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# ADVANCED MATERIALS

Growing Colloidal Crystals

Surface Chemistry of Luminescent Silicon

Molecular Rectification in Polymers

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## Research News

# Growing Large, Well-Oriented Colloidal Crystals\*\*

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## 1. Introduction

Interest in the photonic properties of regular three-dimensional (3D) particle arrangements, or colloidal crystals, dates back to the first people who marveled at the beautiful iridescent colors of opals. Opals are naturally occurring colloidal crystals of silica spheres that formed over many years. In a test tube (model) colloidal particles can crystallize in minutes from sufficiently concentrated dispersions.

The ability to self-organize is a direct consequence of the fact that dispersions of colloids can form thermodynamic equilibrium phases. The colloidal particles, which can range in size between several nm to  $\mu\text{m}$ , travel through phase space towards the lowest free energy state not by atomic free flight, but instead by over-damped diffusion or Brownian motion.<sup>[1]</sup> The time and length scales that are accessible with colloidal dispersions open up possibilities to study first-order phase transitions that are unparalleled in molecular systems. Furthermore, the regular dielectric structures that can be made are built of units with properties that can be chemically modified and with a size close to the wavelength of light.

These features make colloidal crystals interesting for applications in which both the propagation and the spontaneous emission of visible photons can be manipulated.<sup>[2]</sup> Colloidal crystals belong to a class of materials that is sometimes referred to as soft condensed matter, because the crystals are characterized by low elastic constants and are therefore easily influenced by all kinds of external fields.

In the following we will briefly review the ways in which people have tried to manipulate colloidal crystallization either by manipulating the interaction potential or by using external fields. Subsequently, we describe the use of a polymer template and gravity to grow large, single colloidal crystals with well defined crystal orientations both in two and three dimensions.

## 2. Manipulating Colloidal Crystallization

Perhaps the easiest way to grow single colloidal crystals of  $1\text{ cm}^3$  in volume, is to use charged particles dispersed in a liquid with a low ionic strength. If the particles are small and/or the density mismatch with the solvent is small it is possible to grow large, single crystals by extremely fine tuning of the very low ( $\sim 0.001$ ) particle volume fraction.<sup>[3]</sup> This fine tuning is necessary in order to be at the volume fraction where nucleation is so slow that a small number of crystals have the time to grow to a large size. If such crystals are grown between charged glass walls separated by several mm, either single, body centered cubic (BCC) or, at somewhat higher volume fractions, single, face centered cubic (FCC) crystals are formed with their closest packed planes parallel to the wall. Such crystals have been used as optical filters, e.g. to reject the excitation beam in Raman scattering.<sup>[4]</sup>

Applying a steady or oscillatory shear to a dispersion has also been used to influence colloidal crystals or crystallization. Flow fields can both orient or melt crystals; however, large single crystals have not yet been formed in this way.<sup>[5]</sup>

Electric fields at zero or relative low frequencies can be used to induce electrophoretic mobility and in addition to cause hydrodynamic flow patterns that can force colloidal particles to form colloidal crystals. Fields perpendicular<sup>[6,7]</sup> and parallel<sup>[8]</sup> to the wall where the crystals are formed have been used. The crystal thickness is limited to a few crystal layers and the dimension parallel to the wall is not large. Intense light fields have been used to form 2D crystals by forcing particles with a higher refractive index than the solvent to crystallize on the intensity maxima of an interference pattern created by several laser beams.<sup>[9]</sup> In ad-

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dition, these high fields induce dipolar forces between the spheres.<sup>[9]</sup>

The largest 2D crystals, with hexagonal symmetry, have been formed through careful drying of a thin liquid film of colloids. Surface tension and liquid flow caused by solvent evaporation drive the particles into close packed arrangements. Under certain conditions 3D crystals up to 14 layers thick have been created using this method.<sup>[10]</sup>

The largest 3D crystals with a high volume fraction of particles and consisting of many particle layers have been formed under the influence of a gravitational field. For particles with a hard-sphere-like potential, random stacks of close packed planes form perpendicular to gravity, with a crystal width around a mm and sometimes with a height of several centimeters.<sup>[1,11]</sup> Random stacks of close packed planes are not true crystals, however, since they lack order in one direction. Even crystals formed from charged spheres can be compacted to high volume fractions by careful centrifugation.<sup>[12]</sup>

Large crystals with tunable crystal orientation and a high packing fraction of spheres have only been realized recently by a method described in the next section.

