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Self-Assembled Structures of Disc-Like Colloidal Particles

S. Junaid S. Qazi^{1,*}, Göran Karlsson², and Adrian R. Rennie¹

Abstract Self-assembly is an important phenomenon that leads to formation of interesting and novel structures in colloidal dispersions. We present experimental evidence for the existence of a ‘cubatic’ phase in a colloidal dispersion of disc-like particles of nickel hydroxide colloidal dispersions. In this structure, disc-like particles self-assemble as domains of a few parallel discs and the orientation tends to be orthogonal in adjacent domains. This phase has been predicted previously by computer simulations. The domains are approximately equiaxial and are predicted to exist only within a limited range of aspect ratios and volume fractions. We have used the real space technique of cryo-transmission electron microscopy in our studies as this locally ordered structure could not be identified readily using scattering techniques, since the patterns are expected to be similar to those of isotropic liquid phases.

Key words Cubatic Phase • Plate-like colloids • Cryo-transmission electron microscopy

Introduction

Self-assembly is a means to form ordered structures in colloidal dispersions. Interparticle interactions, size-distribution and the thermal motion play vital roles. Ordered structures of anisotropic colloidal particles have significant importance to basic science and are of major practical interests. For example, they provide better mechanical properties

as fillers in composite materials. A variety of different self-assembled structures^{1,2,3,4} are reported for anisotropic particles on changing the concentration and temperature of dispersions.

Polydispersity is important for the structure of colloidal dispersions. It is difficult to synthesise highly monodisperse colloids. Computer simulations of spherical colloids have shown that polydispersity can suppress the formation of crystal phases^{5,6}. Dispersions of hard spheres⁷ with high polydispersity have shown fractionation into several solid phases that coexist with a fluid phase. In contrast, low polydispersity in length does not affect the phase behaviour of rod-like colloids, as nematic order does not depend strongly on length. Polydispersity above 18% was seen to suppress formation of a smectic phase of rods⁸. Polydisperse rods were seen to separate into phases with different length distributions⁹. An experimental study of goethite particles has shown that polydispersity favours the columnar phase over smectic structure that cannot accommodate particles with different lengths¹⁰.

The present work concerns discs. Computer simulations on cut spheres, that approximate discs in shape, are reported

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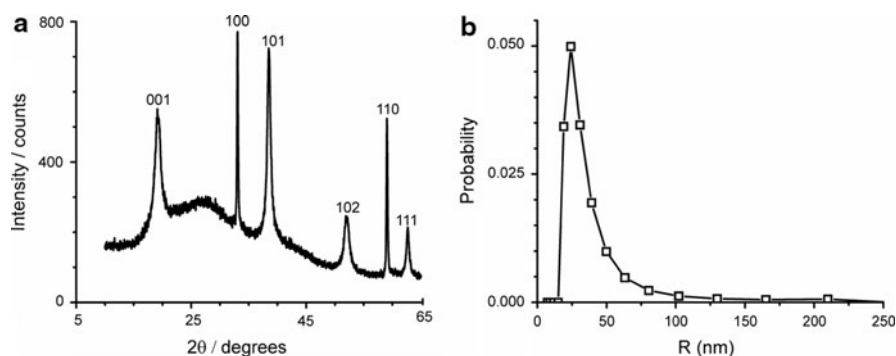


Figure 1 (a) X-ray diffraction pattern for the Ni(OH)_2 dispersions. Diffraction experiments used a monochromatic $\text{Cu K}\alpha$ X-ray beam (wavelength 0.154056 nm). The 001 peak is markedly broader than the 100 peak indicating that the particles are thin along the direction of the 001 plane normal. (b) Distribution of hydrodynamic radius for the nickel hydroxide particles derived from dynamic light scattering data. The data in (b) were obtained at a fixed scattering angle of 90° with a He-Ne laser emitting vertically polarised light at a wavelength of 632.8 nm

in the literature^{11,12}. The phase diagrams with many structures that depend on the concentration as well as the aspect ratio, L/D where L is the thickness of the disc and D is the diameter^{13,14} are described. A cubatic phase was identified^{11,15,16} with self-assembly in domains that consist of a few parallel discs. The orientation tends to be perpendicular in adjacent domains. Cubatic structure has been predicted for $L/D = 0.2$ in the density range $\rho^* 0.5$ to 0.62 where ρ^* is defined as the ratio of the volume fraction of particles to that of a close packed structure. In this article, we describe the observation of cubatic order in a dispersion of disc-like nickel hydroxide particles using cryo-transmission electron microscopy (cryo-TEM).

