

Binary hard-sphere crystals with the cesium chloride structure

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The possibility of binary hard-sphere colloids crystallizing with the cesium chloride (CsCl) structure was examined experimentally using poly (methyl methacrylate) particles dispersed in organic solvents. Towards this end, two dispersions were prepared that contained particles with a radius ratio $\alpha = R_B/R_A$, where A refers to the large particles and B the small, of 0.736. This is close to the optimum ratio of 0.732 at which this structure is predicted to form as determined by space-filling calculations. The phases found within the binary mixture were examined using laser light crystallography and scanning electromicroscopy, and some were shown to have the CsCl structure. Over a period of time some of the CsCl crystals disappeared indicating that they were metastable and that this structure may not be the most enduring phase at this size ratio.

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I. INTRODUCTION

It has been shown both theoretically [1,2] and experimentally [3] that monodisperse hard spheres dispersed in a liquid can spontaneously self-assemble to form a crystalline phase when their volume fraction (ϕ_v) exceeds the value of 0.494. It has also been demonstrated that when two differently sized sets of these hard spheres are mixed together then they can co-crystallize to form binary crystal structures analogous to those seen in atomic systems [4–6]. The exact binary crystal structure formed and its stoichiometry is found to be dependant on the radius ratio of the two different sets of particles and their relative concentrations. To date the binary crystals, AB (face-centered-cubic NaCl structure [6]), AB₂ (hexagonal AlB₂ structure [4,5]), AB₆ (body-centered-cubic C₆₀K₆ structure [7] and cubic CaB₆ structure [8]) and AB₁₃ (cubic NaZn₁₃ structure [4,5]) have been identified experimentally as existing for hard-sphere systems. Binary structures such as CaCu₅ and MgCu₂ have also been identified in nonhard-sphere systems for charged particles [9].

A further crystal that might exist in binary hard-sphere systems is the cubic CsCl structure. This consists of interlocking cubes of each of the two species such that at the center of the cube of atoms of one species, there is an atom of the other (see Fig. 1b). Theoretical calculations exploring the stability of this structure in binary systems using density-functional theory have predicted it to be either stable between radii ratios of 0.865–0.3 [10] or metastable between ratios of 0.86–0.63 [11] whereas those involving cell model calculations [12], simulation [13], and an immiscibility model [14,6], could find no size ratios at which this structure was thermodynamically stable. A qualitative assessment of the stability of possible binary hard-sphere crystal structures can be obtained from the approach of Murray and Sanders [15]. They suggested that such structures will be stable if their total volume fraction when fully compressed exceeds the value, $\pi/3\sqrt{2} \approx 0.74$, which applies to fully compressed one-component systems. For cesium chloride, the optimum size ratio, where the large particles touch each other in a cube and the small particle in the cube center touches all the

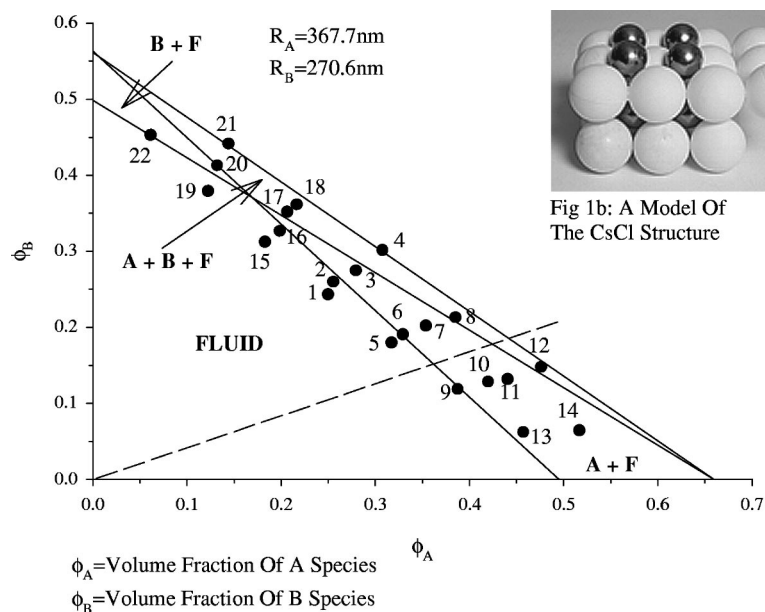


FIG. 1. The concentrations of the samples examined at a size ratio of 0.736 overlain on a theoretical phase diagram generated by Hunt, Jordine, and Bartlett [6] for a similar sized system. The theoretical plot indicates that no binary phases are anticipated to be stable and that only phases of fluid (F), A crystals+fluid, B crystals+fluid, and A crystals+B crystals+fluid are expected to occur. The dashed line across the diagram represents the volume fractions at which the number of A particles equals the number of B particles to give a stoichiometry of 1:1. The inset [Fig. 1(b)] is of a model showing the cubic nature of the CsCl structure.

