crystallisation only requires minor rearrangements. Therefore, the spatial distribution of particle sizes, and hence the realised crystal or fluid arrangement, is determined by an interplay between equilibrium thermodynamics and non-equilibrium effects, such as the presence of the glass transition, unusually large nucleation barriers or slow growth kinetics [3, 5, 11, 12, 20–25]. Furthermore, the shape of the size distribution, for example symmetrical, positively or negatively skewed or multimodal, is crucial. It affects fractionation, crystal nucleation and growth as well as their relation to the particle dynamics. Hence it is also relevant for the size and shape of the formed crystals as well as the presence, number and kinds of defects. For example, a skew of the size distribution to smaller particles results in slower crystallisation and is more detrimental to the crystal structure than a skew to larger particles [24, 25].

The equilibrium phase behavior of polydisperse colloids has been mapped to equivalent binary mixtures [15, 26]. They represent a simple multi-component system. Nevertheless, compared to a one-component system, two additional parameters are introduced to characterise the system; the size ratio \( \alpha = R_l/R_s \) and the relative volume fraction of large particles \( X = \phi_l/\phi \) where \( R_l \) and \( R_s \) are the radii of the large and small particles and \( \phi_l \) is the volume fraction of large particles. In these systems, substitutionally disordered crystals are formed for moderate size ratios [13, 25, 27–31]. Most theoretical approaches predict that they form up to \( \alpha \approx 1.16 \). An empirical rule for metallic alloys, the first Hume-Rothery rule, predicts the existence of crystals up to \( \alpha = 1.14 \) [32].

Crystallisation can be induced by shear. Using experiments and simulations the effect of steady shear [33–36] and oscillatory shear [24, 36–39] has been studied. In oscillatory shear experiments, strain amplitudes of up to about 100% have been found to induce crystallisation [36, 38]. The strain amplitude determines the orientation of the crystal [38–42]. The close packed direction tends to be oriented perpendicular to the shear direction at small strain amplitudes \( \gamma_0 < 0.5 \) but parallel to the shear direction at large strain amplitudes \( \gamma_0 > 0.5 \).

Here, we use binary colloidal hard spheres with radii of about a micron. Due to their size, they can be observed by confocal microscopy [43, 44]. Based on the confocal microscopy images, the particle locations are obtained and subsequently different structural parameters are calculated. Furthermore, each particle’s size and association with a crystalline or amorphous state are determined. Hence the properties of each individual particle can be linked to its local environment. The local environment of the small and large particles are found to become more similar during shear-induced crystallisation. This allows substitutionally disordered crystals to form. Upon increasing the size ratio \( \alpha \), the volume fraction in the crystals decreases and at \( \alpha = 1.18 \) drops below the volume fraction of the amorphous regions. This coincides with the cessation of crystallisation. This suggests that, beyond a maximum size ratio, crystallisation is suppressed by the low volume fraction of the crystals and the high volume fraction of the amorphous regions. This maximum size ratio compares well with predictions for the existence of substitutionally disordered crystals in binary [13, 29–31] and polydisperse samples [5–16] as well as the empirical Hume-Rothery rule for metallic alloys [32].

2. Materials and methods

2.1. Samples

The samples contain locked poly(methyl methacrylate) (PMMA) spheres that are stabilised with poly(12-hydroxy-stearic acid) (PHSA) [45] and are fluorescently labelled with rhodamine B monomerized with methyl methacrylate. After the particle synthesis, the solvent is exchanged for cis-decahydronaphthalene (decalin). Then the samples are centrifuged and the supernatant is removed. The sediment is assumed to be the mixture that almost matches the one of the particles. PMMA particles acquire a charge in CHB7 [47], especially if they are locked [49]. In addition, rhodamine is known to slightly charge the particles [50]. In order to screen the charges, 4 mM tetrabutylammonium chloride (TBAC) is added [47]. This results in hard-sphere-like behaviour [51]. The two-component samples are centrifuged. It again is assumed that this results in random close packing with \( \phi_{RCP} = 0.65 \) [46, 52–57]. Subsequently the samples are diluted to
yield a total volume fraction $\phi = 0.58$ or, for very few samples, $\phi = 0.61$. The uncertainty in the volume fractions is expected to be $\Delta \phi \approx 0.02$ whereas the ratio of the two volume fractions is very accurate [58]. For most experiments, the volume fractions of large ($\phi_l$) and small ($\phi_s$) particles are identical and hence the relative volume fraction of large particles $X = \phi_l / \phi = 0.5$. In addition a few experiments are performed with $X = 0.2$ and 0.8.

Using static light scattering (SLS), the sizes of the particles in decalin are determined (table 1) as well as their polydispersities [59]. The individual polydispersities of the one-component systems have been determined to be about $\sigma_l \approx 0.065$. The particle sizes determined by SLS are used to calculate the size ratios $\alpha = R_l / R_s$ of the mixtures (table 1). The values of these size ratios are confirmed by confocal differential dynamic microscopy measurements in the decalin-CHB7 mixture (typical deviations below 3 %) [60] and scanning electron microscopy measurements in the dried state (typical deviations below 2 %). In the following, the size ratios $\alpha$ determined by SLS are used to refer to the different samples (and not the size ratios $\alpha_c$ determined by classical confocal microscopy [61], see section 2.4).

### 2.2. Application of shear

The samples are sheared and imaged in a home-build shear cell that is an improved version of previously described shear cells [62–64]. The shear cell consists of two parallel glass coverslips with a separation of about 130 $\mu$m. To prevent wall slip, the surfaces of the coverslips are scratched resulting in a rough surface with a depth similar to the particle diameter. In addition, to reduce solvent evaporation the gap between the coverslips is sealed using silicon grease making sure that the silicon grease is not in contact with the sample. Nevertheless, after about three hours first effects of evaporation are noticeable. A piezoelectric actuator moves the bottom plate. The bottom plate is connected to the top plate through a pivoted lever thus driving the top plate in the opposite direction. This increases the available maximum strain amplitude.

