Two-dimensional aggregation and crystallization of a colloidal suspension of latex spheres

P. Richetti, Jacques Prost, P. Barois

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Two-dimensional aggregation and crystallization of a colloidal suspension of latex spheres

P. Richetti, J. Prost and P. Barois

Centre de Recherche Paul Pascal, Domaine Universitaire, 33405 Talence Cedex, France

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Résumé. — Nous présentons une étude expérimentale de cristallisation bidimensionnelle de sphères de latex calibrées, Browniennes en suspension dans l'eau. L'interaction, contrôlée par un champ électrique alternatif, s'avère attractive dans une large gamme de fréquence. Elle conduit à un phénomène d'agrégation de cristallites fractals. La dimension fractale mesurée $D = 1{,}74 \pm 0{,}05$ est en bon accord avec la théorie d'agrégation dynamique des amas. La fusion continue des cristallites intervient lorsque la fréquence augmente. La diffusion de la lumière montre alors l'existence d'une phase intermédiaire de symétrie hexatique.

Abstract. — We present experimental investigations of two-dimensional crystallization of calibrated Brownian spheres in water. The interaction monitored by an external AC electric field is attractive in a wide range of frequency and leads to a clustering of fractal crystallites. The fractal dimension of the structure is measured to be $D = 1.74 \pm 0.05$ in good agreement with the theory of dynamical clustering of clusters. Melting occurs upon increasing frequency and is continuous *via* a phase of hexatic symmetry as seen by light scattering.

1. Introduction.

Colloidal systems are currently under active investigation [1]. They present an interest on their own and also provide us with models which reproduce molecular phenomena in easily accessible ranges of length and time. One particularly interesting limit corresponds to suspensions of large (i.e. : micron range) but still Brownian objects. Indeed, a direct microscopic observation of their behaviour is possible whereas the system still obeys the fundamental laws of statistical physics.

We present here results concerning the two-dimensional field induced aggregation and crystallization of a suspension of calibrated latex spheres in water. After giving in the second section the description of the experimental observations, we discuss their signification in view of the current literature in the third one. In particular we investigate the fractal nature of the obtained texture, and comment on the relevance of our observation of a phase of « hexatic » symmetry between the crystal and the isotropic liquid.

2. Experimental observations.

Suspensions of polystyrene spheres in water are stabilized by repulsive electrostatic forces [2]. Each sphere bears a negative charge [3] resulting from the ionization of terminal end groups

present in the polymerization process or added by the adsorption of the emulsifiers. A careful de-ionization of water allows us to obtain crystals due to monopole-monopole electrostatic repulsion (for volume fraction $\Phi \approx 10\ \%$). In this note we study a different regime, in which the interaction between spheres is monitored by an external AC electric field; the system is in a fluid state in the absence of any external perturbation.

The suspension (2.10 ± 0.02 μm diameter spheres of polyvinyl toluene in water; COO^- end groups) purchased from Rhône-Poulenc was used after de-ionization of water with a mixed bed resin (Biorad AG501-X8). The solution was sandwiched between two conductive transparent slides (Fig. 1). The thickness of the sample determined by mylar spacers was typically set between 8 μm and 15 μm.

Prior to the application of any electric field, as already mentioned, the spheres'system is in a fluid phase, neither translational nor orientational order exist. When an AC voltage V is applied across the cell, for $V < 1$ V nothing dramatic happens. Beyond a threshold field $V_{c1} \approx$ a few volts (1.7 volts at 1 kHz for a 15 μm thick sample with a solid volume fraction $\Phi = 5\ \%$), the particles are suddenly attracted to the surfaces where they progressively aggregate. The attraction to the interface is fast (a few seconds and balistic) on the contrary the aggregation process results from the two-dimensional Brownian motion of single particles (aggregates of a few particles are practically immobile since two-micron spheres are at the upper limit of Brownian behaviour). A typical pattern exhibits the patchy aspect of fractal objects (Fig. 2). If one now decreases the voltage, the structure is stable down to values lower than V_{c1}. Below $V_{c2} < V_{c1}$ (0.8 volt in the above mentioned case) the particles diffuse back into the bulk of the system. A homogeneous suspension is recovered after a few minutes. Thus the process of attraction by the electrodes exhibits hysteresis. The same experiment performed at higher frequencies ($\nu > 5$ kHz) shows no attraction by the electrodes : rather the spheres tend to make small columns perpendicular to the plates; this regime will be discussed elsewhere [4].