Experimental

Uniform hexagonal disc-like particles of nickel (II) hydroxide were prepared and sterically stabilised by adsorbing a layer of sodium polyacrylate on the surface according to the procedure of Brown et al.² who developed the original synthesis of Durand-Keklikian et al.¹⁷. The stabilised sample was then centrifuged and redispersed in water and centrifuged again to the required concentration. Three different concentrations 20% wt., 24% wt. and 30% wt. of nickel hy-

droxide dispersions were prepared for the experiments. The sample, which has shown the cubatic phase, had a concentration of 20% wt..

The disc-like nickel hydroxide particles were characterised by X-ray diffraction and dynamic light scattering to determine the dimensions, thickness of the adsorbed polymer layer and the polydispersity. The 001 peak in the X-ray diffraction pattern, shown in Figure 1a, is broader than the 100 peak. Average dimensions of the Ni(OH)_2 crystals in these directions can be calculated from the peak widths. Details about the methods¹⁸ of analysis and the sample¹⁹ used in the current study have been provided elsewhere. The nickel hydroxide core was found to be 6 nm thick and 80 nm in the diameter. Combining this with light scattering indicates that the overall particle diameter, D , was ~ 103 nm (including both nickel hydroxide and stabiliser), and the thickness, L , was ~ 23 nm. The estimated thickness of the adsorbed polymer layer was 8.5 nm. The size distribution in Figure 1b indicates the presence of some large particles up to 200 nm diameter and a polydispersity index from a cumulant fit of about 0.2. The aspect ratio defined as the overall thickness divided by the overall diameter is thus about 0.22.

Results and Discussions

A cryo-TEM image is shown in Figure 2 that indicates structures with cubatic order.

Cryo-transmission electron microscopy (cryo-TEM) is a technique that is used to study a wide variety of samples in fluid media for which the dispersed structure is important,

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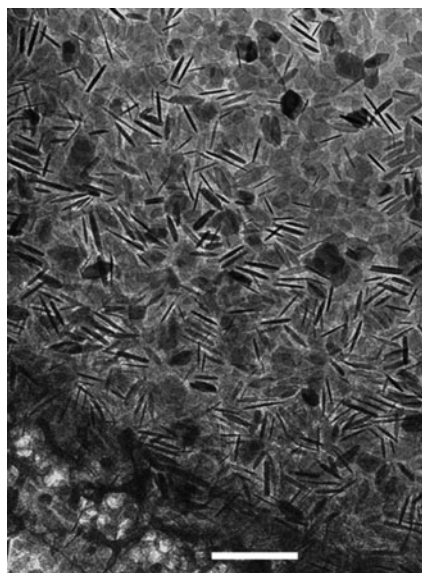


Figure 2 Cryo-TEM micrograph of particles at 20 wt% concentration showing cubatic order. Particles are present in small equiaxial domains of the size of the diameter of the particle. The sample in the thicker regions shows more order which decreases in thinner regions near the top of the micrograph. Scale bar is 200 nm

such as structured liquids^{20,21} where information about texture is vital. The images were taken with a Zeiss EM 902A transmission electron microscope that was operated at 80 keV in zero loss bright field mode. Ultra fast freezing, during the sample preparation process, prevents formation of ice crystals and preserves the sample structure close to its equilibrium state. A general review of the cryo-TEM sample preparation and image recording is available elsewhere²². The perforated polymer film used in the sample preparation for the cryo-TEM analysis was about 300 nm thick. This gives an estimate of the sample thickness near the edges at the bottom of the image in Figure 2. In normal cases, the thickness decreases to less than 50 nm for a dilute sample at the middle of a hole in the grid. In the present case, the sample was concentrated and the sample thickness could be about 100 nm as some edge wise particle are observed close to the middle of holes in a grid (top of the image in Figure 2).

