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LETTER TO THE EDITOR

Programmed symmetry lowering in 2D colloids†

Yeke Tang‡, Rainer M Malzbender‡, R C Mockler‡, W J O'Sullivan‡ and James A Beall§

‡ Department of Physics, University of Colorado, Boulder, Colorado 80309-0390, USA
§ Electromagnetic Technology Division, National Bureau of Standards, Boulder, Colorado 80303, USA

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Abstract. We present a new experimental technique for producing model two-dimensional systems subject to external fields of arbitrary symmetry and variable coupling strength. An aqueous suspension of colloidal microspheres is confined to a single layer between two quartz flats, on one of which a pattern of eroded features is etched using electron-beam lithography combined with plasma etching. By varying the depth of the etched features the strength of the electrostatic wall-particle forces can be adjusted smoothly. We demonstrate the feasibility of the method and discuss possible applications.

When monodisperse synthetic colloidal microspheres are suspended in de-ionised water, the acidic end-group molecules at their surfaces dissociate, leaving a population of spheres having equal negative charges within narrow limits. The spheres and their associated counter-ion distributions interact via repulsive electrostatic forces which are typically approximated by a Yukawa-type potential [1]. If a colloidal particle suspension (CPS) is trapped betweeen parallel dielectric walls, the microspheres experience an additional repulsive wall-particle interaction when the film thickness is reduced to several μm and are eventually driven to form a two-dimensional (2D) distribution [2]. In principle, the statistical properties of single layer CPS can be measured with the same detail afforded by computer simulations. Consequently, single layer CPS bounded by *smooth* surfaces are of current interest in studies of 2D melting and crystallisation [3, 4].

There are, however, compelling reasons to study 2D colloids in spatially varying fields. As an example, consider a single layer CPS under the influence of a periodic electrostatic wall-particle field designed to mimic the effects of a solid substrate on an atomic monolayer. This combination might be a useful analogue of a rare-gas atom monolayer on an ordered substrate, with the advantage of yielding qualitatively and quantitatively improved experimental results.

In this letter we describe a novel method for subjecting 2D distributions of colloidal microspheres to electrostatic fields of selected symmetry, spatial resolution and amplitude, and we include experimental evidence which demonstrates the effects such patterned fields have on the ordering of 2D microsphere distributions. Specifically, we use electron-beam lithography combined with plasma etching to erode programmed features into one boundary surface of a CPS film. The success of this approach depends on the fact that the repulsive wall-particle field contribution to the free energy of the

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suspension decreases as a function of increasing wall separation. Thus, a spatially modulated wall-particle interaction can be imposed on a single layer CPS by etching patterns of μm scale pits or wells on the surface of one boundary. A well acts as an electrostatic particle trap, with a trapping strength which can be controlled by varying its depth and cross section.

To demonstrate the feasibility of the method, a variety of single layer CPS were formed between 3 mm thick fused silica optical flats in a parallel-plate film cell mounted horizontally on the stage of a metallurgical microscope. The films were trapped between 3.2 cm diameter and 1.25 cm diameter flats. The smaller flat is glued to a twin of the first and the cell is sealed by tightening alignment screws in order to press the two larger flats against a silicone rubber O ring; the space between the O ring and the periphery of the smaller flat forms a bulk CPS reservoir. The trap patterns were etched into the surface of the 3.2 cm diameter flat, which serves as the *upper* film boundary, to eliminate the possibility that gravitational settling might influence the results. Photographs of the microsphere distributions were taken in reflected light with exposure times between 4 and 8 s; this, along with the effects of diffraction, resulted in enlarged sphere images.

The method we use to pattern flats begins with spinning a 0.6 μm thick layer of positive electron-beam resist (polymethylmethacrylate) on the flat. The complement of the desired pattern is exposed on the PMMA using a computer controlled electron-beam lithography system. The PMMA is developed, a 50 nm thick Al film is deposited on the flat, and the PMMA is stripped off, leaving an aluminium mask of the desired pattern on the flat. The flat is then placed in a plasma etch system and the pattern is etched into the quartz surface. In the final step the Al is removed.

The etching parameters used in producing the patterns discussed here yielded 0.3 μm deep wells and channels, with 80° side walls and interior surface irregularities smaller than ± 0.1 μm, measured from scanning electron microscope photographs on a fused silica test flat. The depth of an etched area on the flat actually used in this work was subsequently measured with a surface profiler and found to be in agreement with the test flat result.