The following of the note is devoted to the attractive regime. Once a two-dimensional structure is formed, one can monitor the interaction between particles by simply changing the frequency of the applied voltage. The observation shows that the aggregates assume a triangular structure (Fig. 2). If one irradiates with a laser beam a large area (i.e. : large number of clusters : a few mm^2 area) the scattering pattern reveals that the averaged structure is isotropic, and that no long-range positional order exists : indeed the scattering pattern consists of totally isotropic rings (in fact a series of 3 rings corresponding to the successive reticular rows of the triangular structure) which are broader than the optical resolution (the scattering pattern with no applied voltage is just the form factor of the spheres). If one focusses the laser beam down to a few clusters,

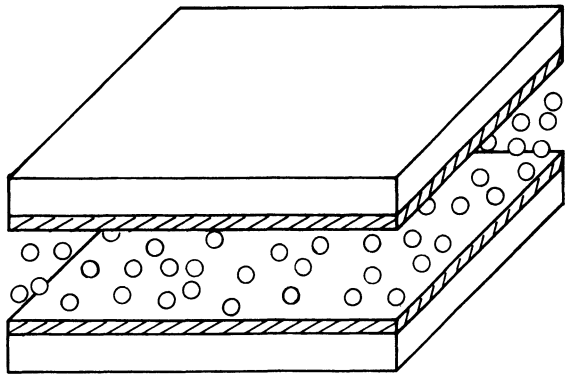

Fig. 1. — Experimental cell. The suspension is confined between two glass slides. Hatched areas represent the conductive coating by means of which the AC voltage is applied.

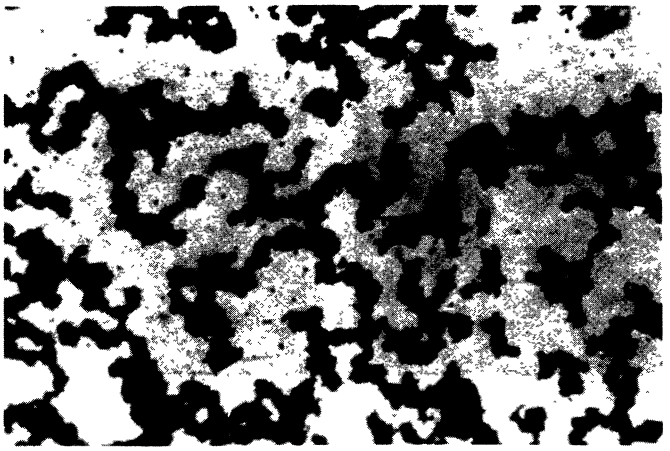

Fig. 2. — Microscopic view (× 500) of the aggregated crystallized phase. $V = 20$ V peak to peak, $\nu = 2.5$ kHz.

well defined spots replace the ring. One can often interpret the scattered image as the superposition of two patterns typical of the triangular lattice and rotated by a $\pi/6$ amount from each other. A direct microscopic observation reveals the existence of $\pi/6$ grain boundaries which explains the existence of the two patterns. Focussing down to single clusters is possible (typically 3 000 μm^2 for the largest) : one observes a « resolution limited » scattering pattern, which is easily identified as the Fourier transform of the triangular lattice (Fig. 3a). Fluctuations are seen with the naked eye both in real and Fourier space, which proves the thermal nature of the investigated state.

