The Various States of Order in Monodispersed Sediments

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Colloidal particles sedimenting under gravity produce ordered layers in which the inter particle distance decreases with depth.

When a monodispersed suspension of particles is subjected to an external field, such as a gravitational field, and the particles are more dense than the surrounding suspension medium, then sedimentation occurs. Under appropriate conditions, the sediment so formed may be highly ordered, and will then show Bragg diffraction of light when the particle spacing is fairly close to the wavelength of the light used. The accurate determination of the angular position of the Bragg peak can be used to calculate the particle size, if the particles are touching, or to determine the centre-to-centre distance when the

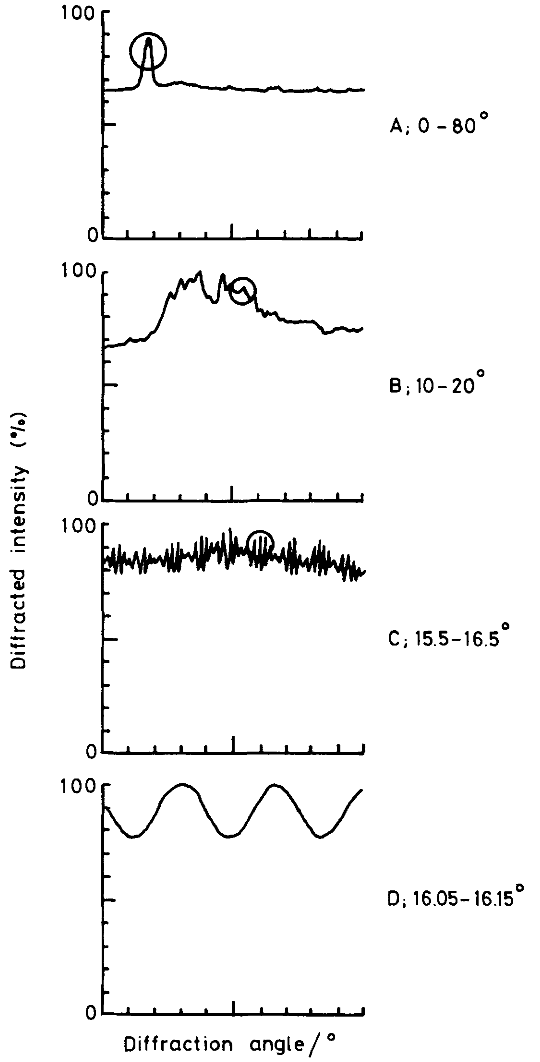

Figure 1. Curve A shows the Bragg peak for a poly(styrene) sample in a scan covering about 80° in the diffraction angle; B shows an expansion of the peak, the scan covering 10°; C and D show interference effects at the walls of the sample cell, C covering an overall angular range of 1°, and D a range of 0.1°.

particles are held apart by repulsive forces, and there are many reports relating to such measurements.[1—4]

During the course of an investigation of the kinetics of sedimentation of a nearly monodispersed silica suspension in ethanol, where the particles had an average diameter of 421 nm, it was discovered that the particle spacing was not uniform with height in the sediment, but decreased in an apparently regular way with increasing depth in the sediment, as judged by the changing position of the Bragg peak. There appear to be no references in the literature to such a variation, and it is believed that this subtle variation in Bragg peak position with depth has eluded detection up to the present time, because of the great precision required of the diffractometer, and the widespread use in the past of white light sources coupled to monochromators to provide the illumination. The choice of this type of light source greatly reduces the vertical resolution available, thus masking the slight height-dependence of the position of the diffraction peak.

A diffractometer has been constructed using a low-power helium neon laser as the light source, with a vertically adjustable sample holder, which allows the position of the Bragg peak to be measured as a function of height in the sediment. This diffractometer has great precision, as shown in Figure 1, where it can be seen that a resolution of about 1/1000 of a degree can be achieved, and this has made it possible to measure the variation in the particle spacing as a function of height, as shown in Figure 2, where a sediment of about 14 mm depth shows a roughly linear variation in the position of the diffraction maximum with height, from A to B. The linear region covers about 2° of diffraction angle, then a pronounced non-linearity sets in from B to C. Whilst there were no visible changes in the state of compaction of the sediment at the time the measurements were made, it is not possible to be certain that equilibrium had been attained in the system. Measurements on this system over a much longer time have been made using an acoustic technique,[5] and show very similar non-uniformity in the particle packing over periods of up to five months, so that it is probable that this is a genuine equilibrium phenomenon.

