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Phase behaviour of binary mixtures of colloidal charged spheres

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Abstract

As a step towards the modelling of binary metal alloys we here report on the shape of the phase boundary of two deionized charged sphere colloidal suspensions as a function of mixing ratio and particle density. Their size ratios are $r = 0.68$ and $r = 0.56$. Both aqueous suspensions of polystyrene copolymer spheres crystallize in a body-centred cubic structure. Interesting differences in the shape of the phase boundary are observed. In the first case a peaked increase of crystal stability was observed for a mixing ratio of $p = 0.2$–0.3, which gives the fraction of small spheres. Also in the second case the stability of the crystalline phase is larger than expected for an ideal solid solution but over a more extended range of small p. In addition at $p = 0.7$–0.8 we find a pronounced suppression of crystallization and furthermore some indications of a precipitation of one species at $p = 0.9$. While the first phase diagram resembles that of a solid solution with possibly the onset of compound formation, the second more resembles a eutectic.

Keywords: Colloidal crystals; Binary mixtures; Phase behaviour; Solid solution; Eutectic

1. Introduction

Like their atomic counterparts, suspensions of colloidal spheres show a rich and fascinating phase behaviour. For one component systems of hard sphere like interactions one observes face-centred cubic (fcc) or hexagonal close packed (hcp) structures resembling that of noble gases [1]. For charged spheres under low salt conditions the electrostatic repulsion dominates and is quite long-ranged. One observes body-centred cubic (bcc) structures at low particle density n and fcc structures at larger n [2–4]. This corresponds to the phase behaviour of many metals, e.g. alkalines or Fe, which show a transition from bcc to close packed structures with increasing pressure or decreasing temperature. With increasing pressure the metal valence electrons change from s to d character giving rise to an atom volume change and allow for an increase of n [5]. For deionized charged colloidal spheres the “native” counter-ions take the role of the electrons, again with a large compressibility and thus the possibility of pressure or rather density induced phase transitions. While the valences (bare or effective particle charges) are, of course, much larger in the colloidal case, the structure determining effective interactions are repulsive in both cases and this analogy between the two kinds of systems became very fruitful. In particular for the study of phase transitions and the corresponding kinetics, colloidal suspensions with their convenient time and length scales, their excellent optical accessibility, and the experimentally variable interaction have by now acquired a prominent position as valuable model systems [6–8]. Recent work turned from single component systems to binary mixtures. First reports of alloy structures have been published already very early [9,10], but only within the last few years the full richness of compound structures has been revealed and explored both experimentally and theoretically [11,12]. In particular, particles of different size ratios and displaying a combination of overall attractive interactions with short ranged repulsions were observed to systematically form series of salt structures, thus mimicking partially covalent binding atomic in atomic systems. In the present contribution we address a related question, namely the phase behaviour in binary mixtures of purely repulsive spheres as a function of composition and particle density. This ultimately aims at a modelling of metal solid solutions, eutectics and alloys. As a first step we here study the shape of the phase boundary. For an ideal (azeotropic) solid solution one would expect a straight line connecting the single component freezing densities, as with increasing concentration $p = n_{\mathrm{small}}/n_{\mathrm{total}}$ the average atom (particle) volume should linearly shrink [13].

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Non-ideality of the solution may for metals result in a finite curvature of this connecting line (e.g. towards lower freezing temperatures for alkalis [14]), the formation of a eutectic, the appearance of a region of enhanced stability, where a stoichiometric compound is formed, or even more complicated scenarios [15]. For charged colloids only little is known, although both straight and more or less curved shapes of the phase boundary have already been observed earlier [16]. The aim of this contribution therefore is to demonstrate the existence of further, more complicated shapes than systems of complete miscibility and to suggest some contributions to their explanation.

In what follows we shortly address the employed techniques of sample preparation and characterization. We then present the two-phase diagrams complemented by some additional observations on morphology and suspension structure. We conclude with a short discussion of our findings.

2. Experimental

We employed three different species of highly charged colloidal spheres. Species PS100B was a commercially available, Carboxyl-modified Polystyrene latex sphere. PnBAPS68 and PnBAPS122 are poly-*n*-butylacrylamide-polystyrene copolymer spheres, stabilized by Sulphate surface groups and a kind gift of BASF, Ludwigshafen, Germany. All three species were comprehensively characterized prior to use in this study. Fig. 1 shows the size distribution of the PnBAPS122 particles measured by ultracentrifugation. The most important parameters of the pure components are compiled in Table 1. All pure samples crystallize in a bcc structure, with a coexistence region separating the crystalline and the fluid phase in the conventional particle density–salt concentration plane of the phase diagram. Note from Table 1 the decrease of the density at the phase boundary with increasing particle size and effective charge.