A subsequent increase of frequency leads to a dramatical change (Figs. 3b, 3c) : the spots which were essentially resolution limited become broad and one observes the pattern expected from a hexatic phase [5]. It should be noted that the structure is very mobile : a high degree of fluctuations is observed, the intensity of the fundamental (diffuse) spots vary significantly with time (over periods of the order of minutes) but the direction of the hexagon appears to be well defined on the same time scale. Figure 3c, obtained at higher frequencies than figure 3b shows a more disordered system, which still keeps the D_{6h} point group symmetry. Presumably many types of defects coexist in this phase, a direct microscopic observation is not easy because of strong thermal motions.

Eventually, increasing further the frequency ($\nu \approx 6$ kHz), the scattering pattern acquires full cylindrical symmetry and corresponds to a 2d (correlated) isotropic liquid (Fig. 3d).

It is important to remark that the spheres remain close to the interface so that the whole process is two-dimensional, except the last stage (isotropic liquid) in which the particles progressively diffuse in the bulk. As far as this kind of direct observation can tell, the frequency dependence is entirely reversible and continuous.

3. Discussion.

If the attraction of the spheres by the electrodes is easily understood in terms of image interactions, the attraction between the spheres in the two-dimensional regime is much less transparent. Indeed a purely dipolar interpretation would lead on the contrary to a repulsion (e.g. : parallel dipoles in a plane perpendicular to their common direction). The positively charged cloud of counter-ions (mainly H^+) obviously plays an important rôle. Due to their high mobility, H^+ ions in water can move back and forth at the frequency of the external field (up to a few