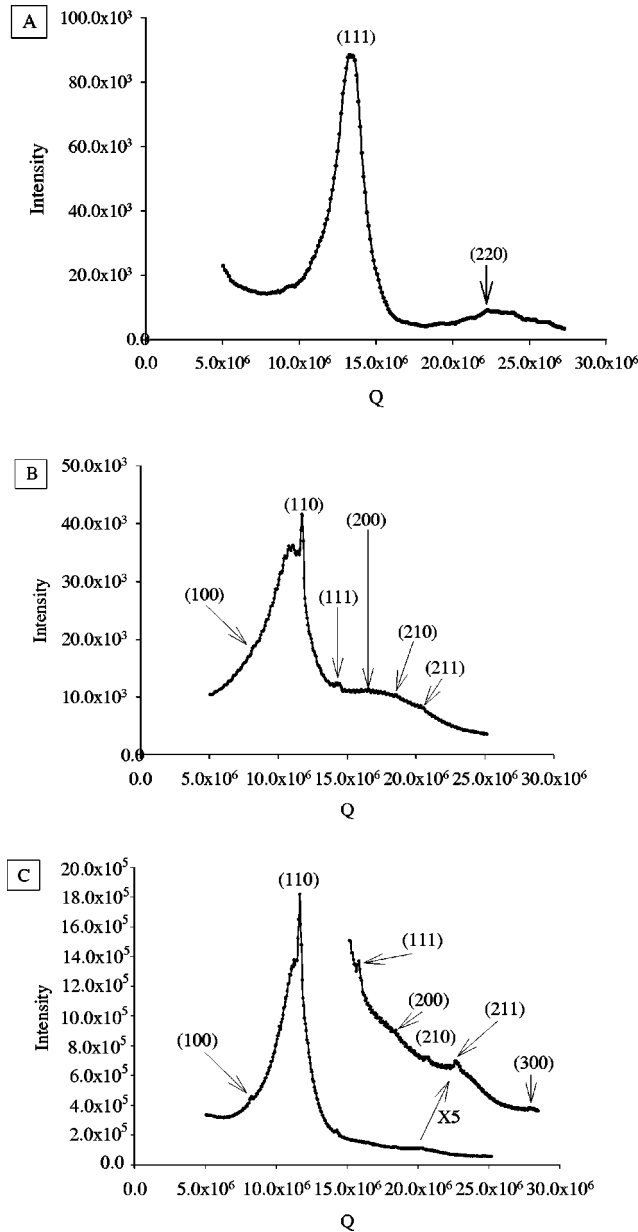


FIG. 2. (a) The laser light crystallography trace for sample 22 showing intensity against scattering vector Q . The peaks are indexed upon a random hexagonal close-packed structure with the main (111) peak corresponding to its position as expected for a pure B crystal. (b) The laser light crystallography trace for sample 12. The Bragg peaks can be indexed upon a cubic lattice. (c) The laser light crystallography trace for sample 6. The Bragg peaks can again be indexed upon a cubic lattice indicating, though not proving, the CsCl structure.

large ones, is $\alpha = \sqrt{3} - 1 = 0.732$. The corresponding maximum volume fraction, $(\pi/6)(1 + \alpha^3) = 0.729$, is a little smaller than 0.74, suggesting that cesium chloride is, at best, marginally stable.

Experimentally, this configuration has been looked for in a hard-sphere mixture by Hunt, Jardine, and Bartlett [6] using a system containing particles with a size ratio of 0.72. They found no evidence that this binary configuration was stable at this size ratio and only found phases containing

crystals solely of the individual components plus a fluid phase, or colloidal glasses. The only work to show this type of structure was reported by Underwood, Megen, and Pusey [16] who used similarly sized particles (size ratio 0.95) apparently with a cross attraction between them, to generate the CsCl configuration.