Three different trap patterns, each filling a 2 mm $\times$ 2 mm square field, were etched in the centre of the flat. The first consists of roughly circular 1.2 μm diameter $\times$0.3 μm deep wells arranged in a square array with a 2.8 μm lattice constant. The second is a narrow channel pattern formed from 2 mm long $\times$1.5 μm wide $\times$0.3 μm deep channels, separated by 1.5 μm barriers. The final, wide channel pattern, consists of 2 mm long $\times$3.0 μm wide $\times$0.3 μm deep channels separated by 0.5 μm barriers. In addition to the patterned regions a 0.3 μm deep thin film reservoir was etched which covered the 2 mm $\times$ 1 mm spaces between the patterns and a 0.5 mm wide band surrounding the outer periphery of the three-pattern grouping. Since the patterns and the thin film reservoir are all etched to a common 0.3 μm depth, the effective film thickness in the region of a trap or within the reservoir is $L + 0.3$ μm, where L is the nominal flat separation.

Suspensions of polystyrene microspheres with carboxyl (1.025 μm diameter; 1.6, 2.5 and 3.9 vol %) and sulphate (1.01 μm diameter; 2.3 vol %) head groups were formed in 18.3 MΩ cm water. The efficient dissociation of the sulphate groups, in contrast with the weak dissociation of COOH, ensures that the sulphate spheres are more highly charged.

To prepare a sample, the film space is first sealed against particle entry by reducing the flat separation to about 1 μm, a suspension of spheres is injected through the

rubber O-ring seal into the bulk reservoir and the cell is rocked gently for about 2 h to allow cleaning of the suspension by ion exchange resin contained in the reservoir. The flats are then pulled apart between 10 and 100 μm and the cell left undisturbed for several hours until a uniform distribution of microspheres fills the gap. By carefully adjusting alignment screws while monitoring an interference pattern, L is reduced to ≈ 2.5 μm (carboxyl spheres) or 3.0 μm (sulphate spheres). The microspheres within the gap bounded by the thin film reservoir assemble within minutes into a 2D triangular lattice crystal, as shown in figure 1. At this point the trap patterns have no observable effect on the particle distributions, but the etched thin film reservoir has stored a large 2D particle population which can exchange spheres with those in the patterned portion of the film. As L is reduced further, the particles redistribute under the influence of the patterned wall fields. 'Melting' is induced by carefully increasing L. This results in an increase in the vibration amplitude of microspheres in the patterned films and an eventual restoration of the 2D triangular solid when L is returned to its former value.

In the process of sealing the film against the O ring, the flats distort spherically about the cell rotation axis with the centre of the film becoming ≈ 0.5 μm thicker than the edge. The wedge that develops away from the centre ($\approx 10^{-4}$ rad) produces a wall-field gradient which generates a radial force acting to drive spheres into the film interior. Consequently, the patterned portions of the film and the thin film reservoir define a common chemical potential, but are decoupled from the outer bulk reservoir with which they are unable to exchange particles.

The qualitative effects of patterning on 2D CPS are apparent in figures 2 and 3. Figure 2 shows carboxyl spheres ordered by the square lattice pattern ($L \approx 1.5$ μm). At low number density (figure 2(a)) the crystal possesses large connected vacancy defects; these are largely eliminated at higher densities (figure 2(b)) where interstitial defects form which appear as crosses in the photograph. In these, a non-coplanar sphere slips into the space between four in-plane lattice spheres, increasing their average spacing in the process. Defect migration can be observed under the microscope as the film separation is increased, until eventually the crystal reorders into the triangular lattice phase.

The sulphate spheres exhibit similar behaviour, except that there is an almost complete absence of interstitials, and at lower densities a square crystal forms with a lattice spacing $\sqrt{2}$ times that of the encoded pattern lattice constant.

Figures 3(a) and (b) are photographs of narrow channel pattern carboxyl and sulphate microsphere 'strings', respectively, along with parts of the interface between the patterned films and the thin film reservoirs. (Although their spatial extent is much greater, these linear row crystals are similar to those formed by crossed laser beam electrostatic trapping [5, 6].) The strings show long-range translational order. Registration across the interface separating the reservoir crystal and the neighbouring channel fixes the linear lattice constant equal to the lattice spacing of the 2D triangular crystal. At the flat separations corresponding to the photographs ($L \approx 1.5$ μm and 2.0 μm for figures 3(a) and (b), respectively) the pattern field is strong enough to impose its 3.0 μm repeat distance on the particle strings.

