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## Classification

Physics Abstracts

61.40 — 64.70K — 68.90 — 82.70

**Thin colloidal crystals : a series of structural transitions (\*)**

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**Résumé.** — Nous étudions des couches minces de cristaux colloïdaux formés de billes de polystyrène de diamètre  $1,1 \mu\text{m}$  en suspension aqueuse. Ces couches minces sont produites par le confinement des cristaux colloïdaux entre deux plaques de verre rapprochées, lesquelles, aux échelles colloïdales, se comportent comme des parois répulsives et parfaitement lisses. Dans le cas où les deux plaques de verre forment un dièdre, nous réalisons le passage continu entre deux et trois dimensions. L'observation directe au microscope optique révèle que ce passage est caractérisé par une série de transitions structurelles consistant en un changement du nombre de couches cristallines mais aussi en un changement de structures dans les couches.

**Abstract.** — We study thin layers of colloidal crystals made of polystyrene balls ( $1.1 \mu\text{m}$  diameter) in aqueous suspension. These thin layers are produced by confining colloidal crystals between two glass planes, which act as repulsive and perfectly smooth boundaries at colloidal scales. When the two planes form a wedge, a continuous passage from 2 to 3 dimensions is realized. Direct observation with an optical microscope reveals that this passage is characterized by a series of structural transitions consisting of changes in the number of layers and also in the structure of each layer.

**1. Introduction.** — Many experiments studying systems between 2 and 3 dimensions have been done with, for instance, multilayers of fatty acid molecules [1] or atoms adsorbed on graphite [2]. In the latter case, an important problem is the interaction with the periodic substrate. Using colloidal crystals for low-dimensional research has many advantages :

- the mono- or multi-layers of colloidal particles are made very simply by confinement between two solid boundaries ;
- at colloidal scales, the surfaces of the boundaries are perfectly smooth and rigid ;
- the observation of the microscopic structure of thin layers is easy with an optical microscope.

In 3 dimensions, the spherical colloidal particles form regular stackings, bcc or fcc, under certain conditions of density and ionic purity [3]. In a previous experiment [4], such crystals, made of rather small ( $0.1 \mu\text{m}$  in diameter) polystyrene balls, were confined between a glass plate and a glass sphere. A system of concentric dislocation loops was observed in this

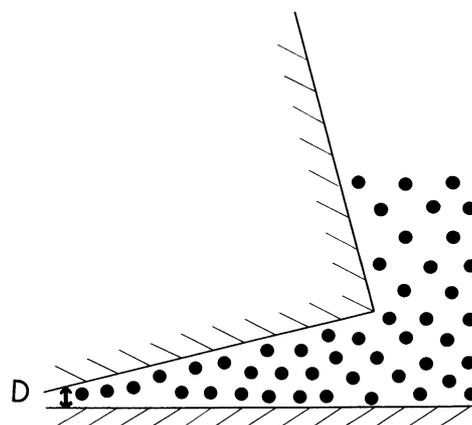


Fig. 1. — Principle of confinement of colloidal crystals between two plane glass boundaries (the real wedge angle is about  $10^{-2}$  rad).

geometry which corresponded to a series of transitions consisting in changes in the number  $n$  of crystalline layers (...  $n - 1 \rightarrow n \rightarrow n + 1$ ...). Using larger particles ( $1.1 \mu\text{m}$  in diameter) made resolution of the intralayer structure easier by allowing direct observations through an optical microscope and revealed the

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(\*\*) Laboratoire associé au CNRS.

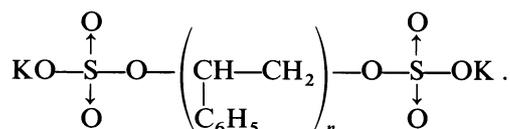
existence of intermediate transitions other than  $n \rightarrow n + 1$ , reported briefly for the first time in [5].