### 3. Colloidal Epitaxy

For particles in the colloidal size-range a glass wall, e.g., a microscope slide, is completely smooth. Conversely, interactions with a wall can be tuned by creating patterns with structural elements the size of the spheres. We created FCC lattice planes of holes close to the micrometer particle size of monodisperse silica colloids in a polymer layer with a thickness close to the particle radius. Subsequently, we let crystals grow on top of the template by gravitational settling from a dilute dispersion of particles that interacted through a hard-sphere-like potential. Contrary to what was mentioned above for hard-sphere sedimentation on a flat wall, pure FCC crystals were formed as large as the template and several thousand layers thick. Once the first layer of spheres has crystallized under the influence of the template it can act as its own template.

FCC crystals were grown both in the (100) direction and in the (110) crystalline direction (see Fig. 1).<sup>[13]</sup> In these two crystal growth directions no twinning could occur, contrary to for instance growth on the densest (111) plane. The use of fluorescent core-shell particles<sup>[14,15]</sup> and confocal microscopy made it possible to obtain particle coordinates with high accuracy, both close to the template, and several hundred layers deep inside the bulk.<sup>[13]</sup> Mismatching of the FCC lattice parameter of the template allowed for a quantitative investigation of defect structures in real-space as well. It has further been shown that crystals with different crystal orientation can be grown next to each other; these structures are important for the creation of waveguides.<sup>[13]</sup> Although the templates have until now been made with electron beam lithography in order to have the most con-

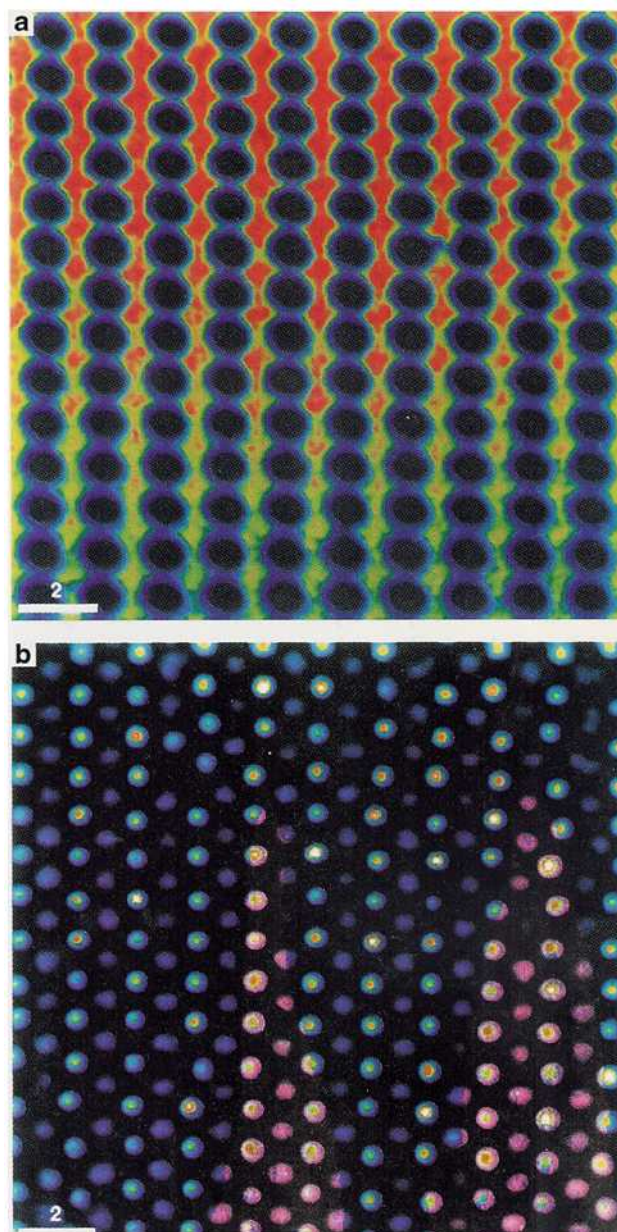


Fig. 1. a) Confocal micrograph of a fluorescently labeled polymer template with a pattern of holes in the symmetry of a FCC (110) plane. b) Confocal micrograph of a (110) FCC crystal plane after crystallization and 50 particle layers above the template of (a). The particle diameter is 1050 nm and the fluorescent core diameter 400 nm. Bars are 2 μm; the false 'rainbow' color table makes it easier to distinguish between intensity differences.

trol over structural features, simpler and cheaper methods are already in industrial use, e.g. in the manufacturing of compact disks.