Shear is applied in several steps. After loading, the sample is left undisturbed for 10 min (step 1). Then shear is applied in a dynamic strain sweep (DSS) with a frequency of 0.7 Hz. The strain amplitude $\gamma_0$ is increased from 0.10 to 0.84 where 20 oscillations are performed at each of the 25 strain amplitude values, which takes a total of about 12 min (step 2). In the next step, the highest strain amplitude $\gamma_0 \approx 0.84$ is maintained but a lower frequency of 0.2 Hz is applied for 200 oscillations (step 3). Subsequently, an inverse DSS with a frequency of 0.7 Hz is performed. The strain amplitude $\gamma_0$ is decreased from 0.84 to 0.10 where, again, 20 oscillations are performed at each of the 25 strain amplitude values (step 4). After each step, no shear is applied for about 3 min to image the sample. The whole experiment takes about 1 h.

### 2.3. Confocal microscopy

The samples are imaged using a Nikon A1R-MP confocal scanning unit mounted on a Nikon Ti-U inverted microscope with a Nikon Plan Apo 100 $\times$ oil immersion objective (numerical aperture 1.4) and a solid state laser with a wavelength of 561 nm. For each sample, ten image stacks are taken. They cover a region between the bottom coverslip and 30 $\mu$m into the sample. The stacks consist of 243 slices (sample with $\alpha = 1.10$ containing the two largest particles) or 363 slices (all other samples) resulting in steps of about 0.124 $\mu$m and 0.083 $\mu$m with the recording taking about 100 s and 132 s respectively. Each slice has 512 $\times$ 512 pixels corresponding to a sample area of $64 \times 64 \mu m^2$ (sample with $\alpha = 1.10$) or, with an additional magnification, $42 \times 42 \mu m^2$ (all other samples). From the image stacks, the particle positions are extracted using an algorithm that also allows for the determination of the size of each particle [61].

### 2.4. Data analysis

Based on the particle sizes determined by confocal microscopy, the size distributions can be obtained. Fitting a sum of two Gaussian distributions to the size distributions, the two mean particle sizes and polydispersities can be determined. Whereas the obtained particle sizes deviate from the ones determined by SLS by up to 30 %, the deviations from the size ratios determined by SLS are small for the small size ratios and increase for

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**Table 1.** Composition of the binary samples. Radii of the large ($R_l$) and small ($R_s$) particles as determined by static light scattering (SLS) and resulting size ratio $\alpha = R_l / R_s$ as well as size ratio determined by confocal microscopy $\alpha_c$. All samples have a total volume fraction $\phi = 0.58$ and a relative volume fraction of large particles $X = \phi_l / \phi = 0.5$, if not explicitly mentioned otherwise. Polydispersity $\sigma$ calculated based on the polydispersity of the one-component systems ($\sigma_l = 0.065$), the size ratio $\alpha$ and the relative volume fraction of large particles $X = 0.5$ (Equations (1), (2)). Polydispersity $\sigma_c$ based on the size distribution determined by confocal microscopy.

| $R_l/$nm | 830 | 1227 | 903 | 1115 | 1115 | 1227 | 1115 | 1227 | 1227 |
|----------|-----|-----|-----|------|------|------|------|------|------|
| $R_s/$nm | 767 | 1115 | 767 | 1227 | 830 | 903 | 767 | 830 | 767 |
| $\alpha$ | 1.08 | 1.10 | 1.18 | 1.23 | 1.34 | 1.36 | 1.45 | 1.48 | 1.40 |
| $\alpha_c$ | 1.10 | 1.09 | 1.19 | 1.36 | 1.46 | 1.50 | 1.62 | 1.56 | 1.82 |
| $\sigma$ | 0.08 | 0.08 | 0.11 | 0.12 | 0.16 | 0.16 | 0.19 | 0.20 | 0.22 |
| $\sigma_c$ | 0.06 | 0.06 | 0.09 | 0.15 | 0.18 | 0.19 | 0.23 | 0.21 | 0.28 |
the larger size ratios to about 12% (table 1). To account for the discrepancy in the particle sizes and exploit the agreement in the relative sizes, the size distributions are normalised by the radii of the small particles. For consistency, the radii as determined by confocal microscopy are used for the normalisation. The fits in addition indicate an average polydispersity of the individual components \( \sigma_1 \approx 0.06 \), which agrees with the value determined by SLS. Furthermore, based on the size distributions determined using confocal microscopy, the polydispersities \( \sigma_c \) of the binary samples are determined (table 1). The values of \( \sigma_c \) can be compared to the polydispersities \( \sigma \) calculated based on the polydispersities of the one-component systems, \( \sigma_1 = 0.065 \) and the size ratio \( \alpha \) (determined by SLS, section 2.1):

\[
\sigma^2 = \frac{1 + (\alpha^2 - 1)\xi}{(1 + (\alpha - 1)\xi)^2} (1 + \sigma_1^2) - 1
\]

where \( \xi \) is the relative number fraction of large particles

\[
\xi = \left\{ 1 + (X^{-1} - 1)\alpha^3 \right\}^{-1} .
\]

The values of \( \sigma \) and \( \sigma_c \) are found to be similar (table 1).