In the present article, we have simplified the geometry of confinement of colloidal crystals by using a variable dihedron (Fig. 1) formed between two glass planes. In this dihedron, the available thickness  $D$  increases continuously and regularly : we may observe the whole series of transitions simultaneously and measurements are easier. These structural transitions are characterized by the change in the number of crystalline layers and by the change in the structure of each layer.

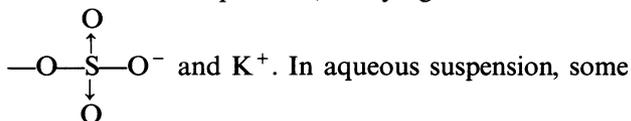
## 2. Preparation and characterization of the samples.

— The colloidal crystals that we used were made from polystyrene balls in aqueous suspension. These balls were prepared in the laboratory using emulsion polymerization [6]; the emulsifiers were SDS ( $C_{12}H_{25}SO_4Na$ ) and Triton X 100 (supplied by Merck) and the catalyser was  $K_2S_2O_8$ . The polystyrene balls were monodisperse (up to 2 % error) and their diameter ( $1.1 \mu m$ ) was measured with an electron microscope, the reference being calibrated polystyrene spheres ( $0.1 \mu m$ ) supplied by Dow Chemical.

The particles themselves are made up of tangled polymeric chains such as :



In aqueous suspension, the end of the chains located at the surface of particles, may get ionized into



of these sites are ionized and the proportion of ionized sites depends on several factors such as the temperature and the ionic strength of the solution. A conductimetric titration gave the maximum mean number of ionizable sites per particle (about  $10^6$ ); hence the mean distance between sites was about  $20 \text{ \AA}$ . In colloidal suspensions, negatively charged particles are surrounded by counterions and other different ions present in the solution. So the interactions between particles are mainly screened, repulsive, electrostatic ones. Following the standard procedure to decrease electrostatic screening, we poured the suspension into closed tubes where it came into contact with ion-exchanging resins. These resins replace ions in solution by  $H^+$  and  $OH^-$  ions and hence the interaction range increases and crystallites characterized by bright iridescence appear in suspension.

We took a few millimeters of the purified suspension which was left floating over the resins which had fallen down to the bottom of the tube and poured them into the experimental cell. At equilibrium in the cell, we measured the distance between adjacent particles obtaining results of the order  $2 \mu m$ ; thus

the distance between the surfaces of neighbouring particles was about  $1 \mu m$  which is near the value of the Debye screening length in pure water. The particle interactions may be changed by controlling the ionic strength of the solution (e.g. by adding salt) : however the number of ionized sites may vary at the same time as the screening length.

### 3. Experimental set-up. — 3.1 THE EXPERIMENTAL CELL.

— The cell used to confine colloidal crystals corresponds to the diagram of figure 2. At the end of the fixed tube T is glued a microscope slide L which is one of the two surfaces of the wedge. Together they form a container which can receive the suspension. The other surface of the wedge is rectangular ( $2 \text{ mm} \times 3 \text{ mm}$ ), made by cutting the optically polished base of a glass cylinder C. This cylinder is rigidly locked to a plate P which is adjusted by means of three Micro-Contrôle screws V (at  $120^\circ$  from each other). In figure 2, the dihedron of figure 1 is situated between the slide L and the base of the cylinder C. The screws V enable us to control the distance between the two surfaces : the gap thickness may vary from less than  $1 \mu m$  to several microns.

It is possible to form the wedge first and then to pour in the suspension : but it is then difficult for the balls to enter into the wedge because of the very small thickness available. Hence, in our experiment, we first poured in the suspension, allowed the particles to form a tridimensional crystal and then we formed the wedge. Everything must be kept very clean, for the slightest impurity can significantly change the screened electrostatic interaction.