At the moment we are extending the template-directed crystallization method to charged spheres by using templates with charged groups and to the drying procedure that was developed to create 2D crystals and 3D crystals of only several layers thick.<sup>[10]</sup> Although the controlled drying method creates crystals through a completely different

mechanism, the first results presented in Figure 2 demonstrate that in this case the template can also induce different, non-close-packed crystalline symmetries. The ability to create crystals with different symmetries, as shown in Figure 2, and the ability to grow crystals with just a small num-

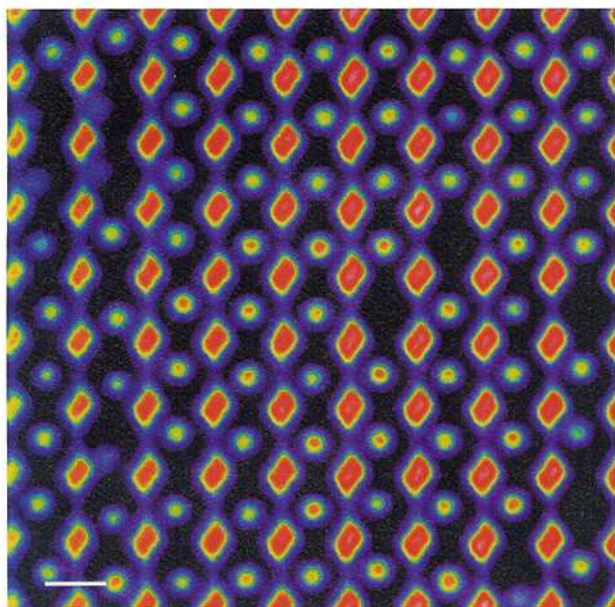


Fig. 2. Confocal micrograph showing a dried 2D crystal with square symmetry of fluorescent spheres, seen as round dots, induced by the fluorescent polymer template of which the 'diamond'-shaped objects are visible as well. Bar is 1  $\mu\text{m}$  and particles are the same as in Figure 1.

ber of layers will be important for the experimental characterization of photonic crystals from particles that interact more strongly with light than the silica spheres used in this study.

#### 4. Conclusion

Temperature, an important and convenient experimental parameter used to tune molecular crystal growth, is not suitable for the control of colloidal crystal growth. This is a

direct consequence of the size of the colloidal particles and their Brownian diffusion. However, the particle size provides ways to manipulate colloidal crystal growth that are impossible on a molecular scale. Template-directed crystallization in a gravitational field, or colloidal epitaxy, is a powerful example of the use of both an external field and the ability to tailor particle-wall interactions on a particle scale in order to grow large single colloidal crystals with well defined orientations. Furthermore, it has been shown that the template can also be used to direct 2D crystal formation through drying of a dilute suspension.

Several questions concerning the method still need to be looked into, for instance, it is not yet completely clear how large the role of the gravitational field exactly is and to what extent crystallization without it will be affected by a templated wall. Also, it is not clear whether the method will work for binary crystals, where colloids of two different sizes would need to be manipulated. Finally, it will be interesting to see which of the other methods mentioned in this short review can be used in combination with a template to achieve even greater control over colloidal crystallization.

- [1] B. Russel, D. A. Saville, W. R. Schowalter, *Colloidal Dispersions*, Cambridge University Press, Cambridge **1989**.
- [2] J. D. Joannopoulos, P. R. Villeneuve, F. Shanhi, *Nature* **1997**, *386*, 134.
- [3] T. Okubo, *Langmuir* **1994**, *10*, 3529.
- [4] P. L. Flaugh, S. E. O'Donnell, S. A. Asher, *Appl. Spectrosc.* **1984**, *38*, 847.
- [5] T. Palberg, W. Mönch, J. Schwarz, P. Leiderer, *J. Chem. Phys.* **1995**, *102*, 5082.
- [6] M. Trau, D. A. Saville, I. A. Aksay, *Science* **1996**, *272*, 706.
- [7] S.-R. Yeh, M. Seul, B. I. Shraiman, *Nature* **1997**, *386*, 57.
- [8] A. E. Larsen, D. G. Grier, *Phys. Rev. Lett.* **1996**, *76*, 3862.
- [9] M. M. Burns, J. M. Fournier, J. A. Golovchenko, *Science* **1990**, *249*, 749.
- [10] N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, K. Nagayama, *Langmuir* **1992**, *8*, 3183.
- [11] K. E. Davis, W. B. Russel, W. J. Glantsching, *Science* **1989**, *245*, 507.
- [12] W. L. Vos, M. Megens, C. M. van Kats, P. Boesecke, unpublished.
- [13] A. van Blaaderen, R. Ruel, P. Wiltzius, *Nature* **1997**, *385*, 321.
- [14] A. van Blaaderen, A. Vrij, *Langmuir* **1993**, *8*, 2921.
- [15] A. M. Verhaegh, A. van Blaaderen, *Langmuir* **1994**, *10*, 1427.