Based on the particle positions, a radial Voronoi tessellation is performed using voro++ [65]. The Voronoi volume of a particle consists of all points in space that are closer to the centre of this particle than to any other particle centre. The radial Voronoi tessellation in contrast considers the distances to the particle volumes or, equivalently, to the particle surfaces instead of the distances to the particle centres. The radial Voronoi tessellation is more appropriate for multicomponent or polydisperse samples. The radical Voronoi volume \( V_V \) is normalised by the volume of the small particles \( V_s = (4\pi/3)R_1^3 \). For the normalisation, the values of \( R_s \) determined by SLS are used because SLS yields more accurate values than confocal microscopy. The particle arrangements are rendered using Ovito [66].

The arrangement of the particles is characterised by two order parameters. First, the average local bond order parameter \( \bar{q}_b(i) \). It is the average of the \( q_b(i) \) values of all considered particles \( i \). The parameter \( \bar{q}_b(i) \) is given by the following sequence of definitions [67, 68]

\[
\bar{q}_b(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}(i)|^2} \]

\[
q_{lm}(i) = \frac{1}{N_b(i)} \sum_{k=0}^{N_b(i)} q_{lm}(k)
\]

\[
q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(r_{ij})
\]

where \( Y_{lm}(r_{ij}) \) are the spherical harmonics with \( r_{ij} \) the vector from the centre of particle \( i \) to the centre of particle \( j \). The sum over \( j \) includes all \( N_b(i) \) nearest neighbours of particle \( i \) whereas the sum over \( k \) includes all nearest neighbours of particle \( i \) as well as particle \( i \) itself \( (k = 0) \). All particles closer than the first minimum in the pair distance distribution function are considered nearest neighbours and are included in the averages. Other nearest neighbour criteria do not significantly change the results. To avoid wall effects, averages only include particles located between 10 \( \mu \)m and 30 \( \mu \)m from the coverslip. A threshold \( \bar{q}_b(i) = 0.33 \) is typically used to distinguish particles participating in a fluid \( \bar{q}_b(i) < 0.33 \) or in a crystal \( \bar{q}_b(i) > 0.33 \).

Information on the crystal structure is obtained through another bond order parameter given by [67, 68]

\[
\bar{\vartheta}(i) = \left( \sum_{m=-l}^{l} |q_{lm}(i)|^2 \right)^{-3/2} \sum_{m_1+m_2+m_3=0}^{l} \left[ \frac{1}{m_1} \frac{1}{m_2} \frac{1}{m_3} \right] \bar{q}_{m_1}(i)\bar{q}_{m_2}(i)\bar{q}_{m_3}(i)
\]

where the term in square brackets is the Wigner 3j symbol and the integers \( m_1, m_2, \) and \( m_3 \) run from \(-l\) to \(+l\) but must obey \( m_1 + m_2 + m_3 = 0 \). We use the bond order parameter \( \bar{\vartheta}(i) \) to determine the stacking order in crystalline regions. The calculations are performed using specifically developed IDL routines.
3. Results and discussion

We investigate two-component samples with different size ratios $\alpha$ and, in most samples, a total volume fraction $\phi = 0.58$ and an equal volume fraction of small and large particles that is a relative volume fraction of large particles $X = 0.5$ (table 1). In these samples, shear-induced crystallisation is studied. Shear is applied in several steps (figure 1, inset to (B)). After loading, the sample is left undisturbed for 10 min (step 1), then it is exposed to a dynamic strain sweep with increasing strain amplitude (step 2), subsequently oscillatory shear at the highest strain amplitude is applied (step 3) and finally a dynamic strain sweep with decreasing strain amplitude is performed (step 4, details are given in section 2.2).

3.1. Quiescent state

First the behaviour in the quiescent state is briefly described. After three weeks of rest, the sample with a small size ratio $\alpha = 1.08$ is fully crystalline, the sample with $\alpha = 1.10$ is only partially crystalline and the sample with $\alpha = 1.18$ does not show crystalline regions in the bulk. Thus crystallisation is observed in samples with polydispersities $\sigma < 0.1$ (table 1). This is consistent with theoretical considerations [5–16, 29–32].

3.2. Local bond order parameter: average $\langle \bar{q}_6(i) \rangle$ and distribution $p(\bar{q}_6)$

To quantify the effects of oscillatory shear on the crystallisation behaviour, the average local bond order parameter $\langle \bar{q}_6(i) \rangle$ (Equations (3)–(5)) is determined. Typically, a value $\langle \bar{q}_6(i) \rangle > 0.33$ is taken to indicate an ordered, crystalline sample and $\langle \bar{q}_6(i) \rangle < 0.33$ to indicate a disordered, amorphous sample.

Before the application of shear (step 1), the sample with size ratio $\alpha = 1.08$ shows the largest value $\langle \bar{q}_6(i) \rangle \approx 0.19$ (figure 1(B)). The observed $\langle \bar{q}_6(i) \rangle$ tend to decrease with increasing $\alpha$. For all samples hence $\langle \bar{q}_6(i) \rangle$ is far below the threshold value of 0.33 indicating that the samples are amorphous. The distribution $p(\bar{q}_6)$ in addition shows that there is no significant contribution beyond $\bar{q}_6 = 0.33$ in any sample (figure 1(A)) and hence initially all samples are amorphous without crystalline regions.

Upon the application of the shear protocol (steps 1–4), $\langle \bar{q}_6(i) \rangle$ significantly increases for the samples with small size ratios $\alpha \leq 1.18$ (figure 1(B)). For the sample with the lowest size ratio, $\alpha = 1.08$, large values $\langle \bar{q}_6(i) \rangle \approx 0.5$, well beyond the threshold of 0.33, are observed suggesting that this sample underwent shear-induced crystallisation. This is supported by the distribution $p(\bar{q}_6)$ after step 4 which indicates that $\bar{q}_6 > 0.33$ for essentially all particles (figure 1(C)) and hence that the sample is fully crystalline with only a few defects. The values of $\langle \bar{q}_6(i) \rangle$ are also beyond 0.33 for the samples with $\alpha = 1.10$ and 1.18. However, their distributions $p(\bar{q}_6)$ imply partial crystallisation since a considerable fraction of particles exist with $\bar{q}_6 < 0.33$. The distribution is particularly broad for the sample with $\alpha = 1.18$. For samples with $\alpha \geq 1.23$, upon application of shear no significant changes are observed, neither in $\langle \bar{q}_6(i) \rangle$ nor in the distribution $p(\bar{q}_6)$. This indicates that these samples remain amorphous. It would be interesting to follow the long time evolution of the sheared samples when left undisturbed. However, this is not possible because evaporation cannot completely be avoided in the shear cell.