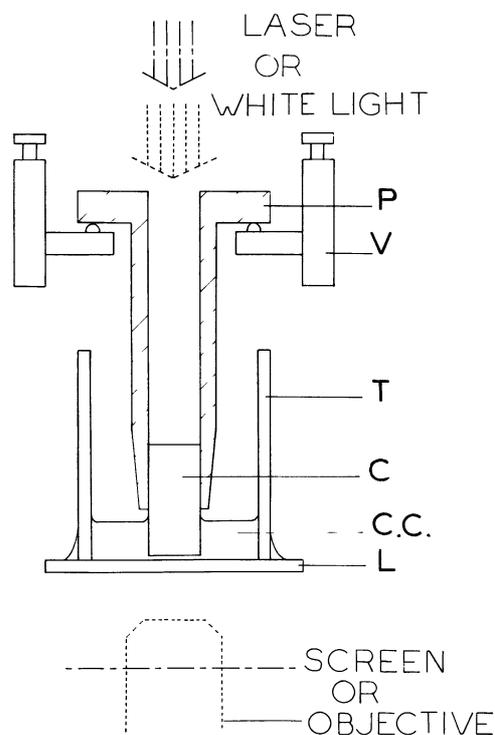


Fig. 2. — Diagram of the experimental set-up : a wedge is made between the fixed glass plane L and the base of the glass cylinder C, moving with the help of 3 screws V).

**3.2 OPTICAL SET-UP.** — The wedge is lit by a collimated beam of white light, incident perpendicular to the layers (Fig. 2). It is observed by means of an optical microscope operating by transmission (such as in Fig. 2) or by reflection and equipped with different objectives ( $\times 2.5$  to  $\times 40$ ). With the objective  $\times 2.5$ , we can see the whole wedge. When the balls are large enough ( $1 \mu\text{m}$  for instance), using the objective  $\times 40$ , we can see the image of each ball; we can detect the Brownian motion of the particles and observe their stackings in crystal lattices.

It is also possible to light the sample with a laser beam focused on a small region of about ten microns in diameter, in order to produce the diffraction pattern of monocrystalline domains.

**3.3 MEASUREMENT OF THE THICKNESS OF THE WEDGE.** — When equilibrium is reached in thin layers, we can measure the wedge thickness in the region where there are no particles (Fig. 3, strip 0). Monochromatic lighting of this region ( $\lambda = 0.546 \mu\text{m}$ ) creates interference fringes («water wedge»,  $n = 1.33$ ) which enable us to measure the wedge angle. The wedge thickness, in the region where the thin layers are, is deduced by extrapolation. In our study, the wedge angle was about  $10^{-2}$  rad (see sect. 5).



Fig. 3. — At point 0, the two surfaces of the wedge are in contact. The gap thickness increases along the X axis ( $\alpha = 1.1 \times 10^{-2}$  rad). Each strip is characterized by the number and the structure of the layers (Sample II).

**3.4 BEHAVIOUR OF THE SUSPENSION IN TIME.** — An important problem is the evolution of suspensions. In freshly prepared samples, electrostatic repulsions were strong enough and had sufficient range to make colloidal crystals occupy the whole available volume  $V$ . We observed the slow and regular increase in the concentration of particles at the bottom of the tube; after a day, this increase was about 20%. This is due to the change in ionic strength because of  $\text{CO}_2$  absorption and perhaps contamination from the glass boundaries. The screening length changes and particles sediment under gravity. After several days,

the deterioration of the samples was irreversible because of the growth of bacteria.

**4. Experimental observations.** — **4.1 OBSERVATION WITH A LOW-MAGNIFICATION OBJECTIVE ( $\times 2.5$ ): SERIES OF COLORED STRIPS.** — Observation with an optical microscope by transmission with the objective  $\times 2.5$  of low aperture ( $6^\circ$ ), revealed a series of parallel strips perpendicular to the X axis (Fig. 3). They are alternately either uniformly colored or made of differently colored domains (except for the first four strips which are all uniformly colored). The number of different colors in the multicolored strips increases with the thickness. Colors depend on the density of particles and hence on the interparticle distance, that is on the interaction range.

