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Influence of the Evaporation Rate on the Packing Order of Polydisperse Latex Monofilms

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A new strategy to create well-ordered latex particle monofilms from polydisperse latex solutions was developed. Due to size-dependent segregation, the spherical particles assemble in grains with a uniform sphere size within each grain. The size-dependent segregation process can be deduced from the action of a single force, the lateral capillary force. A strong temperature dependence can be observed, and the process becomes evident when the substrate is cooled. The samples are characterized by scanning force microscopy. Finally, to prove the theoretical model, a computer simulation is performed, supporting the experimental results.

1. Introduction

Well-ordered latex particle films are interesting for various potential applications in optics,[1] data storage, and adhesive media.[2] They can also be used as calibration standards[3] as well as theoretical models for two-dimensional crystallization.[4] By using such a film as a template, well-ordered metal islands can be produced.[5−7] Standard preparation methods are based on electrophoresis,[8] the Langmuir−Blodgett technique,[9] spin-coating,[2] and the evaporation of a latex particles containing solution on a hydrophilic substrate.

Latex films have been examined by various techniques such as light microscopy, electron microscopy, and scanning probe microscopy. In-situ examinations of the nucleation and growth stage of these two-dimensional crystals have been undertaken with sphere sizes greater than 1 μm by visible light microscopy to determine the nature of the forces between the particles.[10,11]

The phenomenon of size-dependent separation of mixtures of two monodisperse suspensions has been studied systematically by Yamaki and co-workers, who prepared their samples by evaporation of the solution on a mercury surface and a glass substrate.[12]

The aim of many techniques is to minimize the sphere size and to obtain well-ordered latices with very small polymer spheres (<100 nm, e.g.). However, commercially available solutions of this size order are usually polydisperse; i.e., they contain spheres of a certain size distribution. With spheres in the sub-100-nm range, the size distribution usually gets as high as 10% or more. The consequence is a poor packing property resulting in a disordered layer.

By improving the preparation method of Micheletto, who prepared his samples by evaporation of a suspension on a substrate that was fixed on a Peltier cell to keep out any spatial thermal gradients,[13] we are able to control the speed of evaporation by varying the substrate temperature. At low evaporation rates we could observe a much better ordered monolayer from a polydisperse suspension due to size-dependent segregation of the particles. The packing order of the obtained samples was characterized with the scanning force microscopy (SFM) in the tapping mode. A computer simulation was carried out to model the size-dependent segregation procedure of the polydisperse polymer spheres.

2. Theoretical Background

There are three kinds of interparticle forces governing the packing of two-dimensional latex aggregates: lateral capillary forces[14−16] (LCF), flotation forces,[10,16] and convection forces.[10,17,18]

Additionally, an electrostatic force exists when the particles are electrically charged. This Coulomb force is repulsive and hinders the particles forming aggregates in the solution. Since it is a short-range force compared with the other forces, its effect on the film formation is only weak.

The film formation starts when the water film becomes as thin as the particle diameter. The LCF acts solely on particles protruding out of the water surface. Due to meniscus forming between two particles, strong capillary forces arise. Their lateral projection drags the particles together. The LCF is a relatively long-range, attractive force. Its dependence on the distance r between two particles can be expressed through a modified Bessel function,[14] for which a simple asymptotic approximation can be found[15,16]

$$F_{LC} \propto 1/r$$

The flotation force is acting on spheres that are floating on the water surface. With decreased particle size (below 10 μm) this force becomes negligible.[10,16] The convection force is similar to the LCF in its effect but is based on a different mechanism.[10,17] The formation of an aggregate causes a local imbalance of the water film height. At

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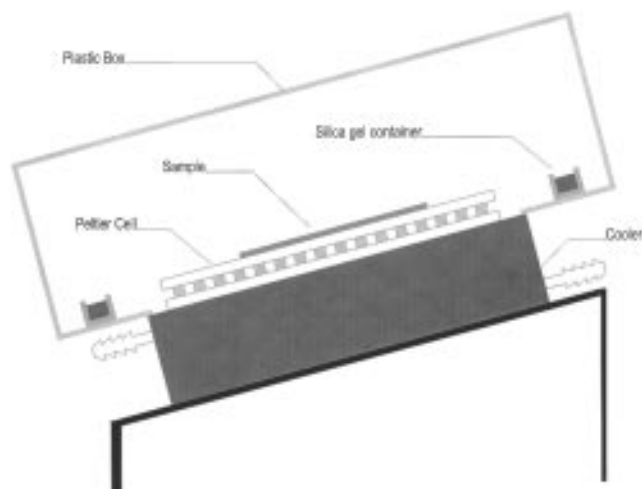
Figure 1. Scheme of the preparation chamber used for the experiments. The substrate is fixed on a Peltier cell that is countercooled by a water cooler. The Plexiglas cover reduces air perturbations and contamination.

already formed aggregates, the water level between the spheres is rising because of the vertical capillary force. When the water evaporates, it has to be replaced by surrounding water, so that a water flux toward the already existing aggregate carries further particles. The convection force on the particles can be deduced from basic hydrodynamic considerations and shows a $1/r$ proportionality like the LCF. Thus, it is difficult to determine whether the LCF or the convection force is dominating the aggregation process.