Crystallisation is expected to depend on the volume fraction $\phi$ and the composition of the sample. The effects of these parameters are studied with samples whose $\langle \bar{q}_6(i) \rangle$ is close to the threshold value 0.33. For these samples, the most pronounced effects are expected. The samples with $\alpha = 1.10$ and $\alpha = 1.18$ (both with $X = 0.5$) show partial crystallisation after the application of shear at a volume fraction $\phi = 0.58$ (figure 1) but

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**Figure 1.** (B) Average local bond order parameter $\langle \bar{q}_6(i) \rangle$ (Equations (3)–(5)) before the application of shear (step 1), after a dynamic strain sweep (step 2), subsequent oscillatory shear (step 3) and additionally an inverse dynamic strain sweep (step 4, indicated by the schematic drawing) as well as the distribution of the local bond order parameter $\bar{q}_6(i)$ (A) before (step 1) and (C) after the application of shear (step 1). The samples contain two components with size ratio $\alpha$ as indicated, total volume fraction $\phi = 0.58$ and relative volume fraction of large particles $X = 0.5$. 

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remain amorphous if the volume fraction is increased to $\phi = 0.61$. The sample with $\alpha = 1.23$ (and again $X = 0.5$) stays amorphous at both volume fractions, $\phi = 0.58$ and 0.61. Thus, an increase in total volume fraction $\phi$ favours the amorphous state. This is attributed to the significant slowing down of the particle dynamics and the crystallisation [5, 12, 25, 69–75].

The composition of the sample is quantified by the relative volume fraction of large particles, $X$. In addition to the samples with $X = 0.5$ (figure 1), samples with $X = 0.2$ and 0.8 are investigated. After the application of shear (steps 1–4), all samples with small size ratios $\alpha \leq 1.18$ show $\langle \bar{q}_6(i) \rangle > 0.33$, whereas all samples with large size ratios $\alpha \geq 1.23$ show $\langle \bar{q}_6(i) \rangle < 0.33$ (figure 2). The general behaviour therefore appears independent of the composition within the investigated range. Nevertheless, asymmetric compositions lead to larger $\langle \bar{q}_6(i) \rangle$ values. This implies that crystallisation is more efficiently suppressed in symmetric mixtures, in agreement with simulations [23], theoretical results [76, 77] and experimental findings in other systems. For example, a metallic alloy with equal amounts of copper and silver is amorphous but shows crystals with a fcc structure for asymmetric compositions [78]. Furthermore, the values of $\langle \bar{q}_6(i) \rangle$ at $X = 0.2$ and 0.8 are similar although the number of large particles at $X = 0.2$ is much smaller than the number of small particles at $X = 0.8$ since $X$ represents the relative volume fraction. Large particles thus appear to be more efficient in disrupting crystallisation, as reported previously [13, 25, 79].

### 3.3. Confocal microscopy images

The effects of shear are further investigated based on confocal microscopy images. In the following, we consider samples with a total volume fraction $\phi = 0.58$ and equal volume fractions of large and small particles, i.e. $X = 0.5$.

The sample with $\alpha = 1.08$ is amorphous before shear, but crystalline after the application of shear. The confocal images reveal the formation of extended crystalline regions which are only interrupted by a few defects (figure 3(A)). Shear aids the healing of the defects. This is consistent with the observed $p(\bar{q}_6)$ and $\langle \bar{q}_6(i) \rangle$ (figure 1). The stacking order can be determined based on the bond order parameter $\bar{p}_4(i)$ (equation (6)). Hexagonal close-packed (hcp) order with stack sequence ABABAB is characterised by $\bar{p}_4 > 0$ and face-centred cubic (fcc) order with stack sequence ABCABC by $\bar{p}_4 < 0$. The analysis based on $\bar{p}_4(i)$ indicates that the sample contains a random mixture of hcp and fcc arrangements but no significant amounts of body-centred cubic (bcc), simple cubic (sc) or icosahedral (ico) orderings. This crystalline order is in agreement with previous work [38]. The orientation of the crystal was previously found to depend on the strain amplitude [38–42]. At large strain amplitudes $\gamma_0 > 0.5$, the close packed direction was reported to orient parallel to the shear direction whereas it tends to be perpendicular to the shear direction at small strain amplitudes $\gamma_0 < 0.5$. In the crystalline samples investigated here, however, no systematic orientation is observed. This could be due to the applied shear protocol that contains a range of strain amplitudes $0.10 \leq \gamma_0 \leq 0.84$ covering small as well as large strain amplitudes.

If the size ratio is increased to $\alpha = 1.18$ (figure 3(B)), shear results in a partially crystalline sample. The crystalline domains are randomly-distributed and separated by amorphous regions. Again, no particular orientation of the crystallites is observed.