**4.2 OBSERVATION WITH HIGH-MAGNIFICATION OBJECTIVES ( $\times 20$  AND  $\times 40$ ): SERIES OF MICROSCOPIC STRUCTURES.** — With these objectives, we could determine the microscopic structures of the colored strips. These structures are nothing but stackings of an integral number of two-dimensional crystalline layers. The monocolored strips correspond to layers with a square structure (for instance  $2 \square$  in Fig. 4b and  $3 \square$  in Fig. 4c). The multi-colored strips correspond to layers with a triangular structure ( $3 \Delta$  in Fig. 4c).

*Remark :* One may notice that there are two ways to stack two triangular layers, usually written AB and AC, related to each other by a  $60^\circ$  rotation. For  $n$  triangular layers ( $n > 2$ ),  $2^{n-2}$  different stackings are possible. For instance for  $n = 3$ , the two different stackings are ABC, the beginning of a fcc compact structure, and ABA, the beginning of a hcp compact structure. In [7], we explain that the colors in the strips are due to interference between rays which cross the balls and those which do not; the phase shift is due to the difference in the refractive index of polystyrene and water which is  $1.59 - 1.33 = 0.26$ . The phase shifts may be different for different stackings and give different colors. For instance in the ABA structure, the light has to cross two spheres vertically whereas it does not in the ABC structure. Therefore the bicolored triangular-structured strip is a stacking of three layers, so this strip is called  $3 \Delta$ . When the layers have a square structure of for the case of one and two triangular-structured layers, only one stacking is possible and only one color is observed in these strips.

When the thickness increases from 0, the series of structures is :  $0 - 1 \Delta(1) - 2 \square(1) - 2 \Delta(1) - 3 \square(1) - 3 \Delta(2) - 4 \square(1) - 4 \Delta(3) \dots$  where, for example,  $3 \Delta(2)$  is a stacking of 3 triangular structured layers with domains of 2 different colors.

**4.3 DIFFRACTION PATTERNS.** — The symmetry of the Bragg spots in the diffraction pattern of each strip was in agreement with the structures observed with the microscope. Besides the Bragg spots, we observed a strongly fluctuating continuous background. This

