

Effect of local curvature on the interaction between hydrophobic surfaces

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ABSTRACT

Surface structure, including roughness and chemical heterogeneities, is known to be of importance for the surface interaction forces observed between hydrophobic and superhydrophobic surfaces. In this study, silica particles have been used to prepare structured particulated surfaces with a controlled roughness using Langmuir-Blodgett deposition or a drop coating technique. The surfaces were characterized by SEM and AFM. The AFM colloidal probe technique was employed for probing the interaction between a micro-size hydrophobic particle and hydrophobic surfaces with a sintered and silanized nano-sized silica particle monolayer. These measurements indicate that the adhesion force is increased by a decrease in particle size. Larger roughness gives larger crevices on the surface and more air/vapor accumulation but the capillary growth is impaired since the three-phase line (solid-liquid-air) has to move over a longer distance with an increase in the size of the surface features.

Keywords: surface forces, AFM, capillary force, hydrophobic interaction, surface roughness

1 INTRODUCTION

The first direct measurements of the attractive interaction between hydrophobic macroscopic surfaces was reported in 1982 and the study showed that long-range forces that are considerably stronger than the van der Waals force dominate the interaction [1]. It was later suggested that cavitation or bridging bubbles between the surfaces could be responsible for the long-range nature of the attractive force observed on bringing the surfaces together [2-4]. The hydrophobicity of the surfaces involved is not solely responsible for the range and magnitude of the interaction between hydrophobic surfaces in aqueous solutions. Observations have shown that surface roughness and chemical heterogeneities are of vital importance for the long-range attractive forces. Air pockets created within the rough and heterogeneous surface are likely to be the reason for that [5-6].

Particulated surfaces with a densely packed and well-ordered structure can give valuable information about how the bubble/cavity induced attractive forces are influenced by topography and roughness. Recently, Wallqvist et al.[7], reported how the adhesive and long-range capillary forces between slightly hydrophobic surfaces are influenced by the

surface topography of disordered particulated surfaces. Langmuir-Blodgett (LB) deposition is well-known to be capable of preparing films with a highly ordered structure and controlled roughness. Previously, hexagonally close-packed films with silica particles of sizes 0.5, 1.0 and 1.5 μm have been created by Tsai et al [8].

This study aims at gaining information about how the range and magnitude of the hydrophobic interaction are affected by the surface roughness of the interacting surface by measuring forces between a colloidal probe and a surface coated with particles of the same size range as the probe as well as particles more than 100 times smaller than the probe. Focus has been on the preparations of the structured surfaces and characterization of particles from which the surfaces are created.

2 EXPERIMENTAL

2.1 Materials

Silica particles of 30, 90, 200, 800 and 4000 nm in diameter were purchased from G. Kisker GmbH Germany. The cationic surfactant hexadecyltrimethylammonium bromide (HTMAB, Sigma, UK) was used to physically modify the particle surfaces. To hydrophobize the particle surfaces, dodecyl-dimethyl-chlorosilane (Sigma, UK) was used. Polystyrene particles with a radius of 5 μm (G. Kisker GmbH, Germany) were used as probes in AFM force measurements.

2.2 Surface preparation

Modification of the silica particles to be used for LB deposition was done following a protocol developed by Lee et al and Tsai et al [8-9]. Water was removed from the silica particle suspensions by careful heating in an oven. Then the particles were redispersed in 2-propanol by sonication for 2 h followed by addition of 1000 ppm HTMAB and sonication for another hour. The dispersion was left to equilibrate for 24 h followed by removal of the solvent. Finally, chloroform was added to give a particle concentration of 20 mg/mL.

The deposition of particles and monolayer experiments were conducted in a Langmuir trough (KSV Instruments, Finland). The particles were spread on a clean water subphase by using a microsyringe (705N, Hamilton Co, USA) followed by a 15 min waiting period to let the solvent

evaporate. The amount of particles added to the trough differed with respect to particle size and an optimal amount was decided through surface pressure-area (π -A) isotherms. For all types of experiments; π -A isotherms and film deposition, the monolayer at the air-water interface was compressed at a speed of 10 mm/min. Glass microscope slides thoroughly cleaned in ethanol and water with dimensions of 15 mm x 15 mm x 1 mm were used as substrates for film deposition. The particles were deposited at a speed of 1 mm/min in the upstroke direction at the selected surface pressure.

Drop coating was performed by putting a droplet of the aqueous silica particle stock solution on a glass microscope slide and letting it dry.

In order to obtain stable and organics free particulated films, the deposited films were heated in a furnace for 5 min at 650 °C. The sintered surfaces were cleaned in a plasma cleaner (PDC-3XG, Harrick Scientific, USA) for 15 min. In the next step, the surfaces were exposed to dodecyl-dimethyl-chlorosilane in gas phase by placing them in a desiccator next to a few droplets of the silane for 15 hours. Finally, the surfaces were rinsed consecutively in chloroform, heptane, 2-propanol, ethanol and Milli-Q water.