The samples with even larger size ratios, $\alpha = 1.23$ and 1.45 (figures 3(C) and (D)), do not show any crystallisation but only an amorphous arrangement of the particles before and after the application of shear.
Figure 3. Reconstructed images based on confocal microscopy images of samples with size ratios $\alpha = 1.08$ (A), 1.18 (B), 1.23 (C) and 1.45 (D) before (step 1, left) and after the application of shear (steps 2–4, left to right). The total volume fraction is $\phi = 0.58$ and the relative volume fraction of large particles is $X = 0.5$. Circle sizes represent the particle sizes and circle colours represent the local bond order parameter $\bar{q}_6$ of the particles. Blue indicates $\bar{q}_6(i) < 0.33$ and hence a particle participating in an amorphous arrangement whereas red indicates $\bar{q}_6 > 0.33$ and hence a particle participating in a crystalline arrangement. The shear direction is indicated.

These microscopic observations of the ordering are in agreement with the values of $\langle \bar{q}_6(i) \rangle$ and the distributions $p(\bar{q}_6)$ described above (figure 1). The confocal microscopy images in addition reveal the spatial distribution of crystalline and amorphous particles in the partially and fully crystalline samples. The amorphous particles represent defects in the fully crystalline sample but participate in extended, randomly-distributed regions in the partially crystalline samples.

With confocal microscopy also the spatial distribution of small and large particles is accessible [61]. In all samples before, during and after shear, the small and large particles are randomly distributed (figure 4). In particular, neither segregation nor fractionation of the small or large particles is observed.

3.4. Number of nearest neighbours

To characterise the crystallisation behaviour in more detail, the local topology around each particle is investigated. It is characterised by the number of nearest neighbours ($N_n$). In two-component systems it is difficult to unambiguously define nearest neighbours by a cut-off criterion. Thus, the criterion is based on the radical Voronoi tessellation. Two particles are defined nearest neighbours if their Voronoi cells share a face. Then the number of faces of the Voronoi cell is identical to the number of nearest neighbours. This criterion does not take into account the size of a face. Very small faces might correspond to spurious nearest neighbours that result in a larger number of nearest neighbours than other criteria. However, for small $\alpha$ we checked that the Voronoi criterion yields qualitatively similar results as a cut-off criterion based on the first main minimum of the pair distance distribution function.

The distribution of the number of nearest neighbours, $p(N_n)$, is determined for all particles and separately for the small and the large particles as well as crystalline ($\bar{q}_6(i) > 0.45$) and amorphous ($\bar{q}_6(i) < 0.25$) particles where only particles with $\bar{q}_6(i)$ values well within the crystalline and amorphous ranges are considered to avoid ambiguities.

First the distributions obtained before the application of shear are considered. They represent the intrinsic distributions without external interference. These distributions are found to reflect the binary nature of the samples (figure 5, dashed lines). The distributions for all particles are asymmetric, which is especially pronounced for large $\alpha$. This is due to the significantly larger number fraction of small particles (equation (2)) for an equal volume fraction of small and large particles ($X = 0.5$). Since the relative number
Figure 4. Reconstructed images based on confocal microscopy images of samples with size ratios $\alpha = 1.08$ (A), 1.18 (B), 1.23 (C) and 1.45 (D) before (step 1, left) and after the application of shear (step 4, right). The total volume fraction is $\phi = 0.58$ and the relative volume fraction of large particles is $X = 0.5$. Circle sizes and colours represent the particle sizes: green indicates small and purple large particles. The shear direction is indicated.

fraction depends on the size mismatch, the effect becomes more pronounced for large size ratios $\alpha$. As the size ratio $\alpha$ increases, the distributions for the small and large particles successively move apart as expected. For the small particles, the most likely number of neighbours $N_{\text{n},s}$ and the average number of neighbours $\langle N_{\text{n}} \rangle_s$ decrease with increasing size ratio $\alpha$. Simultaneously, for the large particles the most likely number of neighbours $N_{\text{n},l}$ and the average number of neighbours $\langle N_{\text{n}} \rangle_l$ increase (table A1 in appendix). Thus, their ratio increases. A simple geometrical model predicts $N_{\text{n},l}/N_{\text{n},s} = \alpha$ (appendix). This is in reasonable agreement with the data. Furthermore, in an experimental study of a one-component colloidal glass [80] and in theoretical studies of binary amorphous packings [55, 56, 81, 82] similar values and distributions have been obtained.

The application of shear does not significantly change the distributions $p(N_{\text{n}})$ for size ratios $\alpha \geq 1.23$ (figures 5(C) and (D); solid lines). This is consistent with the distribution, $p(\bar{q}_6)$, and the average, $\langle \bar{q}_6 \rangle_i$, of the local bond order parameter (figure 1) as well as the appearance of the confocal microscopy images (figures 3 and 4). They also remain essentially unchanged upon the application of shear. The distribution $p(N_{\text{n}})$ for all particles is very broad for $\alpha = 1.23$ and bimodal for $\alpha = 1.45$. Accordingly, the distributions $p(N_{\text{n}})$ for small and large particles are almost separated for $\alpha = 1.23$ and well separated for $\alpha = 1.45$. This suggests that the local topologies of the small and large particles are significantly different in the amorphous samples.