In Figure 2, more columnar stacks are observed in the thicker regions where the sample shows bulk structure of the order of few hundreds of nanometres. The very dark full hexagonal regions in the image are certainly not a single particle but could be stacks of several particles. Images from cryo-TEM are two-dimensional which make it impossible to

determine how many particles lie in stacks with their large face in the plane of the sample. The stacks of discs lying edge wise out of the image are clear and they tend to be equiaxial as seen in Figure 2. In areas where the sample is thinner, the stacks are tilted and one such tilted stack is highlighted in Figure 3a. This tilt could arise from the sample preparation: flow and blotting during the preparation can distort the short columns in to tilted stacks. These regions of the sample may be too thin to allow equiaxial domains with particles of the diameter used in the present study.

Columnar stacks shown in Figures 3b,c and d illustrate some structural effects that can arise from polydispersity. Small discs (b) have more free space locally. Particles with large diameters can fit within a column (c) by tilting with respect to neighbouring particles. In some cases, (d) tilt is about 90 degrees if the gap between two particles is of the order of the diameter of a disc. The observed tilt of particles may arise from thermal motion with a sample quenched so as to reveal a range of orientations. However, on average, particles prefer to assemble in a short column of the order of the average diameter of the particle.

Analysis of several micrographs from different regions of the sample allows us to quantify the order in the structure. An average of 4.1 particles per stack in the sample is consistent with cubatic order. The length of an average column compares well with the mean diameter of particles as expected in a cubatic phase. The number of particles in a stack decreases with increasing concentration and no stacks were seen in a sample at a concentration of 30% wt. as discussed previously¹⁹. The average gap between the particles in a stack, determined from the cryo-TEM micrographs, is ~13 nm. This is less than twice the estimated polymer thickness (17 nm). However, if the particles are not laying exactly edge wise in the cryo-TEM images they will appear thicker and obscure the polymer regions. Both polydispersity and thermal motion of the particles are expected to have significant effects on the cubatic phase. The sample used in the current studies had a polydispersity index of 0.2 in the particle radius as discussed earlier. A cubatic phase for slightly polydisperse thin circular discs is shown schematically in Figure 4a.

Particles bigger in diameter than the column can be incorporated with tilt. If a tilted particle occurs, it may be preferentially at the end of a stack where there is more space. This might favour the cubatic structure as shown schematically in Figure 4b rather than long columns. We have observed that the particles with different dimensions separate in different columns (not shown in the micrographs in the paper). In such case, whole columns with bigger particles are tilted to obtain a column width, W , that is smaller than D , the diameter of particle in the stack. One such example is shown schematically in Figure 4b. These different structures for a polydisperse

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Figure 3 Illustrations of irregular packing in columns. (a) Tilt in an entire column, (b) packing of small particles within a column, (c) tilt of individual particles with respect to its neighbours in a column and (d) in some cases, smaller particle get more space between its neighbouring particles and can rotate. Scale bar is 200 nm