There appears to be a qualitative difference in the effective interaction between sulphate and carboxyl spheres. While the former assemble in a distorted triangular lattice (body-centred rectangular), surprisingly, the carboxyl spheres prefer to align into strings across the channels and form a rectangular lattice. This suggests the existence of an attractive component in the interparticle force, at least in the presence of the channels. Aside from an increase in the transverse channel particle motion in

the former case, the ordering effects of the wide and narrow channel patterns are the same.

To summarise, with the increasing availability of image processing computers, experiments involving 2D suspensions of colloidal microspheres are likely to become important tools for studying statistical physics in two dimensions. Unlike atomic and molecular systems, the time and length scales of colloids allow the determination of more detailed physical quantities, such as higher-order correlations. In this regard they are similar to computer simulations. However, while the section of a 2D CPS sampled at a given time may contain up to several tens of thousands of particles, depending on the size of the illuminated region, the portion within which conditions of constant film thickness, chemical potential and average number density prevail can contain $\sim 10^8$ particles. Thus, they can be established as thermodynamic systems, and artefacts due to boundary conditions and sample size and shape are reduced. Finally, the ability to calculate the same quantities provided by simulations may permit experiments using 2D CPS to provide independent checks of the simulations.

In this letter we have shown the effectiveness of using electron-beam lithography and plasma etching techniques to produce spatially varying external fields in a 2D colloid as a means of lowering the symmetry of the system. This development will expand the class of problems in 2D condensed phase physics to which such colloidal suspensions can be applied. It has several advantages over multiple laser-beam methods of electrostatic field trapping [5, 6]. Large sample populations can be formed under fields having well controlled spatial resolution and amplitude. Qualitatively different patterns such as periodic lattices, fractals, quasiperiodic structures and random fields can be simply generated in software.

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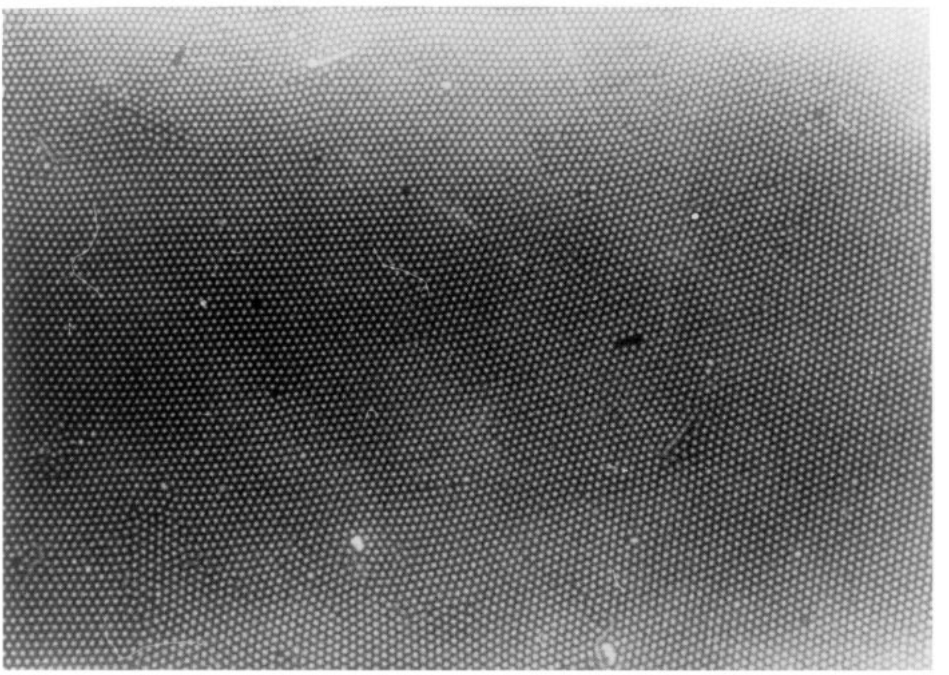
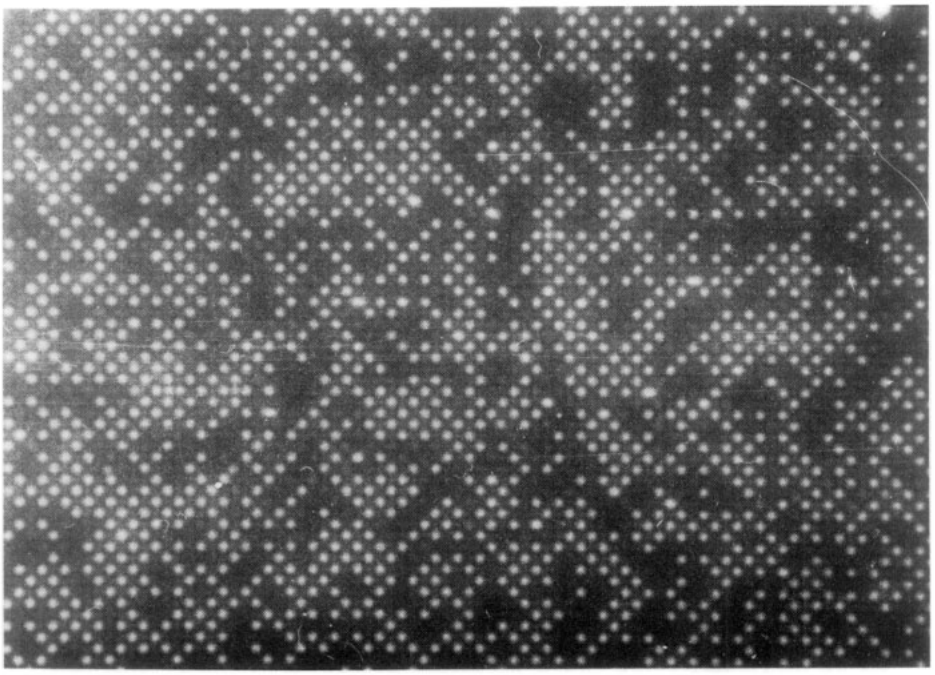