Finally, the Brownian motion has to be taken into account. Due to the viscosity of the water, especially in a thin layer, this motion is slowed down significantly.

Our approach to control the evaporation velocity is to decrease the temperature. As is well-known, the evaporation rate of water is equivalent to the vapor pressure, which is exponentially dependent on the temperature:

$$p \propto e^{-W/RT}$$

where W represents the molar evaporation energy. For example, the evaporation rate at 2 °C is $^1/_{10}$ of the evaporation rate at 25 °C. The decrease of the Brownian motion of the particles in the water is negligible as the thermal energy of the particles changes only by 8%.

The convection force is directly dependent on the evaporation rate, so it will be decreased by the same factor,

while the LCF as the only additional acting force is not affected by the temperature in the considered range.

3. Experimental Section

Our experimental setup consists of a Peltier cell with a temperature controller surrounded by a small Plexiglas container to keep out external air flow and contamination (Figure 1). The volume of that box is about 300 cm³. The setup is similar to that described by Micheletto et al.[13] However, in our setup the temperature can be precisely adjusted. It is worth mentioning that at low temperatures of about 2 °C condensation from the ambient air becomes greater than the evaporation from the solution; thus it is necessary to control the air humidity inside the preparation chamber. For this purpose, some small containers filled with silica gel were placed around the preparation zone to avoid high humidity originating from the evaporation process. The chamber can also be floated with nitrogen gas. The Peltier cell is countercooled with water to prevent any vibrations. The substrate is fixed on the cold side of the Peltier cell. The useful preparation area is about 2 × 2 cm. The whole system is tilted by about 10° such that the evaporation process starts from the top of the substrate. The temperature can be controlled in the range of 2–25 °C with a precision of ±0.1 °C. The Peltier cell is the most effective way to minimize spatial thermal gradients on the preparation area. Together with a carefully cleaned substrate, this method is suitable to achieve a very homogeneous evaporation.

Silicon is used as a substrate. A silicon slide is first cleaned with Milli-Q water (15 min, ultrasonic bath). To obtain a hydrophilic surface, the sample is placed in a mixture of NH_3 solution (25%), H_2O_2 (40%), and Milli-Q H_2O in a ratio of 1:1:5, for 60 min at 82 °C. All chemicals are in HPLC grade. Finally, the silicon is carefully rinsed with at least 2 L of Milli-Q water. The substrate is kept under water and used within 3 h after cleaning.

A droplet (20 μL) of the suspension is spread on the dried, precooled substrate. Since the substrate is tilted, a thin water film forms and the residual water forms a droplet at the lower side of the substrate which can be easily absorbed with a piece of filter paper. The concentration of the suspension is not critical. As a rule of thumb, a 1% solid concentration will fit in most cases.

We used a latex suspension with a mean diameter of 80 nm and CV = 15% at a solid concentration of 1% as the polydisperse system, and a suspension with a mean diameter of 220 nm and CV < 2% as the monodisperse system.

Preparations are performed at different temperatures from 2 to 20 °C. Depending on the temperature, the evaporation process takes up to 2 h to complete.

