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Modeling of structure formation in Langmuir films of nanoparticles

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INTRODUCTION

In the colloid chemical approach of nanotechnology, molecules and nanoparticles are the building blocks of the new materials. The macroscopic properties of these nanostructures are determined not only by the characteristics of the individual particles but also by their spatial order. Thus, if the mechanisms of the structure formation are known, their physical and chemical properties can be designed in a more systematic way. This is where computer simulations can support us: as opposed to the real world, a computer model makes it easy to move in the multidimensional space of input parameters, thus correlations between the measurable quantities and the microscopic mechanisms are much easier to reveal.

Structuring a material on the nano-scale can provide new physical or chemical characteristics, e.g. modulating the dielectric permittivity on the length scale comparable to the wavelength of light results in photonic crystals or antireflective coatings. The electronic band structure of nanometer sized particles may differ from the macroscopic bulk characteristics due to size-quantized effects. The relatively simple and inexpensive Langmuir-Blodgett (LB) technique allows us to exploit these novel properties on the macroscopic scale. By fabricating multilayers from the films of various types of nanoparticles, optical, catalytic, electronic, magnetic or even mechanical properties of the materials can be combined.

To gain a better understanding of the structure formation of Langmuir-films, we developed a computer simulation that permits the modeling of film balance experiments of partially wettable, spherical nanoparticles. Using this model we interpreted the collapse mechanisms of particulate films, assessed the contact angle of Stöber silica particles

and revealed the relationship between the size distribution and the evolving structure. We proposed a correction method for the determination of interparticle potentials from surface pressure vs. area isotherms and investigated the structure of multilayers fabricated by LB technique. To strengthen the conclusions of the computational work, we carried out real film balance experiments on the model system of microparticles having partial wettability.

METHODS

- Molecular dynamics computer model was developed to reproduce the macroscopic behaviour of real systems and thus reveal the microscopic mechanisms on the length scale of the individual particles.
- A two-liquid Wilhelmy film balance was built, and monolayers of easily visualized, surface modified glass microparticles were compressed at various liquid-fluid interfaces.

Our conclusions were drawn from the comparison of real and simulated experiments on Stöber silica systems, and the argument was validated by the results of experimental work on microparticulate model systems.

RESULTS

1. Molecular dynamics computer simulation has been developed to model the compression of Langmuir films of spherical nanoparticles. Arbitrary particle size distribution, contact angle, compression rate and central pair interaction can be set in the model. Since the particles are allowed to move perpendicular to the liquid-fluid

APPLICATIONS

Using the LB technique, photonic crystals, nanolithographic masks, planar waveguides and other nanostructured coatings can be fabricated from the Langmuir films of nanoparticles. The quality of the thin film on the substrate is determined by the structure of the particulate monolayer at the liquid-fluid interface. The demonstrated computer simulation permits the investigation of particulate monolayers of arbitrary size distribution, contact angle and particle interactions, thus it can be used as a design tool for tailoring nanostructures. (Fig. 4) In real systems, a few nanometer thick liquid film can be present between the particles due to their repulsion; the polydispersity is often in the range of 10-20%, and the structure of the monolayer is hexatic, at the best. Our computer simulation can account for the effects of these imperfections and thus facilitate the optimization of the structure of LB thin films.

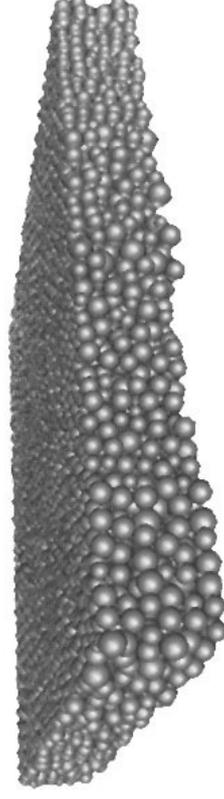


Figure 4: Simulated structure of an LB multilayer. The 6 sublayers were taken at 10 mN/m surface pressure and consist of averagely 44 nm diameter Stöber silica particles.

7. We developed a computer model to investigate the structure of multilayers fabricated by LB technique. The inputs of this model were the monolayer structures gained from the simulation of Langmuir films of the same particulate sample. The results indicate that the porosity as a function of distance from the substrate has local maxima. The values of these maxima are continuously decreasing, and the variance of the distance of particles belonging to the same layer levels off after 4-5 layers. (Fig. 3) By means of this model we were able to investigate the structure of multilayers fabricated from realistic Langmuir films, i.e. monolayers of polydisperse particles not only in close packed, perfect hexagonal order.