Figure 1. Photograph showing part of a sulphate sphere 2D crystal established in the thin film reservoir ($L \approx 3\,\mu$m; the nearest-neighbour sphere separation is $\approx 1.3\,\mu$m). While there are roughly 10^4 particles in the photograph, the actual crystal comprised over 10^5 particles.

[facing page 192]

(a)



(b)

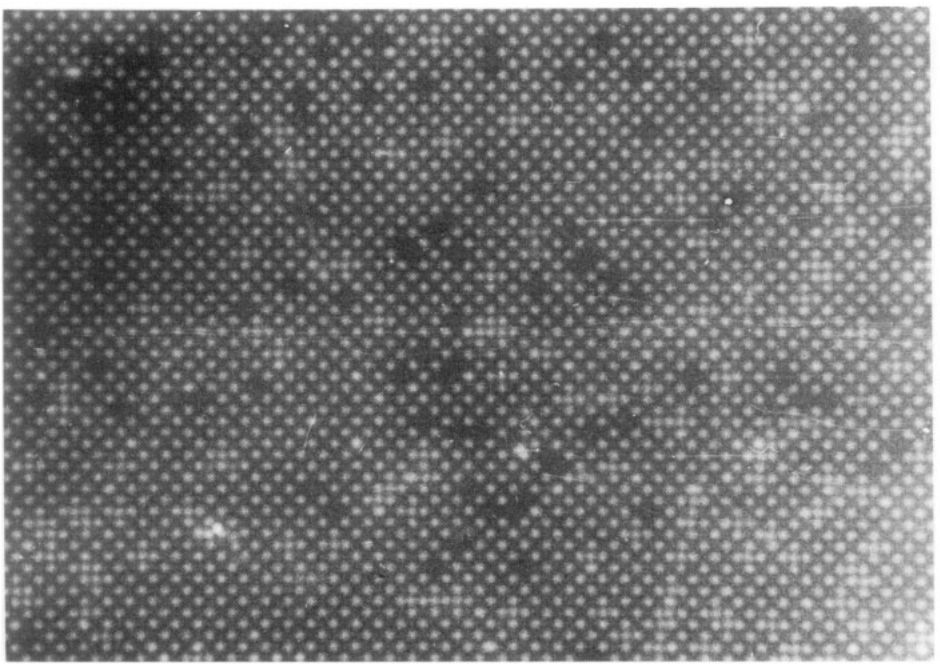
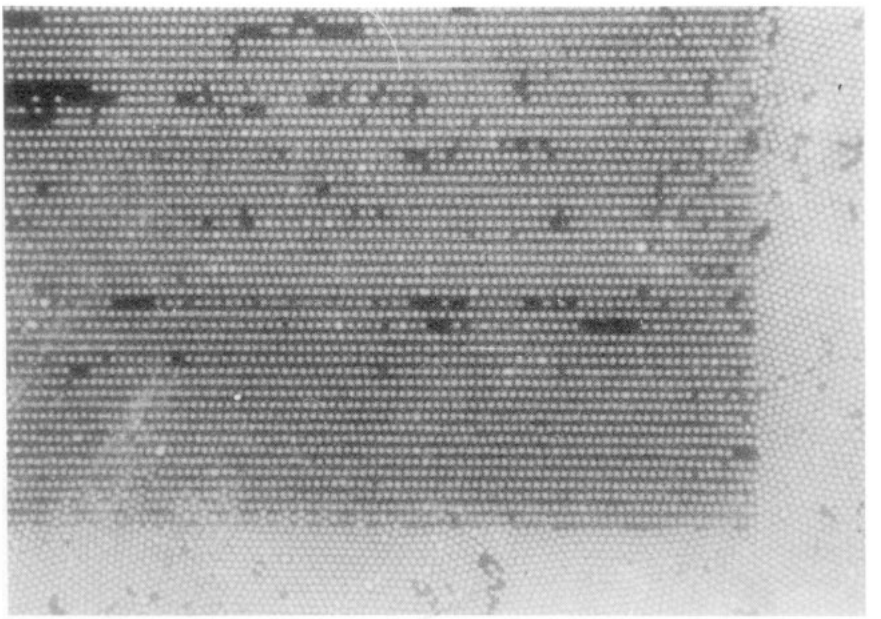