In contrast, shear changes the distributions $p(N_{\text{n}})$ for small size ratios $\alpha \leq 1.18$ (figures 5(A) and (B)). The distributions for all particles are unimodal and become narrower when shear is applied. Correspondingly, the distributions for small and large particles move slightly towards each other. For the fully crystalline sample with size ratio $\alpha = 1.08$, $p(N_{\text{n}})$ shows the highest probability for $N_{\text{n}} = 14$ nearest neighbours for all, the small and the large particles, whereas the average number of neighbours $\langle N_{\text{n}} \rangle$ is slightly different for the small and large particles. As discussed above, the actual values depend on the definition of nearest neighbours. For example, if the cut-off distance is based on the first main minimum of the pair distance distribution function instead of the Voronoi tesselation, the number of nearest neighbours is centred around about 12.
Figure 5. Distribution of the number of nearest neighbours $p(N_n)$, which is taken to be the number of faces of the Voronoi cell, before (step 1, dashed lines) and after (step 4, solid lines) the application of shear. The particles have size ratios $\alpha = 1.08$ (A), 1.18 (B), 1.23 (C) and 1.45 (D). The distributions are shown for all (black), the small (green) and the large (purple) particles and, for the sample with $\alpha = 1.18$, the distributions for the crystalline ($\bar{q}_6(i) > 0.45$, red) and the amorphous ($\bar{q}_6(i) < 0.25$, blue) particles. In the other samples, the fractions of amorphous ($\alpha = 1.08$) or crystalline ($\alpha = 1.23, 1.45$) particles are too small to render individual distributions meaningful. For clarity the distributions of the small and large particles are normalised such that the sums of their integrals, not their individual integrals, are unity. Similarly, the distributions of the crystalline and amorphous particles are normalised such that the sum of their integrals are unity although part of the particles, those with $0.25 \leq \bar{q}_6(i) \leq 0.45$, are not considered. The total volume fraction is $\phi = 0.58$ and the relative volume fraction of large particles is $X = 0.5$.

Upon increasing the size ratio $\alpha$ to 1.18, the distributions for the small and large particles are slightly further apart. Since the sample is partially crystalline, the crystalline and amorphous regions can be investigated separately. The distribution $p(N_n)$ for crystalline particles is narrower than the distribution for amorphous particles, as expected for ordered and disordered arrangements respectively. The distribution $p(N_n)$ for amorphous particles is essentially identical to the distribution of all particles before application of shear when the whole sample was amorphous. Thus, the distribution of nearest neighbours is unchanged in the amorphous regions. This is identical to the case of the samples with $\alpha \geq 1.23$ which remain amorphous throughout. For the other partially-crystalline sample ($\alpha = 1.10$) similar distributions are obtained (data not shown).

Independent of the size ratio $\alpha$, the distributions for crystalline particles are found to be very similar. This indicates that all crystalline regions have a similar topology. In addition, the convergence of the distributions of the small and large particles indicates that the local topologies of the small and large particles are more similar in crystalline regions. This is consistent with substitutionally disordered crystals in which particles are incorporated into the crystal lattice irrespective of their size. The existence of substitutional crystals for size ratios $\alpha \leq 1.18$ is in agreement with previous findings based on simulations and density functional theory [13, 27–31]. Since confocal microscopy suggests that fractionation does not occur (figure 4), crystallisation seems to rely on the accidental spatial distribution of particle sizes and short-range rearrangements. This is supported by the moderate changes in the distributions of the nearest neighbours, $p(N_n)$. Moreover, it is consistent with a simulation study on a sample with $\alpha = 1.1$ that found crystallites to form in places with a favorable composition [23].

3.5. Voronoi volume and particle size distributions

Having investigated the number of faces of the Voronoi cells, now the volume of the Voronoi cells is considered. The distribution of Voronoi volumes $p(V_V)$ for all, crystalline ($\bar{q}_6 > 0.45$) and amorphous
Distribution of radical Voronoi volumes $p(V_V)$, distribution of particle sizes $p(R)$ and radical Voronoi volume $V_V$ as a function of particle volume $V_p \sim R^3$ where each particle is represented by a point. Colours indicate all (black), crystalline ($\bar{q}_6(i) > 0.45$, red) and amorphous ($\bar{q}_6(i) < 0.25$, blue) particles. Dashed lines represent data obtained in the initial state (step 1), solid lines and points in (I–L) indicate data obtained after the application of shear (step 4). The line in (I–L) has slope $1/\phi$. The Voronoi volume $V_V$ is normalised by the volume of the small particles, $V_s = (4\pi/3)R_s^3$ (with $R_s$ as determined by SLS), the radius $R$ is normalised by the radius of the small particle $R_s$ (as determined by confocal microscopy in the specific measurement, i.e. step 1 and step 4 are normalised individually). The particles have size ratios (A,E,I) $\alpha = 1.08$, (B,F,J) 1.10, (C,G,K) 1.18 and (D,H,L) 1.23, total volume fraction $\phi = 0.58$ and relative volume fraction of large particles $X = 0.5$.

The particle size distributions $p(R)$ of all, crystalline and amorphous particles are also determined. The size distributions $p(R)$ exhibit two peaks which are not fully separated for small $\alpha$, i.e. the crystalline and partially crystalline samples, but are clearly separated for large $\alpha$, i.e. the amorphous sample (figures 6(E)–(H)). The distributions for the amorphous particles tend to broaden and, correspondingly, the very large and very small particles are underrepresented in the distributions for the crystalline particles. Hence there is a preference for similar Voronoi volumes which reduces the polydispersity of the Voronoi volumes in the crystalline regions. This is consistent with the formation of substitutionally disordered crystals. Furthermore, it reflects the difficulty to incorporate the largest particles in crystals (figure 2) and the preference for crystallisation in regions depleted of very small particles.

The similarity between the two distributions $p(V_V)$ and $p(R)$ suggests that the small and large particles are associated with the small and large Voronoi volumes respectively. To verify this hypothesis, the particle volume $V_p = (4\pi/3)R^3$ and Voronoi volume $V_V$ of each particle are represented in the $V_V - V_p$ plane where both volumes are normalised by the corresponding volumes of the small particles (figures 6(I)–(L)). The small particles are indeed found to occupy small Voronoi volumes and the large particles large Voronoi volumes. The mean local volume fraction $\langle \Phi \rangle = \langle V_p/V_V \rangle = \phi$ is indicated by a line with slope $1/\phi$ (figures 6(I)–(L), solid lines). A comparison with this dependence shows that the data points are close to this line, which provides confidence in the normalisation procedure and the determination of the volume fraction.
\( \phi = 0.58 \). A closer inspection reveals that the Voronoi volumes of the small particles are relatively large whereas the Voronoi volumes of the large particles are relatively small. This effect is observed for crystalline and amorphous particles. However, it is particularly pronounced for the crystalline particles in the partially crystalline samples with \( \alpha = 1.10 \) and 1.18. This again indicates that the characteristics of the large and small particles become more similar in the crystalline regions.