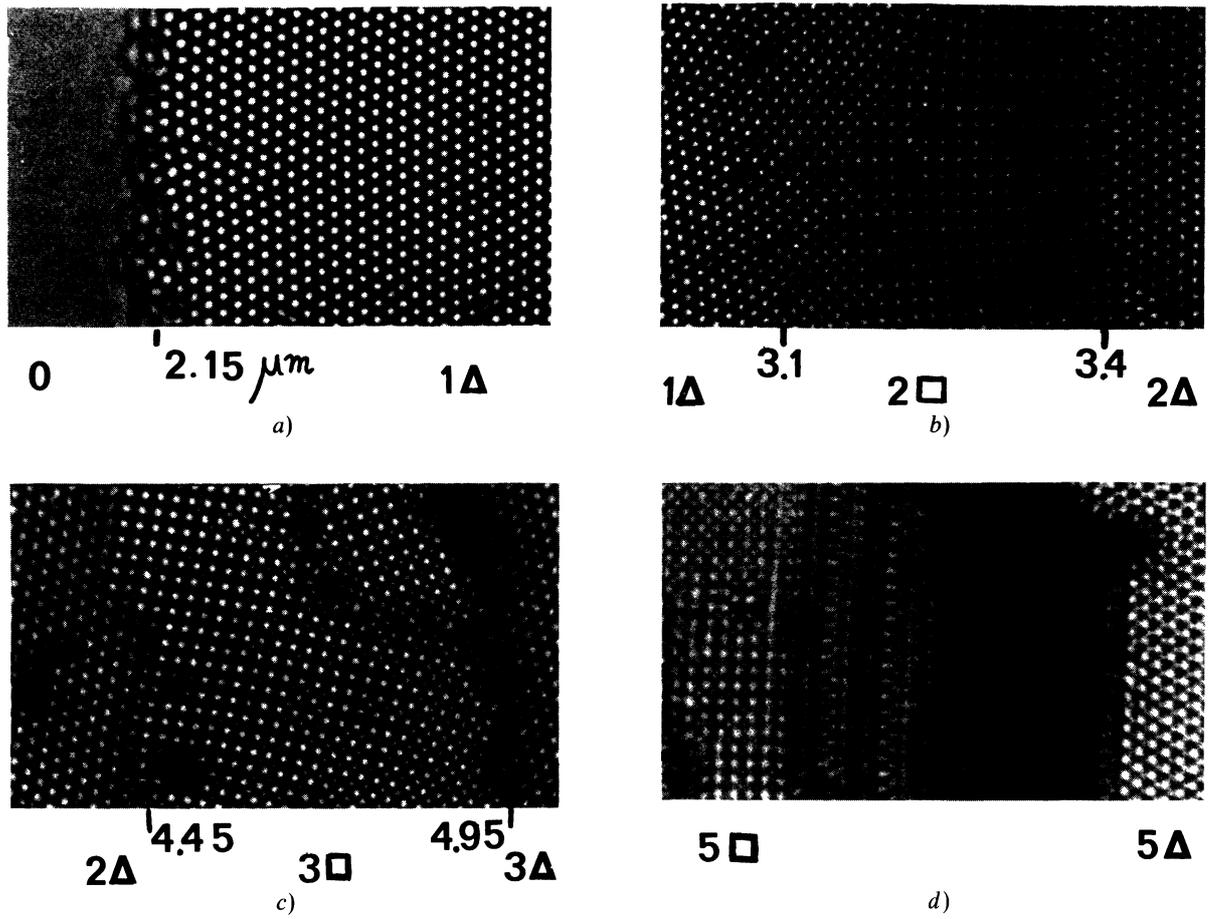


Fig. 4. — Observation of the microscope structure of different strips (Sample III). We give the gap thickness corresponding to the start of each structure in microns.

background is interesting for the dynamical study of multilayers and of colloidal crystals [8].

**4.4 OBSERVATION OF THE WALLS BETWEEN THE STRIPS.** — The walls corresponding to the  $n\Delta \rightarrow (n+1)\square$  transition, where both the number of layers and the structure in each layer change, are sharp (except for  $n=1$ ). We may slightly change the gap thickness with the help of the V screws and so move the walls; an important hysteresis phenomenon for these walls is observed. The  $n\square \leftrightarrow n\Delta$  walls, where only the structure in each layer changes, are broader and for  $n$  large enough ( $> 5$  in the samples) made up of « scores » (Fig. 4d) parallel to symmetry axes of both structures (square and triangular). Moving these walls is easier with less hysteresis.

**5. Measurements.** — For our samples, using photographs such as those shown in figures 3 and 4, we measured the following parameters (results are given in table I) :

— The wedge angle (cf. paragraph 3.3) : in sample I, its value is  $9.9 \times 10^{-3}$  rad, in samples II and III, its value is  $1.1 \times 10^{-2}$  rad.

— The thickness  $D_{\text{crit}}$  where the different structures

Table I. — For different samples I, II and III, values of : — the gap thickness  $D_{\text{crit}}$  of the wedge corresponding to the start of the different strips ( $1\Delta, \dots$ ) in microns ; — the width  $l$  of each strip, in microns ; — the average distance  $a$  between the spheres in each strip in microns. The error in these values is about 5%.

	I			II			III		
	$D_{\text{crit}}$	$l$	$a$	$D_{\text{crit}}$	$l$	$a$	$D_{\text{crit}}$	$l$	$a$
$1\Delta$	1.43	100	1.43	2.80	100	2.15	2.15	86	1.90
$2\square$	2.41	25	1.48	3.91	47	2.4	3.10	28	1.89
$2\Delta$	2.65	71	1.45	4.43	95	2.11	3.41	96	1.88
$3\square$	3.35	36	1.48	5.47	53	2.10	4.47	49	1.93
$3\Delta$	3.70	71	1.47	6.05	91	2.09	4.95	75	1.85
$4\square$	4.40	44	1.48	7.05	50	2.10	5.77	53	1.85
$4\Delta$	4.85	76	1.47	7.6	112	2.10	6.35	78	1.85

appear (Fig. 4). The error  $\Delta D_{\text{crit}}$  in this value is due to several factors :

- The boundary between different structures is not always well defined. For instance, at the  $1 \triangle \leftrightarrow 2 \square$  transition, there is an intermediate zone where the structure is difficult to determine because of strong fluctuations, especially vertical motions. Another example is the  $n \square \leftrightarrow n \triangle$  ( $n > 5$ ) transition characterized by a zone with « scores » (Fig. 4d).