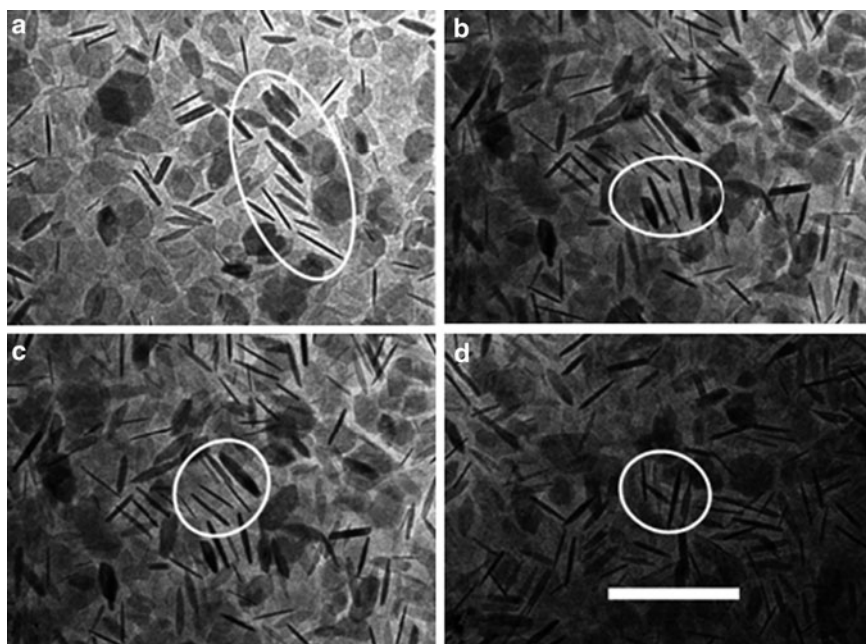
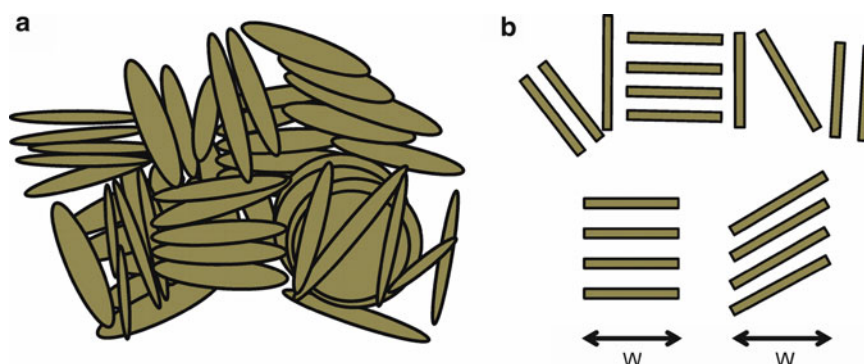


Figure 4 Diagram of cubatic phase for thin circular discs that includes particles with different diameters: (a). The domains that are locally orthogonal are shown schematically. (b). Means to pack bigger particles with tilt. If the width of the stack, W , is smaller than the diameter of the discs, D , then whole stack is tilted. Single larger or smaller particles can be inserted with tilt away from the average orientation in a stack



sample strongly alter the maximum packing density as discussed in a previous paper¹⁹. For perfect monodisperse hexagonal discs, the maximum packing fraction is 1. If one assumes that particles up to one standard deviation above the mean diameter will pack in columns of width defined by the mean diameter, then the maximum packing fraction for the size distribution, used in the current experiments, would be decreased to roughly 0.5. The ratio of volume fraction to maximum packing, ρ^* , would then be increased¹⁹. The effect on ρ^* would be even larger if we include the particles from the tail of the size distribution in Figure 1b.

It is very important to understand the effect of size shape and polydispersity on the ordered mesostructures in the design of materials with organization at nanometre length scale. This study provides a further indication of how polydispersity might alter the packing of discs and complements the observations of columnar phases^{3,4}. Previous studies of dispersions of disc-like particles using X-ray and neutron

scattering have not identified cubatic structure but the similarity of the scattering patterns to those of isotropic liquids would make this very difficult.

Conclusions

Locally order has been observed in cryo-TEM micrographs that resembles the computer simulations of a cubatic phase. Disc-like particles form approximately equiaxial stacks that tend to be orthogonal in adjacent domains. The structure is dominant in the thick regions. In thin regions, the sample is not thick enough to retain an equilibrium structure of several hundred nanometres and the regions may be perturbed by flow. Moderate polydispersity affects strongly on the packing of disc-like particles, it causes a large excluded volume and reduces the packing density. Incorporation of different

size particles in the observed structure indicates that the boundaries of different ordered phases with respect to concentration may be altered by a large factor. Further computer simulations would be helpful to account for the free energy of polydisperse colloids.

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