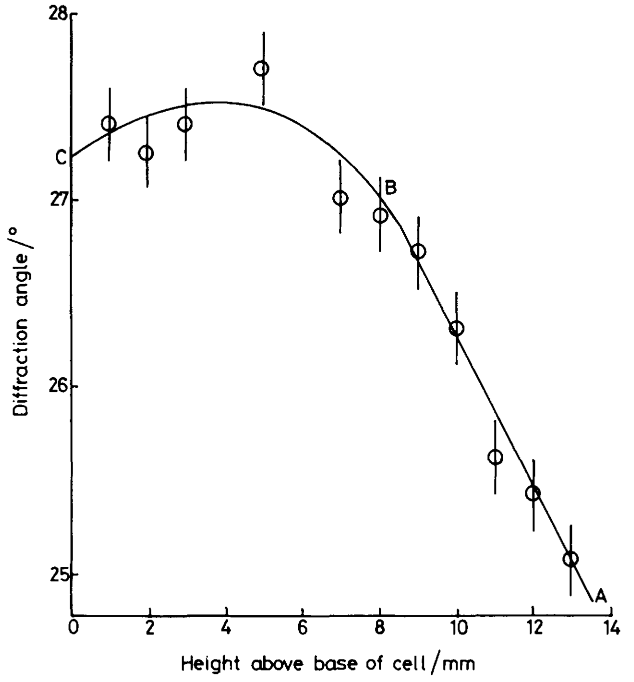

Figure 2 The Bragg angle for a silica sediment of diameter 421 nm, with a coefficient of variation of 8%, as a function of height above the base of the cell. From A to B, the change in diffraction angle is approximately linear with height, an increase in the Bragg angle indicating a decrease in the particle spacing. From B to C, the fractionation of the particles as they sediment gives an increase in interparticle spacing, because the biggest particles accumulate at the base of the cell. The slope from A to B is probably related to the 'softness' of the repulsion between the particles.

The silica particles are not completely monodispersed, having a coefficient of variation in the particle diameter of about 8%. With an ideally monodispersed sample (*i.e.* one with a coefficient of variation of 0%) it is expected that the monotonic increase in the Bragg angle shown between A and B would persist through to C. The observed reversal of slope between B and C is probably due to fractionation of the particles by size during the complex sedimentation process, with a higher proportion of the largest particles reaching the base of the cell first.

From the angular position of the Bragg peak, the particle spacing can be calculated if the refractive index of the suspension is known. The refractive index depends upon the volume fraction of the suspension, and as the present observations show, this varies with depth in the sediment. In previous papers on this subject,[1—3] this refractive index has been assumed to be constant (a reasonable assumption bearing in mind that it was not known that the volume fraction was a function of depth). It is not possible at present to calculate accurately the refractive index of the sediments in these experiments, and the results are therefore quoted only as Bragg peak positions. An estimate of the spacing can be made by making reasonable assumptions about the volume fraction in the sediment, and making no allowance for the variability of this quantity, the spacings calculated for the present sediments give values larger than expected if the particles were touching thus implying the presence of some 'soft' repulsion between the particles. This soft repulsion is likely to be electrostatic in origin, given that it is practically impossible to completely exclude water from the system. Even if there was no water present, the dielectric constant of ethanol is large enough to ensure some long-range repulsion in the case of charged silica sols.

The significance of these observations is three-fold. First, the variation in particle spacing can, in principle, be related to the pressure being exerted as a function of depth by the weight of sediment above the level at which the observation is made, and thus indirectly, to the force–distance curve for the interparticle interaction. In order to do this, the 'ideal' hard sphere contribution to the osmotic pressure should be deducted from the overall pressure, thus leaving the part attributable to the interparticle forces. An approximate calculation shows that the hard sphere contribution is relatively small in this system. Secondly, the slope of the graph of the spacing as a function of height gives an immediate means of assessing the 'hardness' of the repulsion term, with a large slope indicating a hard repulsion, and a small slope showing a soft repulsion (again, after allowance for the hard sphere contribution has been deducted). Thirdly, if an adsorbing polymer is added to the suspension, and the system is left to come to equilibrium, the variation in Bragg peak position with depth in the sediment will similarly give the force–distance curve for the interaction of the adsorbed polymer layers. The measurement of such force–distance curves is the subject of much current research,[6—8] and the present method appears to be a complementary approach to the more usual force-balance techniques currently employed for such measurements, though inconveniently large sediment depths might be needed to achieve the high compressional forces attainable with the force balance.

Whilst some sediments appeared to be quite uniform, for example the one on which the measurements in Figure 2 were conducted, others showed a visibly layered structure, this being particularly obvious when mixed solvents, such as benzyl alcohol–ethyl alcohol mixtures, were used. The layers often appeared to be alternately crystalline and glassy. In some instances, layers of crystalline material were adjacent to each other, but the crystal axes were oriented differently in these layers. Quite commonly in such cases, one layer had a 'palisade' structure, with closely packed crystals all orientated vertically, whilst in the adjacent layer (usually nearer the top of the sediment) the orientation was more random. Typically, the bottom layer was glassy, and showed no clear crystal structure. These phenomena need to be studied in more detail before clear conclusions emerge, but seem to indicate the great importance of kinetic factors, and particularly, the importance of nucleation in determining which phases are formed under the prevailing conditions. Since nucleation kinetics are very sensitive to the viscosity of the suspension, it may be inferred that the viscosity and its variation with volume fraction may be the governing factor in the explanation of these subtle phase effects. In this context, it should be noted that the particle flux is analogous to the rate of cooling in a melt or solution, and above a certain critical flux (or cooling rate) glasses are expected to be formed.[9]

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