- When the boundary is sufficiently sharp, it is usually not quite straight.

- The way we deduce the gap thickness, by extrapolation of an interference pattern, introduces a systematic error into the measurement of  $D_{\text{crit}}$ . The average relative error  $\Delta D/D$  in the measured value of  $D$  is about 5 %.

— The distance  $a$  between the particles at equilibrium and hence the surface density of particles in each layer. We measured  $a$  in monocrystalline domains of size  $m \times a$ , where  $m$  is an integer usually greater than 10. For an error  $e$  in the size of the domain, the error in the measured value of  $a$  is  $e/m$ . To increase the accuracy of this measure, the domains we choose have to be sufficiently large. On the other hand, the variation of the gap thickness in these domains is  $\delta D = (ma) \alpha$  and if too large, may give rise to appreciable variations in the distance  $a$  between the centres of the balls. In our samples ( $\alpha \sim 10^{-2}$  rad) possible variations in the surface density over a strip were difficult to detect and in table I, are given the mean values of  $a$  in different strips.

**6. Discussion.** — In spite of all the uncertainties, several remarks may be made :

— The strips with the triangular structure are about twice as broad as the strips with the square structure (table I, Fig. 3).

— The mean interparticle distance is the same in the square layers as in the triangular layers.

Therefore, each sample is characterized by the distance between adjacent particles in a layer (1.47  $\mu\text{m}$  in sample I for instance). This distance may be considered as an apparent diameter of the spheres.

— In sample I and III, this mean distance is equal to the gap thickness at which the particles can enter into the wedge, which is linked to the repulsive interaction between the particles and the glass planes. It is not true in sample II where the interaction range is greater. Hence, in the samples where the interaction range is lowest, the colloidal particles act as spheres

whose apparent diameter  $\phi$  is greater than the real diameter of the particles  $\phi_0$  measured with an electronic microscope (1.1  $\mu\text{m}$ ). The apparent diameter  $\phi$  depends on the sample and therefore on the interaction range. For instance this diameter is 1.45  $\mu\text{m}$  in sample I and 1.9  $\mu\text{m}$  in sample III. A good approximation is to consider colloidal particles as hard spheres of diameter  $\phi$ , greater than the real diameter  $\phi_0$  of the particles.

**7. Conclusion.** — This experiment has confirmed the existence of a series of structural transitions when colloidal crystals are confined between 2 and 3 dimensions. These transitions consist not only of a change in the number of layers but also a change in the structure of each layer (square or triangular). Another new fact is that, for most samples, particles act as hard spheres both in interactions with other particles and in interactions with the glass planes. The apparent diameter of the balls depends on the sample, particularly on the interaction range. In our next article [9], we propose a model of hard-sphere stackings to explain this series of transitions. Besides this problem, the experiment raises new questions of experimental and theoretical interest :

— The existence of bright colors, observed in the thin layers, with a low aperture objective, sets an unusual problem in optics. Because of the size of the particles, we have to take into account the phase shift when the light crosses the spheres, the diffraction by each ball and the diffraction by the crystalline periodic grating.

— The Brownian motion of the particles in the crystalline structures, is not all chaotic. The collective motions in the multilayers impose correlations between the particles. When the structure changes, at the monolayer-bilayer transition for instance, soft modes must appear and be detectable by studying Brownian motions.

— The study of defects in multilayers (particularly in the bilayers) is interesting in itself.

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