II. EXPERIMENT

The hard spheres used in this work consisted of poly (methyl methacrylate) particles stabilized by thin layers of poly-12-hydroxy stearic acid, prepared by the method of Antl *et al.* [17]. Dispersions of each type of particles were made and redispersed in an organic solvent mixture of decahydronaphthalene and tetrahydronaphthalene such that the refractive index of the mixture was 1.5, similar to that of the particles. This meant that the dispersions were virtually transparent and that any changes within them, or in the binary mixtures made from them, could be observed visually by eye and optically with a laser light crystallography setup [18]. To measure the radii of the particles within the two dispersions, they were first concentrated using centrifugation until the volume fraction of the system was within the “two-phase” region of the single species phase diagram. Here, the single species crystal phase ($\phi_v = 0.545$) coexists with the fluid phase ($\phi_v = 0.494$) and an accurate particle radius can be determined by laser light crystallography using the process described in Schofield, Pusey and Radcliffe [19]. For the systems under study here the particle radii were found to be 367.7 and 270.6 nm, giving a radius ratio $\alpha = 0.736$. When the sample is in this region of the phase diagram the volume fraction of the particles can be determined accurately from the relative proportion of the fluid and crystal phases within the sample, i.e., $\phi_v = (0.545V_{\text{Crystal}}/V_{\text{Total}}) + (0.494V_{\text{Fluid}}/V_{\text{Total}})$. The binary mixtures were then made by mixing known amounts of these two dispersions together and altering their concentration by either adding or removing solvent. Figure 1 shows the concentrations of the binary samples examined.

The binary mixtures were allowed to stand undisturbed in a temperature controlled room and were visually examined every day for signs of change within them. This was usually indicated by the appearance of opalescence within the sample, which is due to light being diffracted by crystal grains. The structure of these crystals was first examined using laser light crystallography, a technique in which an expanded laser beam is shone through the randomly orientated crystals to give a powder pattern analogous to that obtained from x-ray diffraction from an atomic system. To look at the packing of the particles in these crystals a second sample was then prepared, leaving the first sample for further visual and laser studies, and allowed to dry under ambient conditions to leave a white residue, which hopefully still contained particles packed with the same crystal arrangement as was seen in the first sample. This residue was scraped out of the sample vial, glued onto a microscope stub using carbon cement, and then sputter coated with gold to make it conductive to the electrons used in the imaging process. The sample was then examined using a Cambridge S250 scan-

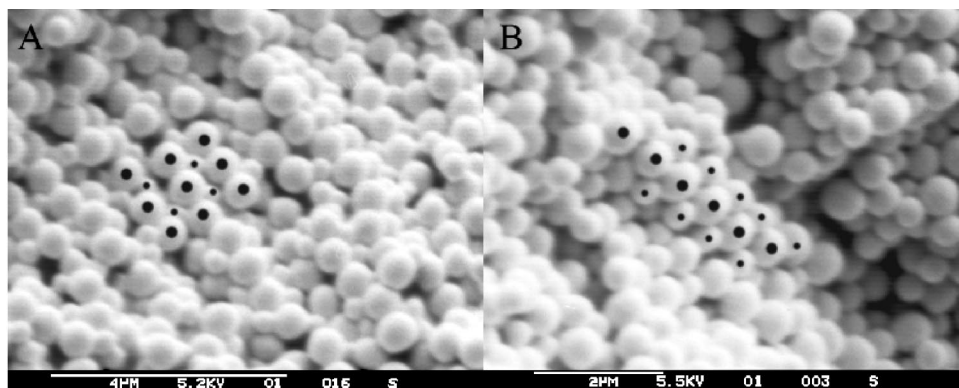


FIG. 3. Scanning electron microscope pictures of the particle packing in the binary crystals. (a) This shows a large region of CsCl ordering with square packing of the large spheres (dotted with the larger, black circles) with small spheres set at their center. (b) The central portion shows the square face of cubes made up of small spheres with a large sphere at the middle of each.

ning electron microscope and photographs of the particle packing obtained.

III. RESULTS

Visual examination of the samples revealed that 6, 7, 8, 10, 11, 12, 16, and 22 all showed the formation of crystals with the position of the crystal phase relative to the fluid phase within the sample cell breaking down into three distinct groups. First, the crystals in sample 22 appeared as a thin band at the bottom of its container after 4 days, the crystals in samples 7, 8, 10, 11, and 12 appeared after 7 to 12 days as very thin layers at the top of the sample cell just under the meniscus, and those in samples 6 and 16 appeared after 7 days and 19 days, respectively, as a diffuse band within the center of the cell. The crystals in sample 16 all also seemed to be attached to the cell wall. The other samples all remained amorphous.