The samples were characterized by SFM. Because the operation in contact mode led to the destruction of the soft samples, we used the instrument in the tapping mode. A commercial SFM (Dimension 3000, Digital Instruments) was used together with silicon tips (Nanosensor) having spring
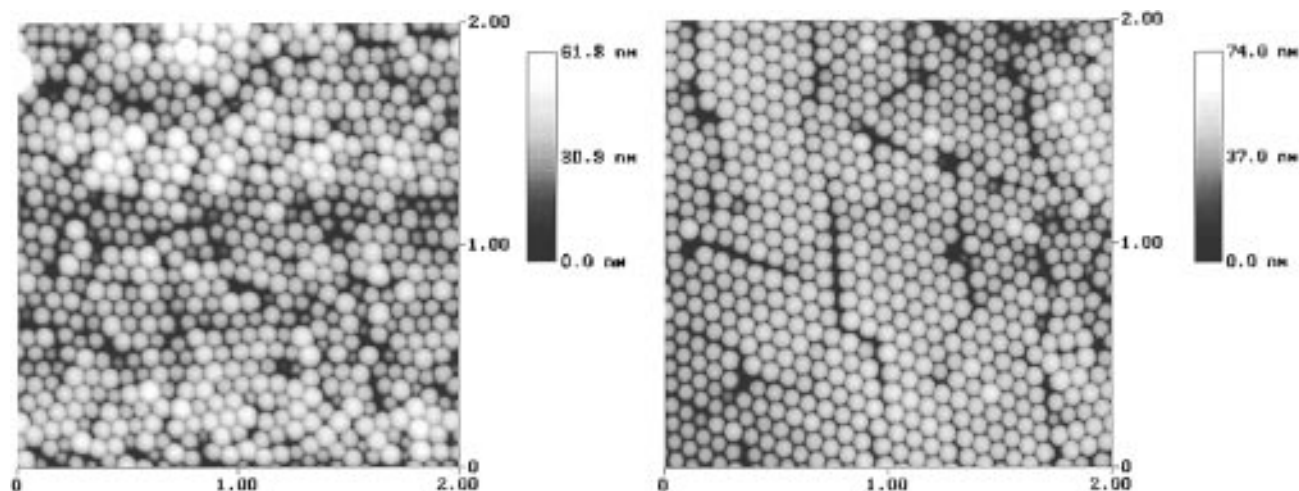
Figure 2. SFM micrographs (2 μm) of a polydisperse (CV = 15%) latex film prepared at 20 °C (a), and 2 °C (b). The improved packing order at the low temperature is obvious.
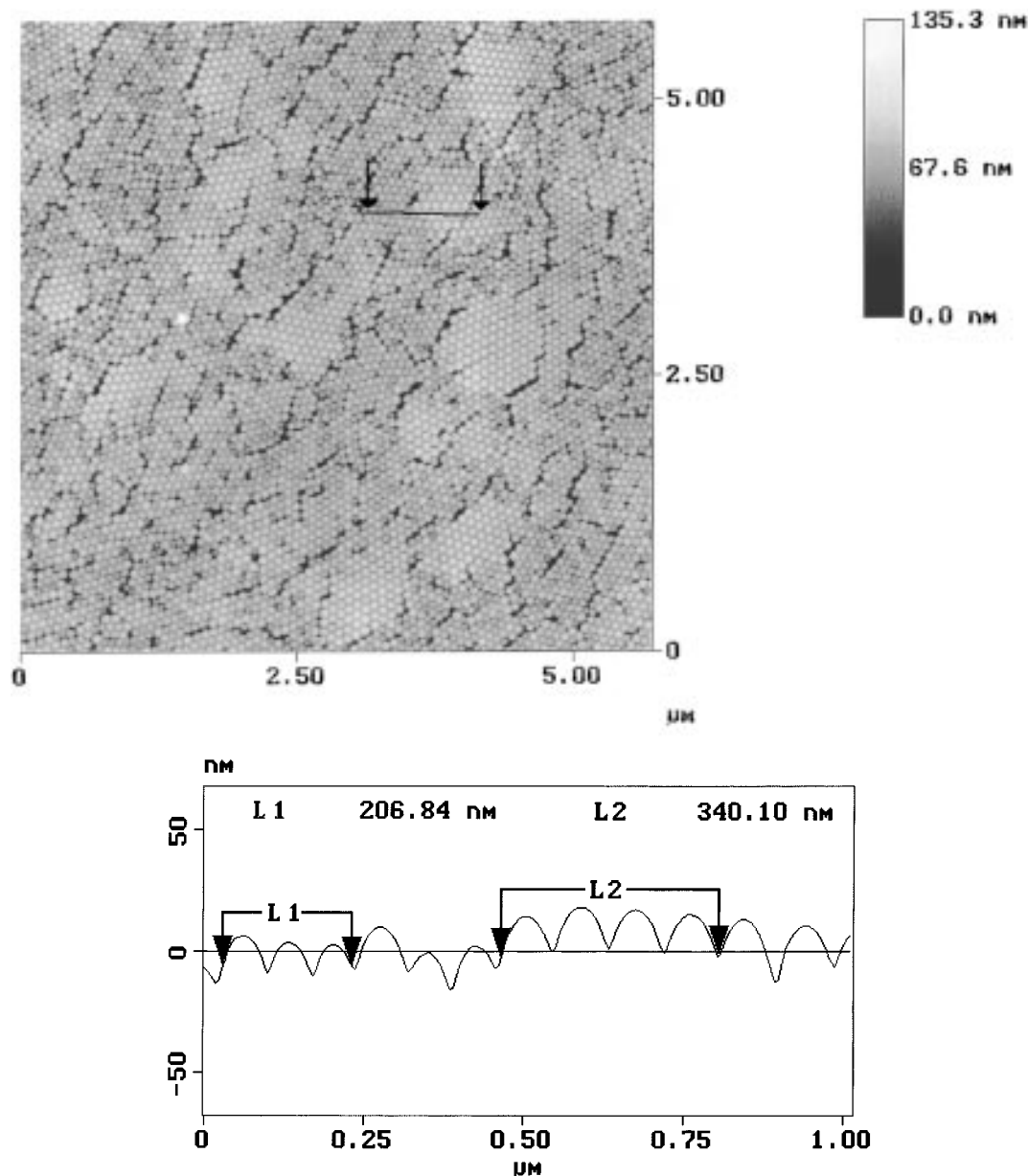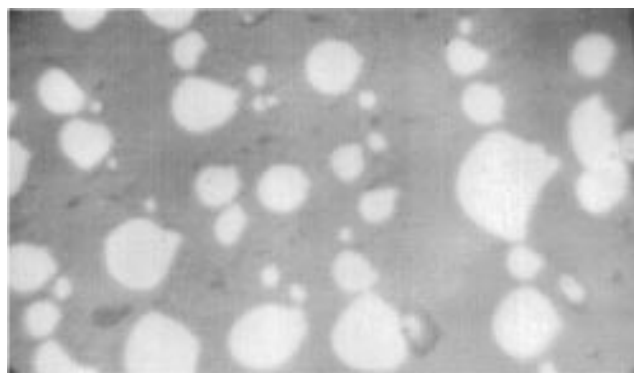
Figure 3. SFM micrograph (a) of a latex film prepared at 4 °C. The particles form grains containing spheres of a uniform size. The black line indicates where the height vs distance chart (b) is taken from. The chart shows the different sphere sizes in different grains. Within two grains the sphere sizes are measured. L_1 and L_2 denote the overall width of tree spheres in grain 1 and four spheres in grain 2, respectively. The single sphere sizes result from this measurement: $d_1 = 69$ nm; $d_2 = 85$ nm. The height values are not evaluated here.