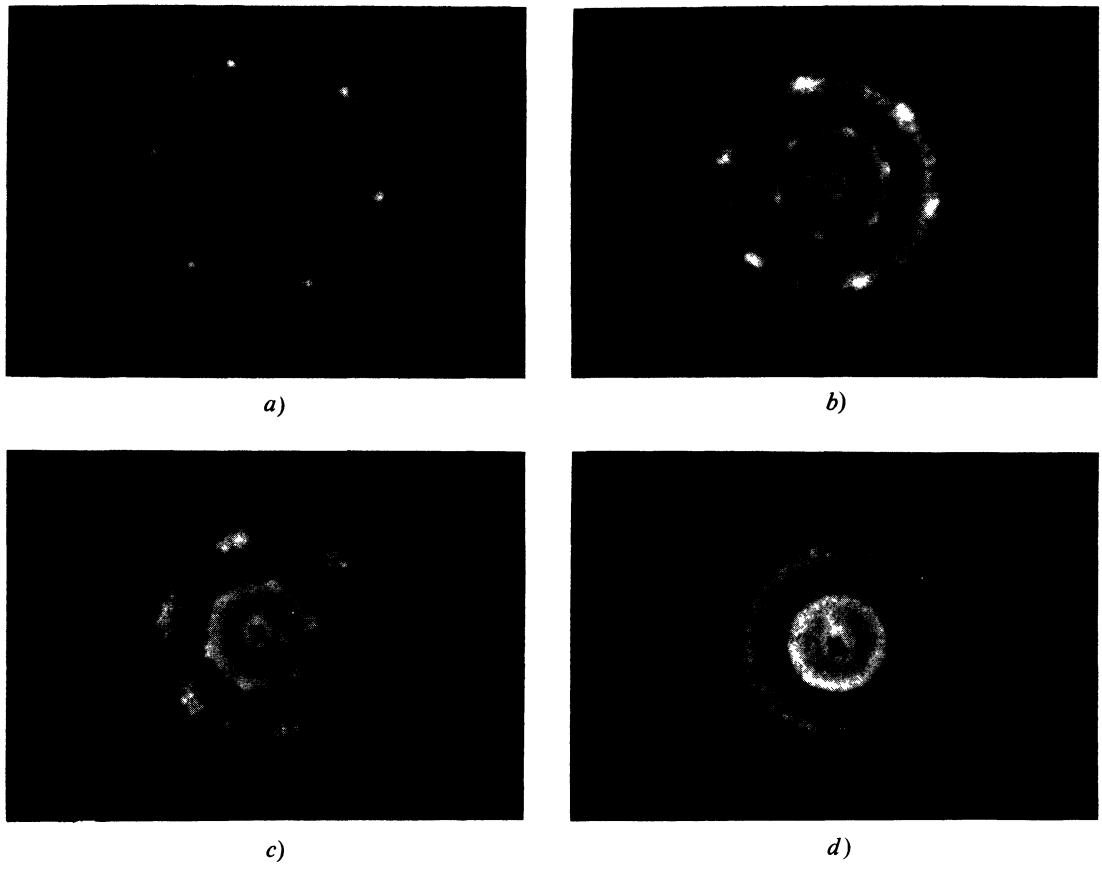

Fig. 3. — Light scattering patterns. He-Ne Laser, $V = 20$ V peak to peak. (a) $\nu = 2.5$ kHz : crystal like diffraction pattern clearly showing the six fold symmetry of the triangular lattice. The exposure times of the second and third rings are respectively multiplied by a factor 2 and 4 with respect to the first one to make them clearly visible on that view. The laser essentially irradiates a single crystallite since the sharpness of the quasi-Bragg peaks is comparable to that of the direct beam. Note that the contribution of other crystallite with rotated axis is visible and tends to complete the hexagone to a ring. (b) and (c) Hexatic like phase : (b) $\nu = 3.5$ kHz : close to the crystal; (c) $\nu = 5.0$ kHz : close to the liquid. The six fold symmetry of the cluster is still visible but the peaks are clearly diffuse. The exposure time of the outer ring is again twice that of the first one. Note that the third one has almost completely disappeared. (d) $\nu = 6.0$ kHz : liquid phase. Note the perfect cylindrical symmetry and the large width of the ring. The mean interparticle distance grows continuously upon increasing frequency (about + 15 % from a to d).

10^4 Hz). A net density of positive charges is thus forced between the particles. This could lead to an attractive interaction. The exact shape of this density and the average effect (attractive or not) in the vicinity of the conducting plane cannot be qualitatively predicted : a complete electrohydrodynamical treatment should be undertaken.

For short separations $L \leqslant \xi$ (ξ Debye screening length) the direct monopole-monopole repulsion should take over : the equilibrium distance between particles is indeed found to be appreciably larger than r (radius of the spheres).

The fractal character of the aggregates has been identified numerically by the study of the

relation between the number of particles in a given aggregate, and its gyration radius. Indeed, one expects a power law of the type

$$R \propto N^{1/D}$$

in which N is the particle number, R the gyration radius and D the fractal dimension ($D < d$ Euclidean dimension). A typical log-log plot is displayed in figure 4 : the existence of a single power law is clear. The exponents obtained for different magnifications and densities are gathered in table I. We find over one decade of radii

$$D = 1.74 \pm 0.05 .$$

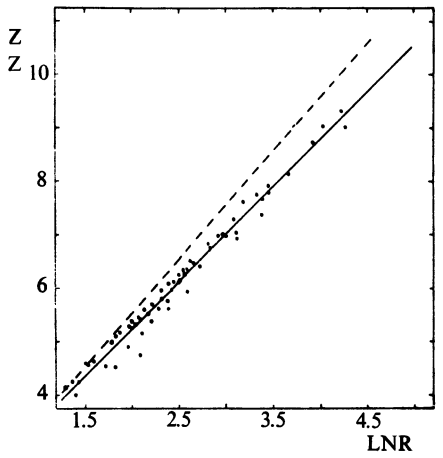

Fig. 4. — Log-log plot of gyration radius of clusters *versus* number of particles. The dashed line would correspond to $d = 2$.