Instead of the large and small particles, now the crystalline and amorphous particles are considered. Based on the particle volume \( V_p \) and Voronoi volume \( V_V \) of each particle, the local volume fraction \( \Phi \) of each particle is calculated. This allows us to compare the average local volume fractions of crystalline and amorphous particles in the partially crystalline samples (\( \alpha = 1.10, 1.18 \)). They are expected to be different, as suggested by the differences in the distributions \( p(R) \) and \( p(V_V) \) for crystalline and amorphous particles. The comparison is based on the ratio of the average local volume fractions of crystalline and amorphous particles, \( \langle \Phi_i \rangle_C / \langle \Phi_i \rangle_A \). This quantity is more reliable than the average local volume fractions, \( \langle \Phi_i \rangle_C \) and \( \langle \Phi_i \rangle_A \), because the size determination allows for a reliable comparison of particle sizes determined in the same experiment whereas the individual particle sizes are associated with a rather large uncertainty. The ratio \( \langle \Phi_i \rangle_C / \langle \Phi_i \rangle_A \) is found to decrease with increasing size ratio. It is 1.04 and 0.99 in the case of \( \alpha = 1.10 \) and 1.18 respectively. Both values are smaller than the ratio of a one-component system, which is the ratio of the volume fractions at its melting and freezing transition 0.545/0.494 = 1.10 [1, 5].

In the crystalline regions, cells formed by larger than average particles force the crystal to expand whereas cells with smaller than average particles cannot shrink since the crystal order has to be maintained. As the size mismatch increases, therefore, the volume fraction within the crystalline regions decreases [9]. Within the amorphous regions, in contrast, large and small particles can locally rearrange to establish another amorphous arrangement. The size mismatch even allows for a slightly more efficient packing because the differently-sized particles can be distributed among the differently-sized spaces in the random structure. The volume fraction hence slightly increases with increasing size ratio \( \alpha \) [9, 54–57]. The decreasing volume fraction within the crystalline regions and the increasing volume fraction in the amorphous regions is also reflected in the phase behaviour of polydisperse hard spheres [5, 6, 8, 10, 15].

Beyond a size ratio \( \alpha \approx 1.18 \), the ratio \( \langle \Phi_i \rangle_C / \langle \Phi_i \rangle_A \) is found to be smaller than one and hence packing in a crystal is less efficient than in an amorphous arrangement, which is in contrast to monodisperse systems [1–3]. Since the volume fraction in the amorphous regions is already initially high or increases during crystallisation, the dynamics is slow or even arrested if the volume fraction is pushed beyond the glass transition. As a result, crystallisation is very slow or arrested and the sample remains partially crystalline or does not crystallise at all. This could be a reason why crystallisation is not observed for \( \alpha > 1.18 \).

4. Conclusion

Binary mixtures with modest size ratios \( \alpha \leq 1.60 \) and, in most cases, a total volume fraction \( \phi = 0.58 \) and a relative volume fraction of large spheres \( X = 0.5 \) are studied. They are exposed to oscillatory shear to investigate shear-induced crystallisation. Structural changes on the single particle level are observed using confocal microscopy. Each particle is attributed to the crystalline or amorphous regions and its size, Voronoi volume, local topology and local volume fraction are considered.

The sample with a small size ratio \( \alpha = 1.08 \) fully crystallises upon the application of shear, samples with an intermediate size ratio \( 1.10 \leq \alpha \leq 1.18 \) partially crystallise and samples with a large size ratio \( \alpha \geq 1.23 \) remain amorphous.

The amorphous samples as well as the amorphous regions of the partially crystalline samples show only minor changes in the investigated quantities compared to the initial state. In contrast, where shear-induced crystallisation occurs, changes are observed: the average local bond order parameter \( q_b \) is significantly higher, the distribution of the nearest neighbours \( p(N) \) and the distribution of Voronoi volumes \( p(V) \) and hence the local topologies of the small and large particles become more similar. In general, the characteristics of the small and large crystalline particles match more closely. This is consistent with the formation of substitutionally disordered crystals.

The total volume fraction \( \phi = 0.58 \) is kept constant in the main series of experiments. Nevertheless, the local volume fraction in substitutionally disordered crystals decreases. Correspondingly the local volume fraction in the amorphous regions has to increase as the size ratio \( \alpha \) is increased. An increasing size mismatch indeed allows for a more efficient random packing. However, the increased volume fraction slows down the dynamics, especially long-range movements. This prevents fractionation and the formation of several crystalline phases with different lattice spacings (two in the case of binary systems), which is in agreement with our observations. Crystallisation thus occurs in regions where the conditions are already favourable and only small-scale movements are required to realise an ordered crystalline arrangement. The formed crystals are expected to reflect the initial spatial distribution of particle sizes. This is indeed observed.
The experiments reveal that beyond a size ratio \( \alpha \approx 1.18 \) the volume fraction in the amorphous regions is higher than in the crystalline regions. This coincides with the maximum size ratio, \( \alpha = 1.18 \), up to which crystallisation is observed. Moreover, this value is consistent with the Hume-Rothery rule for metallic alloys [32]. It corresponds to a polydispersity of about 0.1 (table 1). Crystallisation is expected to cease around such a polydispersity with the actual value of the terminal polydispersity depending on the shape of the size distribution [1–3, 5–16].