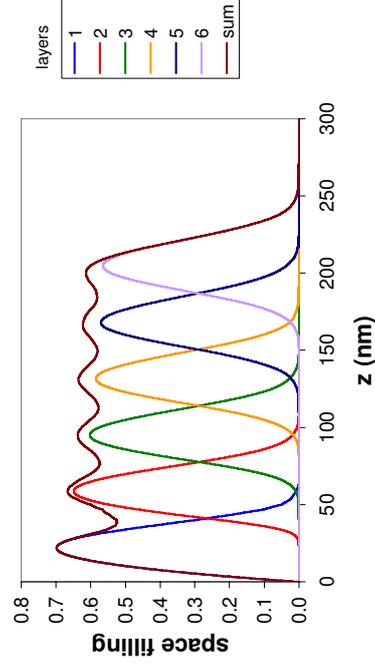


Figure 3: Space filling of a simulated multilayer structure and its sublayers as a function of distance from the substrate. The sublayers are outputs of the simulation of Langmuir films and consist of 44 nm diameter Stöber silica particles.

interface, the structure formation can be investigated after the onset of the collapse.

2. By means of the simulation we proved, that at a given surface coverage a real particulate film has higher surface pressure than an idealistic monodisperse, hexagonally packed system due to the uniaxial compression of real films and the polydispersity of nanoparticles. Consequently, the usual assumption in the determination of interparticle potentials from the surface pressure vs. area isotherms (i.e. monodisperse particles in perfect hexagonal order), leads to a systematic overestimation of the characteristic length of the interaction. Based on the results of the simulation we proposed a correction method to improve the traditional way of determining the interparticle potentials.
3. A Langmuir film consisting of narrow size distribution, spherical particles can have two types of collapse mechanism: buckling, where the whole layer folds and wrinkles, or expelling, where particles are displaced from the interface. According to the congruent results of the experiments on microparticles and the simulation, the mechanism of collapse is primarily determined by the wettability of particles. Expelling mechanism is expected if the particles are well wetted by the subphase, whereas the layer folds during collapse for less wettable particles. In terms of contact angles, the mechanism change is between 40 and 50 degrees. In the case of expelling collapse mechanism the increasing polydispersity of particles results in lower collapse pressure.

4. We showed experimentally that the contact angle determination based on integrating the surface pressure vs. area isotherms considerably overestimates the contact angle of particles. Instead of that, we proposed a new method based on the results of the computer model. At given particle-particle interactions and size distribution the collapse pressure of a Langmuir film is a monotonous function of the contact angle and the simulation can reveal this correlation. (Fig. 1) That contact angle will be accepted at which the simulation provides the experimentally measured collapse pressure.

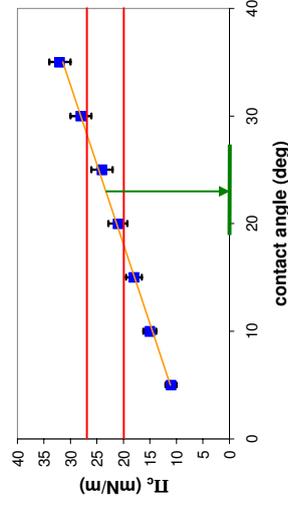


Figure 1: The contact angle of particles can be estimated by comparing the experimental (red) and the simulated (orange) collapse pressures (Π_c).

5. The correlation between the size distribution of particles and several structural parameters (decay length of pair-correlation function, global orientational order parameter, mean and standard deviation of number of neighbours) has been explored. We found that domain-structured films can be formed only below 7-8% polydispersity and showed how the computer model can support the design of nanostructures. By means of the simulation one can find the ideal size distribution - surface pressure combination to fabricate Langmuir-Blodgett films of desired surface coverage and order.

6. The particulate Langmuir films are continuously restructuring in course of the uniaxial compression. According to the results of the computer simulation the adjacent particles usually shift in the same direction, therefore the local structure is mostly preserved. Units consisting of numerous particles move collectively to follow the constraint dictated by the barrier. (Fig 2.) Because of the uniaxial compression and the stiffness of the particulate layer, the surface pressure is not a scalar field, its value depends on the direction angle. In systems of smaller polydispersity bigger units move in course of restructuring, thus the ratio of eigenvalues of the local pressure tensor fluctuates more during compression. According to the simulation, the narrower the size distribution the more significant the difference between the values of surface pressure parallel and perpendicular to the barrier.

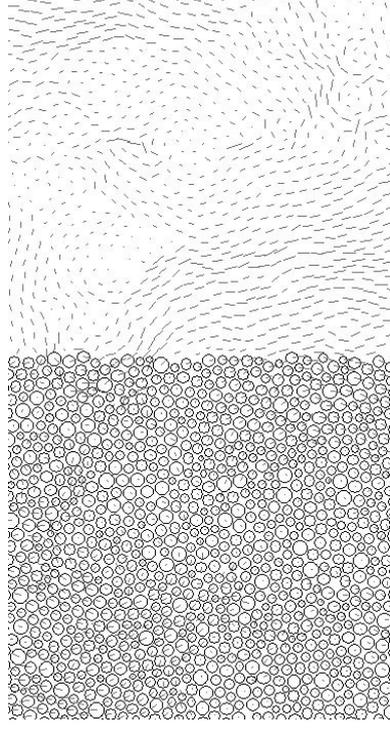


Figure 2: Simulated restructuring of 44 nm diameter Stöber silica particles. The lines ending in the center of particles show the directions where particles arrived from. The direction of compression is vertical in the figure.