Properties of mixed colloidal crystals

Abstract We prepared colloidal crystals from aqueous suspensions of spherical, charged polystyrene spheres under deionised conditions. Using a home-built multipurpose light scattering apparatus we measured the static structure factor, the static shear modulus and the intermediate scattering function. In addition we also monitored the conductivity as a function of the composition and the particle number density. For the mixture investigated the data are well described assuming the formation of randomly substituted body-centered-cubic crystals.

Key words Colloids · Charged spheres · Mixtures · Light scattering

Introduction

Colloidal crystals are the subject of intense research for several reasons. First, owing to their specific length and time scales their properties are readily accessible by various forms of light scattering and microscopy. Second, a number of interesting questions of fundamental interest in condensed matter physics can be addressed in a well-defined model systems. This concerns both equilibrium properties (like diffusive dynamics, structure or phase behaviour), response to external fields (like electrokinetic properties or sedimentation) and situations far from equilibrium (like the glass transition, shear-melting or crystallisation kinetics). Third, however, important applications may also result from a better understanding of the generic properties. Optical-band-gap materials are one of these.

Recently focus has shifted from single-component suspensions to mixtures. The most prominent examples deal with hard-sphere or hard-sphere-polymer mixtures of large size difference, where phase separation is observed owing to attractive terms in the potential of the mean force [1, 2]. Much less is known about charged mixtures. Only a few reports exist on the phase behaviour [3, 4, 5], and fewer on even other properties, like shear rigidity [6], diffusion [7, 8] or crystallisation kinetics.

We report on a mixture of two species of polystyrene latex spheres in deionised aqueous suspension. Their size ratio is \( \Gamma = 0.85 \). Such a small value should not induce an entropically driven instability. Nevertheless, the phase behaviour is not immediately obvious. The formation of alloy structures of glasses or of precipitates can be expected. Alloys may either be compositionally ordered (e.g. of NaCl structure) or disordered (e.g. Cu/Au). We conducted a number of different experiments to comprehensively characterise the resulting solids. Besides the static structure factor, \( S(q) \), we also measured the conductivity, \( \sigma \), and the static shear modulus, \( G \). The former is very sensitive to the formation of precipitates; the latter has been shown to yield valuable information about the local crystal structure [9]. Finally, we also report some of the first dynamic light scattering measurements on polycrystalline samples. Their interpretation can be qualitative only, since a rigorous scattering theory of such nonergodic and inhomogeneous materials is still demanded. The combination of our results shows that at low-to-intermediate particle concentrations randomly substituted alloys of body-centered-cubic (bcc) structure are formed.
Table 1 Properties of the pure components. Sample name, source, nominal diameter, $2a_{nom}$, effective charges, $Z^*_e$ and $Z^*_G$, from conductivity and shear modulus measurements, shear modulus, $G$, at the particle number density used for the mixture as well as the number densities at freezing and melting are given

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source</th>
<th>$2a_{nom}$</th>
<th>$Z^*_e$</th>
<th>$Z^*_G$</th>
<th>$G$ at $n = 1 , \text{µm}^{-3}$</th>
<th>$n_F$ at $n = 1 , \text{µm}^{-3}$</th>
<th>$n_M$ at $n = 1 , \text{µm}^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS85</td>
<td>IDC Batch No 767.1</td>
<td>85 nm</td>
<td>530 ± 32</td>
<td>350 ± 20</td>
<td>0.786 Pa</td>
<td>3.8 ± 0.5</td>
<td>4.4 ± 0.5</td>
</tr>
<tr>
<td>PS100</td>
<td>Banys Lab. Batch No. 3512</td>
<td>100 nm</td>
<td>530 ± 38</td>
<td>327 ± 10</td>
<td>0.8 Pa</td>
<td>4.0 ± 0.5</td>
<td>7.0 ± 0.5</td>
</tr>
</tbody>
</table>

**Experimental**

Two species of commercially available polystyrene latex spheres were investigated. The particle parameters are compiled in Table 1. All the suspensions were prepared from diluted and precleaned stock suspensions of approximately 1% packing fraction. The suspensions were thoroughly deionized using advanced continuous conditioning methods. Details of this have been given elsewhere [10]. Both individual species were comprehensively characterised before conducting experiments on the mixtures.

Both pure samples crystalline at low particle number densities in a bcc structure. Measurements of $S(q)$ were further used to calibrate measurements of the conductivity, $\sigma$. The particle number density dependence of $\sigma$ was observed to be strictly linear and independent of the phase state of the suspension. The data for thoroughly deionised suspensions are well described by $\sigma = n e Z^*_e (\mu_+ + \mu_-) + \sigma_B$, with the elementary charge $e$, the particle and proton mobilities $\mu_-$ and $\mu_+$ and the background conductivity $\sigma_B$ (mainly stemming from dissociated water and ionic impurities). The effectively transported charge, $Z^*_e$, was determined as a fit parameter. It is tabulated in Table 1. The shear modulus, $G$, is in good agreement with theoretical fits yielding an effective shear modulus charge $Z^*_G$ as the only free parameter. We note that $Z^*_G$ is observed to be somewhat smaller than the effectively transported charge.

Mixtures were prepared at fixed particle number density under thoroughly deionised conditions. The background concentration of ionic impurities was below $5 \times 10^{-7} \, \text{M}$. Under these conditions the samples were completely solidified. Colloidal solids, however, show very low yield moduli and may easily be shear-melted by mechanical treatment. Since for some properties the sample morphology may have a severe influence on the results, it was of great importance to leave the samples undisturbed once crystallised. To this end all measurements were performed using a recently reported multipurpose light scattering apparatus. In this static structure, the shear modulus and the dynamic structure factors may be measured quasi simultaneously on the same crystalline sample. The apparatus is equipped with a double-arm goniometer. It uses two counterpropagating illumination/detection schemes for static and dynamic light scattering and a third independently adjustable scheme for the torsional resonance detection. Details have recently been given elsewhere [11].

**Properties of mixed colloidal crystals**

Our results are given in Figs. 1, 2, 3 and 4.

The conductivity varies linearly with the composition. It is well described (solid line) using an extension of Hessinger’s conductivity model of independent ion migration with exchange of icons across the plane of shear [12].

$$\sigma = n e \left( X Z^*_e (\mu_+ + \mu_-) + (1 - X) Z^*_G (\mu_2 + \mu_1^+) \right) + \sigma_B,$$

where $X$ is the fraction of component 1, $e$ is the elementary charge and $\mu_i$ is the independently measurable electrophoretic mobility of particle species $i$. The effective charges, $Z^*_e$, used in the fit were taken from the single-component measurements and the background conductivity indicates a background concentration of impurities of some 0.5 $\mu$M.

The structure of the mixtures stays bcc independent of composition. Note the constancy of the position of the (1 1 0) Bragg reflection, indicating constant particle density.

Together with the conductivity data this rules out any phase separation or correlation between particle positions. In the first case the conductivity should show deviations from the theoretical expectations; in the latter case the appearance of superstructure peaks is expected. This demonstrates the formation of an alloy with a random distribution of particles on the bcc lattice sites.

This can be checked via $G$. Here a prediction of Lindsay and Chaikin [13] exists for the shear modulus of a randomly substituted alloy:

![Fig. 1 Background-corrected conductivity, $\sigma - \sigma_B$, of the PS85/PS100 mixture as a function of composition](image-url)