Figure 2. (*a*) Square crystal 'grown' at low sphere number density and (*b*) at higher number density. In both examples the crystals are formed of carboxyl spheres.

(a)



(b)

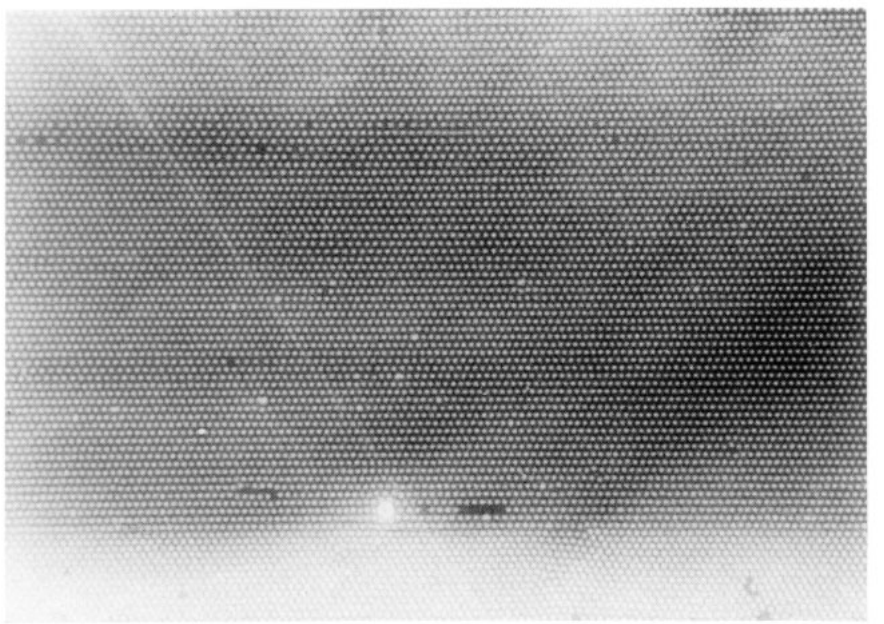


Figure 3. (*a*) Carboxyl sphere strings formed under the influence of the CHN pattern ($L \approx 1.5\ \mu$m; nearest-neighbour separation within the strings and in the surrrounding 2D crystal is $\approx 2.3\ \mu$m); (*b*) sulphate sphere strings formed under the influence of the CHN pattern ($L \approx 2.0\ \mu$m; nearest-neighbour separation within the strings and in the surrounding 2D crystal is $\approx 2.8\ \mu$m). Because of their large vibration amplitude, the microspheres in the 2D crystal within the thin film reservoir appear larger and brighter than those in the strings.