Laser light crystallography on the crystal band in sample 22 was difficult due to the thinness of the layer, which meant that there were not enough randomly orientated crystallites to give a good scattering pattern and that the liquid layer above contributed significantly to it. The crystallography trace measured is shown in Fig. 2(a) and the main peaks within it can be indexed on a random-hexagonal-close-packed pattern [18]. This is indicative of the pattern seen for the pure B crystals and this is supported by the fact that the position of the main (111) peak is at the correct scattering vector for this crystal phase. The problem of thin crystal bands was also encountered in samples 7, 8, 10, 11, and 12, which in some case had layers that were so thin that it was virtually impossible to determine the position of the crystal Bragg peaks relative to the background in the crystallography traces. Figure 2(b) shows the trace obtained from sample 12 and the peaks with this can be indexed upon a cubic lattice, which is what is expected for a CsCl structure. However, this cannot be used as conclusive proof that this is the configuration found as there are other binary crystal types with a cubic arrangement that will show this type of crystallography plot. Also, seen in the trace in Fig. 2(b) is that the Bragg peaks are situated within a background that is believed to be due to the liquid phase. For samples 6 and 16 problems were encountered in obtaining a good crystallography plot, not because of the thinness of the layer, but because that there were few crystals within it making it again difficult to

get crystal Bragg peaks that were significantly greater than the liquid background. Figure 2(c) shows the laser crystallography plot for sample 6 and again the peaks can be indexed on a cubic lattice.

Due to the fact that the CsCl phase occurred as a thin band in most samples it was decided that only a copy of sample 6 had any chance of producing enough crystals to make a scanning electron microscopy (SEM) investigation feasible. When this was prepared it was found that some crystals had survived the drying process and SEM photographs of these can be seen in Fig. 3. They show that both the large and small spheres pack with a cubic arrangement and, furthermore, at the center of each of these squares can be seen a sphere of the second species indicating that the packing is the CsCl structure.

IV. DISCUSSION

An examination of the phase diagram shows that the samples with binary behavior occur (with the exception of sample 16) where the ratio of A to B particles is approximately 1:1, which is what is expected for a CsCl arrangement. The position of the crystals also suggests that they may form by a heterogeneous route, i.e., they need a surface, such as a meniscus or wall, onto which to nucleate. This was particularly noticeable in sample 8 where the crystals seemed to nucleate out from a small slither of dust or dried colloid that had fallen from the cell lid onto the top of the sample.

Although the results described give clear indication of the formation of crystals with the CsCl structure, there is also evidence that the crystals are metastable or, at best, marginally stable. First, unlike systems where stable binary structures are found, the samples never exhibited extensive crystallization and relatively small numbers of crystallites were observed either in thin layers or dispersed sparsely through broader bands. Second, it was noted that after 10 months, some of the binary crystal layers had disappeared to be replaced by fluid and that only samples 6, 8, and 12 still contained them. If the CsCl crystals are metastable relative to the fluid phase, then why they should form in the first place is open to debate. It is possible that there is some small deviation of the interparticle interaction from the pure hard-sphere case towards a slightly softer potential, but what effect this will have is uncertain and no theoretical or experimental work has been reported for such mixtures. Also, as

TABLE I. The edge length and volume fraction of the CsCl structures found.

Sample number	Unit cell edge length (nm)	Unit cell volume fraction
6	762	0.6582
8	748	0.6959
12	762	0.6582
16	738	0.7246

pointed out in Ref. [16], a weak cross attraction of unknown origin between the two differently sized particles (while the A-A and B-B attractions are weaker or absent) tends to stabilize the CsCl structure.

Using the laser light crystallography results and the position of the (100) or (110) peak we can determine the CsCl unit-cell dimensions and volume fraction and these are shown in Table I for those samples whose crystallography trace were of sufficient quality to allow this analysis to take

place. As can be seen the binary CsCl structure had a volume fraction between 0.65 and 0.72 which, when compared with its volume fraction of 0.729 at close packing, shows that the crystals are slightly expanded.

V. CONCLUSIONS

Hard-sphere colloids with a size ratio of 0.736 were mixed together to produce a binary crystal with the CsCl structure; the first time this configuration has been seen for such a system. The majority of samples showing this arrangement had a particle to particle number ratio of 1:1 and the crystals appeared either as thin bands at the top of the sample container or as diffuse crystal regions within the center of the cell.

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