Table I. — *Fractal dimension as a function of surface density.*

Fractal dimension	Surface density
1.70	0.33
1.69	0.34
1.76	0.39
1.78	0.40
1.75	0.37
1.77	0.34
1.77	0.32
1.70	0.34

These results are slightly but systematically higher than the 5/3 value of two-dimensional diffusion limited aggregation (DLA) [6]. This is not quite surprising since, in the DLA model, one single cluster is allowed to grow from a seed particle, whereas in our case a « homogeneous clustering » occurs by the aggregation of a collection of particles. The most appropriate model is the clustering of clusters developed by Kolb, Botet and Jullien [7] and Meakin [8]. Two regimes may be distinguished [9] : a low density one corresponding to flocculation in which scaling is observed with a small fractal dimension ($D \simeq 1.38$); a high density one ($\rho_{\text{eff}} = N_c(R)/S \simeq 1$ with N_c total number of clusters, R mean cluster radius, S total area) corresponding to the sol-gel transition. Close to this transition, fractal structures are again found, but with a larger dimension : $D \simeq 1.72 \pm 0.1$ [10]. The latter value agrees well with our experimental result, both numerically and conceptually. It is for instance very clear on figure 2 that our experiments were performed in a regime very close to the sol-gel transition. Note that a percolation analogy would lead to $D \simeq 1.8$ which we cannot rule out [11], and that two-dimensional non-Brownian aggregation gives significantly lower values [12].

Eventually we comment on the melting process. The current belief is that it can occur either continuously in two steps including the so called « hexatic » phase, or discontinuously directly to the isotropic state [13]. In some cases computer simulations suggest the existence of the hexatic phase [14, 15] but often favour a first-order transition [16]. The largest cluster we have investigated contains about 1 000 particles which corresponds to most computer simulations (except the very last one which bears on 10 864 particles) [16]. Our observations reveal a continuous change from a (limited size) crystal to an isotropic liquid, *via* a phase which possesses the hexatic symmetry (Figs. 3b, 3c).

One can wonder if our observation corresponds to a genuine phase or if the continuity results from a dense distribution of discontinuous behaviours due to the fractal nature of the overall structure. It is worth pointing out that this experiment has been performed on one of the largest clusters, in a rather dense case. The crystal pattern shows that since the peaks are practically resolution limited the cluster has essentially the size of the irradiated area. The existence of diffuse scattering outside the peaks reveals that this affirmation is not totally correct : a few smaller clusters contribute to the diffuse ring. However, our point is that these smaller clusters do not contribute to the sharp { 1,0 }, { 2,1 } and { 2,0 } peaks of figure 3a. The evolution towards figures 3b and 3c is obtained through a broadening of these peaks, which prompts us to think that we really probe the structure of the large cluster. The fluctuation level being very high (almost as high as in the isotropic liquid) and the phase very mobile, we think that we are dealing with a state of thermodynamical equilibrium. The average aspect of the pattern is indeed stabilized after a few minutes (the fluctuations may be such that sometimes a { 2,1 } spot may disappear for a few seconds, but it always reappears at the same location). The possibility of directly observing the six fold symmetry is obviously related to the limited size of the cluster. since angular correlations should die off algebraically in a 2d system.

Whether this phase corresponds exactly to the Nelson Halperin picture or not is beyond the scope of this note [17]. We remark that it is in agreement with the existence of hexatic B 3d liquid crystals [18], and also with recent work on two layers freely suspended smectic films [19].

As a conclusion we believe that the study of systems near the Brownian-non Brownian limit is useful to illustrate the behaviour of more conventional systems. In this note, we have analysed the most salient features of our observations : of course more quantitative work is required and will be performed. Let us point out that even this first approach may suggest new ideas on long studied systems : one of the problem in the understanding of the behaviour of Langmuir films in the absence of any plateau in the $\pi(A)$ curve (π surface pressure, A specific area) at the expanded phase-condensed phase transition. Just like in our experiment there is no coupling to gravity, and one can conjecture that the condensed phase tends to aggregate and leads to a fractal object. It is then clear that the $\pi(A)$ curve will have nothing to do with the three-dimensional $P(V)$ plateau, since the transition conditions depend locally on the cluster size.

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