From the shipped materials stock solutions of a few percent volume fraction were prepared by dilution with doubly distilled water (Purelab Classic DI, ELGA, UK) and stored over mixed bed ion exchange resin (Amberlite UP 604, Rohm & Haas, France). After filtering (syringe filter with pore size 1.2 μm to remove ion exchange debris, dust, and coagulate, regularly occurring at first contact of suspensions with ion exchange resin) a second series of stock suspensions were prepared with the desired mixing ratios. From these the actual samples were prepared by further dilution and under regular control of the particle number density *via* the position of Bragg reflections in static light scattering. To maintain deionized conditions either an advanced continuous deionization technique was employed (PS100B/PnBAPS68) or the standard batch procedure was used (both mixtures). The former technique (details of which are given in [17]) is fast, gradient free and allows to monitor the progress of deionization *via* conductivity measurements. At the same time it is more suitable for a high n resolution (reproducible adjustment of n with a residual uncertainty of 0.2 μm^{-3} at $n = 5\ \mu m^{-3}$) but too substance consuming for a high p-resolution. The batch method needs only small amounts of materials, as some 2 ml of suspension are filled in a Teflon® septum screw cap vial containing approximately 1 ml of ion exchange resin. The vial then is tightly closed and stored up side down to avoid the formation of ion concentration gradients, which may lead to artefacts [18]. First appearance of crystals takes some hours to days. When samples are shaken up and left to re-crystallize, equilibrium of preparation is notable from constant short crystallization times (seconds to several minutes depending on n). Equilibrium is usually reached after a week and the residual ion concentration then is estimated to be on the order of the dissociation product of water. For control of n both kinds of samples are placed in a standard static light scattering apparatus and from the positions of the bcc (1 1 0) reflection the lattice constants (and thus n) is inferred [2].

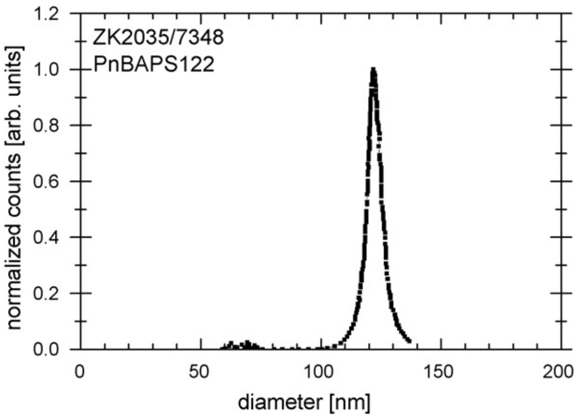

Fig. 1. Size distribution of PnBAPS122 particles measured by the manufacturer by ultracentrifugation.

Crystallization was usually determined directly from visual observation. Crystals are identified from the brilliant Bragg reflections they display under illumination with white light. An example is shown in Fig. 2. From left to right we show the featureless fluid structure at $p = 0.9$ and $n = 5.92 \pm 0.01\ \mu m^{-3}$; the columnar wall crystals in the coexistence region at $p = 0.15$ and

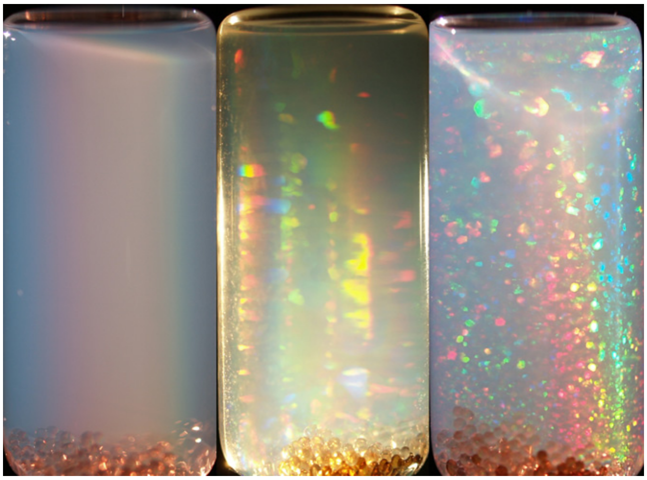

Fig. 2. Images of the sample vials for different compositions p and particle number densities n. Image size approx. 14 mm × 35 mm. (From left to right) Featureless fluid structure at $p = 0.9$ and $n = 5.92 \pm 0.01\ \mu m^{-3}$; columnar wall based crystals at coexistence at $p = 0.15$ and $n = 0.53 \pm 0.05\ \mu m^{-3}$; bulk nucleated crystals at coexistence at $p = 0.9$ and $n = 0.59\ \mu m^{-3}$ and a polycrystalline sample at $p = 0.15$ and $n = 1.24 \pm 0.12\ \mu m^{-3}$.