constants of 30−50 N/m and quality factors of 300−500 at a resonance frequency in the range from 300 to 365 kHz.

4. Results and Evaluation

Figure 2 shows SFM pictures of 2 μm scans performed on samples prepared at 2 and 20 °C. As can be easily seen, the sample prepared at 2 °C (Figure 2b) exhibits a higher degree of order than the other one (Figure 2a). In the 5 μm scan, the granular structure of a sample prepared at 4 °C is easy to observe (Figure 3a). A height vs distance plot shows the unique sphere size within each grain (Figure 3b).

A light microscopic picture (Figure 4) shows that only about three-fourths of the area of the substrate is covered with a monolayer. However, this monolayer is partially interspersed with areas which are not covered. We believe that such regions are due to ruptures of the water film during evaporation. We observed different sizes of these regions on different kinds of silicon; thus they may be caused by surface roughness. An SFM measurement

Figure 4. Optical micrograph (1 mm) of a latex film prepared on silicon. The bright spots represent the substrate; the dark areas represent the monolayer.

acquired at a film−substrate border shows the film height to be equal to the sphere diameter (picture not shown here).

To obtain a quantitative result, SFM images were taken
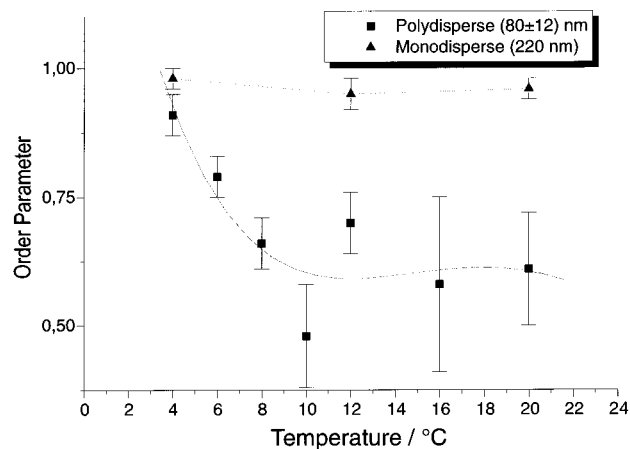
Figure 5. Order parameter vs temperature plot. The packing order of the polydisperse latex film is strongly improved by low temperature, while the packing order of the monodisperse latex is not affected.