2.3 Methods

Surface modified silica particles were characterized by measuring their size with dynamic light scattering (Zetasizer Nano, Malvern Instruments, UK). Water contact angles were measured using a dynamic contact angle and absorption tester (FibroDAT 1100, FibroSystems AB, Sweden). Images of the surfaces were recorded using an Atomic force microscope (AFM, Nanoscope III, Digital Instruments, USA) in tapping mode with non-contact silicon cantilevers (NCH-VS2-W, Nanoworld, Switzerland) or by using a Scanning electron microscope (SEM, XL30, Philips FEI, USA). The forces between the hydrophobized surfaces and a hydrophobic colloidal probe were measured using the same AFM as employed for imaging equipped with a liquid cell. The cantilevers (NSC12/tipless/No Al, Mikromasch, Estonia) were calibrated using the method proposed by Sader et al.¹⁰ Measurements were performed in aqueous 10 mM NaCl.

3 RESULTS AND DISCUSSION

The size of the silica particles both before and after modification with the cationic surfactant was measured and gave an indication that the smaller particles, 30 and 90 nm, tend to aggregate during the drying process and are impossible to disperse by using ultrasonication after they have aggregated (Figure 1). However, a filter with a pore size of 500 nm could be used to remove most of the aggregates.

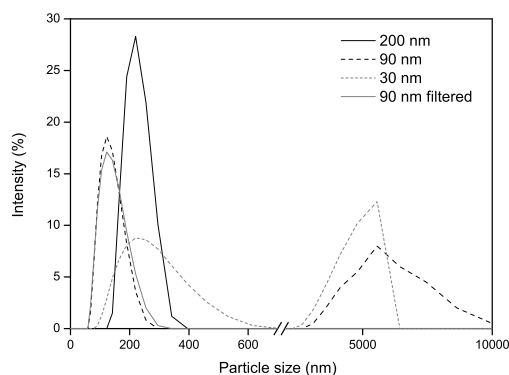


Figure 1: Size measurements of silica particle suspensions using dynamic light scattering.

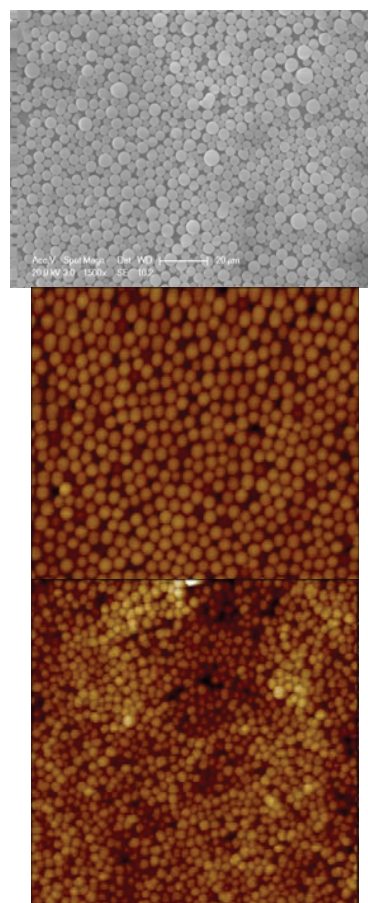


Figure 2: Particulated surfaces A) 4000 nm particles deposited by LB, recorded by SEM, B) 200 nm particles deposited by LB, recorded by AFM ($5 \times 5 \mu\text{m}^2$) C) 30 nm particles deposited by drop coating, recorded by AFM ($2 \times 2 \mu\text{m}^2$)

The images displayed in Figure 2A and 2B illustrate Langmuir-Blodgett (LB) deposited surfaces. LB deposition

of 30 and 90 nm particles gave surfaces that contained large particle aggregates.

According to the previously described particle size measurements, the aggregates are present already before spreading of the particles in the Langmuir trough. Particle filtration before LB deposition resulted in films without any apparent aggregates. Drop coated surfaces with 30 nm particles are shown in Figure 2C which displays a well-ordered surface. However, the surface coverage tends not to be complete and large holes without particles were sometimes visible on the surface.

Contact angle measurements of silanized particulated surfaces showed that the macroscopic contact angles of LB deposited films were 120-125°, compared to a clean hydrophobized glass slide which exhibited a contact angle of 108° (Figure 3). As expected, an increase in surface roughness due to the deposited particles gives an increased hydrophobicity of the surfaces. However, the particle size has an insignificant effect on the contact angle. As mentioned above, due to lower surface coverage on the drop coated surfaces, the contact angle is slightly lower than those exhibited by the LB surfaces.

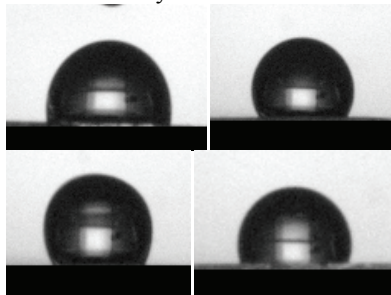


Figure 3: Water contact angles on A) Flat silanized glass surface, 108°, B) LB film of 4000 nm particles 122°, C) LB film of 200 nm particles 124°, D) Drop coated film of 90 nm particles 116°.