In future, further quantities could be determined and could provide more detailed information on the crystalline and amorphous regions. We suspect that also changes in the amorphous regions could be detected if other quantities more suited for random arrangements are considered. Moreover, the individual particles should be followed during shear-induced crystallisation. This would clarify to what extent initially existing configurations are exploited and to what extent they are modified. Furthermore, this would reveal whether and to what extent the distribution of nearest neighbours is isotropic or anisotropic during shear [83–85]. Varying the shear protocol would furthermore reveal its impact on crystallisation. It could, for example, be interesting to compare the efficiency of different shear protocols to induce crystallisation [86] but also to lead to different crystal orientations or to induce (re-entrant) shear melting. The investigations could also be extended to samples with different size distributions, for example with different symmetry or skewness [24, 25], or to other soft matter systems, such as polymers and liquid crystals, as well as granular materials and metals. In these systems, structural ordering is also of great importance and of very significant relevance for technological and industrial applications.

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**Appendix — Number of neighbours**

To investigate the local environment of the particles, the number of neighbours of each particle is determined. This allows us to calculate the distribution of nearest neighbours \( p(N_n) \) for all particles as well as separately for the small and large particles, the particles in the crystalline and amorphous regions (section 3.4, figure 5). As the size ratio \( \alpha \) increases, the distributions for the small and large particles successively move apart. This is quantified by the most likely \( \langle N_{n,l} \rangle \) and mean \( \langle N_{n,l} \rangle \) number of neighbours of the large and small particles (table A1). For the large particles, the most likely and mean number of neighbours increase as the size ratio \( \alpha \) is increased, whereas simultaneously these numbers decrease for the small particles. Because their ratio depends less on the specific definition of nearest neighbours than the individual values, also the ratios \( N_{n,l}/N_{n,a} \) and \( \langle N_{n,l} \rangle / \langle N_{n,a} \rangle \), are considered. They increase with increasing size ratio \( \alpha \) and are similar to \( \alpha \).

To estimate the number of neighbours, a simple geometrical model is proposed (figure A1). This model is inspired by similar previously proposed models, including in the context of metallic glasses [87, 88]. The centres of the large and small particles are located at distances \( d_{i,1} = f(R_i + R_l) \) and \( d_{i,s} = f(R_i + R_s) \) from the centre of the central particle respectively, where the radius of the central particle, \( R_i \), is either \( R_l \) or \( R_s \) and the factor \( f \) depends on the average particle distance and hence the volume fraction \( \phi \). The equatorial planes of the large and small particles are located in these concentric spherical surfaces with radii \( d_{i,1} \) and \( d_{i,s} \), respectively where curvature effects are neglected (figure A1). The samples appear homogeneous and hence each particle is surrounded by small and large particles according to the sample composition \( X = 0.5 \). In a concentric spherical surface thus the relative surface fraction of large particles \( \chi \) is given by:

\[
\chi = \frac{\xi R_l^2}{\xi R_l^2 + (1 - \xi) R_s^2} = (1 + (X^{-1} - 1)\alpha)^{-1}
\]

(A1)

where \( \xi \) is the number fraction of large particles (equation (2)). Accordingly, the relative surface fraction of small particles is \( 1 - \chi \). The number of neighbours is given by

\[
N_{n,i} = \int \int \int \frac{4\chi(R_i + R_l)^2 + 4(1 - \chi)(R_i + R_s)^2}{\chi R_l^2 + (1 - \chi) R_s^2}
\]

(A2)
Table A1. Most likely $\langle N_{n,l} \rangle$ and mean $\langle N_{n,s} \rangle$ number of neighbours of the large and small particles as well as the ratios of these quantities for different size ratios $\alpha$. The total volume fraction is $\phi = 0.58$ and the relative volume fraction of large particles is $X = 0.5$.

| size ratio | large $N_{n,l}$ | small $N_{n,s}$ | ratio $N_{n,l}/N_{n,s}$ | large $\langle N_{n,l} \rangle$ | small $\langle N_{n,s} \rangle$ | ratio $\langle N_{n,l} \rangle/\langle N_{n,s} \rangle$ |
|------------|-----------------|-----------------|---------------------------|-------------------------------|-----------------------------|---------------------------------|
| 1.08       | 14              | 14              | 1.00                      | 14.8                         | 13.8                        | 1.07                            |
| 1.18       | 15              | 13              | 1.15                      | 15.2                         | 13.4                        | 1.13                            |
| 1.23       | 15              | 13              | 1.23                      | 15.7                         | 13.3                        | 1.18                            |
| 1.45       | 17              | 13              | 1.31                      | 17.3                         | 12.8                        | 1.35                            |

Figure A1. Schematic representation of the simple geometrical model used to estimate the number of nearest neighbours. Small (green) and large (purple) particles surround a central particle $i$, here a large particle. The two species occupy spherical shells (light green and light purple lines). The volume fraction determines the particle separation, which is taken into account by the factor $\hat{f}$. This results in distances of the centres of the small and large particle from the centre of particle $i$ of $\hat{f}(R_i + R_s)$ and $\hat{f}(R_i + R_l)$, as indicated.

where $f$ is the packing fraction in the surface surrounding the particle [82, 87, 88]. The ratio of the number of neighbours of the large and small particles then is given by

$$\frac{N_{n,l}}{N_{n,s}} = \frac{4\alpha^2 + (X^{-1} - 1)\alpha(\alpha + 1)^2}{4(X^{-1} - 1)\alpha + (\alpha + 1)^2}. \tag{A3}$$

In the present case the relative volume fraction of large particles is $X = 0.5$. This simplifies the relationship to $N_{n,l}/N_{n,s} = \alpha$. Given the simplicity of the model, this is in reasonable agreement with the ratios determined in the experiments (table A1). Similar ratios can be extracted from a theoretical study of binary amorphous packings [55].

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