from samples prepared at 4, 6, 8, 10, 12, 16, and 20 °C. Three pictures have been taken at random spots for each sample. To numerically evaluate the results, a computer program based on the algorithms proposed by Yoshida et al.[19] was applied on the SFM images. Simply spoken, this program counts all direct neighbors for each sphere and divides the number by 6. Finally, the mean value of all the calculated values is determined. An order parameter of 1 represents a perfect close-packed aggregate; a value of zero represents a perfect statistical order in which there is no next neighbor ordering. In a dense-packed statistical order any sphere should have about three neighbors, so we expect a value of 0.5 for this case. The order parameter was calculated and plotted vs temperature (Figure 5). At the lower temperatures, a strong improvement of the order parameter can be observed. Obviously, the effect of improved ordering is caused by the size-dependent segregation of the particles. We also performed experiments with spheres with a smaller size distribution. In these experiments, no effect of the temperature on the packing order can be observed.

5. Discussion

The mechanism of size-dependent segregation is based on one dominating force which is the LCF.[12] When the water film becomes as thin as the diameter of the largest spheres, these start to protrude the surface, and the LCF acts only on these spheres. At first, the large spheres form aggregates that act as nuclei for further crystallization. During further thinning of the water film the smaller spheres protrude out of the surface and start to move toward the already existing aggregates, or start to form new aggregates. As mentioned above, it is difficult to distinguish between the LCF and convection force, since both forces are $1/r$ dependent. However, the convection force should not contribute to the size-dependent segregation process, since it acts only when the aggregates have already partly formed.

To prove that only the LCF is necessary to cause the effect of size-dependent segregation, we performed a computer simulation which accounts in addition to the Brownian motion only for the LCF. As simulation parameters the size distribution of the spheres and the evaporation speed of the water can be changed. The iterative simulation algorithm consists of two stages which are performed within each iteration step. In the first stage, according to the Brownian motion, a random displacement
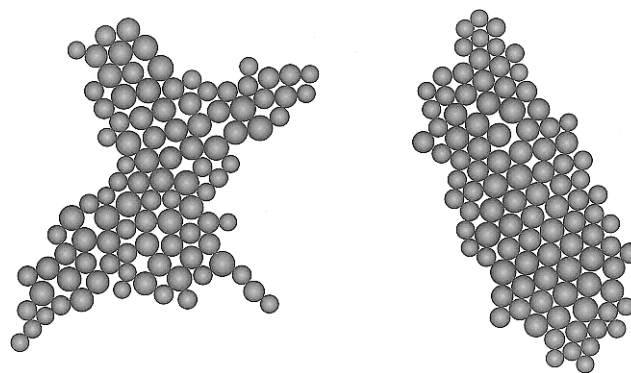
Figure 6. Simulation results of a fast evaporation (left) and a slow evaporation (right) as it occurs at low temperatures. The latter picture shows the improved ordering.

in a random direction for each sphere is set up. In the next stage, for each protruding sphere the lateral capillary forces on any other protruding sphere are calculated under the condition that no third protruding sphere is present in the distance between the two considered spheres. After each stage, motions that would cause overlaps are reduced to the maximum allowed range. After each iteration step the water film height is reduced for an adjustable quantity, e.g., 10 pm/step. The algorithm terminates when the water film height has reached zero, i.e., when all water has evaporated. Thus, about 50 000 iteration steps are necessary for a complete run of the program. A more detailed description of the simulation algorithms is given in ref 20. The simulation results for a fast (10 pm/step) and a slow (0.5 pm/step) evaporation are shown (Figure 6). As a result of the slow evaporation, a well-ordered aggregate is obtained, while in the fast evaporation the aggregate has no order.

The simulation indicates that the LCF dominates the size-dependent segregation procedure of the polydisperse spheres at low temperatures, which induces a better packing of the spheres. The convection force is acting on all the particles no matter if they protrude out of the water surface or not and are thus not effective on the size-dependent segregation. In the case of a high evaporation rate the convection force would be equal to or even greater than the LCF but has no effect on the packing order. With decrease of the evaporation speed of the solvent, the convection force becomes smaller, and the LCF becomes the dominating force.

6. Conclusions

We demonstrate that it is possible to obtain a highly ordered latex particle monolayer from a polydisperse solution by reducing the evaporation rate of the water. The packing order is strongly dependent on the substrate temperature. In contrast, the packing order of a film deposited from a monodisperse solution is not affected by the temperature. The images acquired with the SFM show a granular structure of the polydisperse monolayer. Each grain is hexagonally packed and shows a single sphere size. Supported by the results of a computer simulation we conclude that the size-dependent segregation process at low temperature is dominated by the lateral capillary forces.

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