The force measurements presented here were done by measuring interactions between a polystyrene colloidal probe and a LB deposited particulated surface. Figure 4 displays force curves measured on 30, 90 and 200 nm particle surfaces. These measurements indicate that the adhesion force is increased by a decrease in particle size. This is in line with measurements reported, indicating the strong influence of air/vapour cavities contributing to capillary forces between the surfaces [7]. In the present study, the measurements were extended to larger particle sizes and to higher macroscopic contact angles. The interaction forces are larger when the nanoscale roughness is smaller. There is more air/vapour accumulation due to larger crevices on rougher surfaces but the capillary growth is impaired since the three-phase line (solid-liquid-air) has to move over a longer distance with an increase in the size of the surface features.

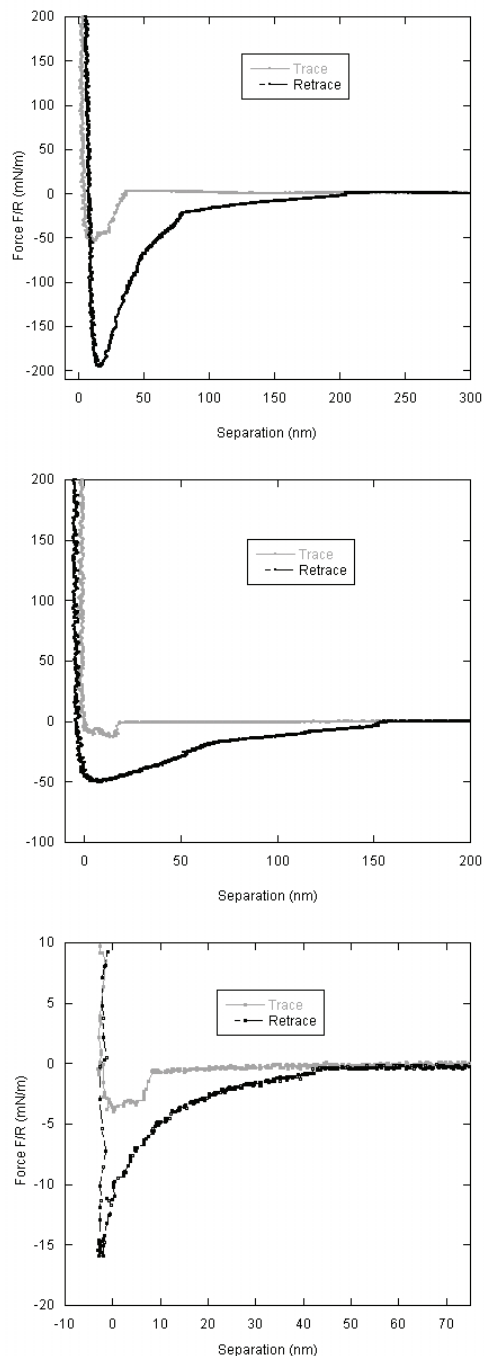


Figure 4: Force measurements on approach (jump-in) and separation (adhesion) between a polystyrene probe and LB deposited hydrophobic particulated surface. Particle size for the surfaces: A) 30 nm, B) 90 nm and C) 200 nm.

4 CONCLUSIONS

Silica particles of diameters 30, 90, 200, 800 and 4000 nm were surface-modified with a cationic surfactant and used for preparation of structured particulated monolayer films by using Langmuir-Blodgett deposition or drop coating. The smaller particles displayed a higher tendency to aggregate during the process of surface modification.

After hydrophobization of the particulated surfaces, forces between them and a hydrophobic colloidal probe were measured. The first results indicate strong interaction forces between hydrophobic particulated surfaces and hydrophobic probe due to capillary forces and a significant influence of the size of the surface features.

REFERENCES

- [1] Israelachvili, J. & Pashley, R. "The Hydrophobic Interaction Is Long-Range, Decaying Exponentially With Distance." *Nature*, 300, 341-342, 1982.
- [2] Christenson, H. K. & Claesson, P. M. "Cavitation And The Interaction Between Macroscopic Hydrophobic Surfaces." *Science*, 239, 390-392, 1988.
- [3] Parker, J. L., Claesson, P. M. & Attard, P. "Bubbles, Cavities, And The Long-Ranged Attraction Between Hydrophobic Surfaces." *J. Phys. Chem.* 98, 8468-8480, 1994.
- [4] Carambassis, A., Jonker, L. C., Attard, P. & Rutland, M. W. "Forces measured between hydrophobic surfaces due to a submicroscopic bridging bubble." *Physical Review Letters*, 80, 5357-5360, 1998.
- [5] Hato, M. "Attractive forces between surfaces of controlled "hydrophobicity" across water: A possible range of "hydrophobic interactions" between macroscopic hydrophobic surfaces across water." *J. Phys. Chem.* 100, 18530-18538, 1996.
- [6] Nguyen, A. V., Nalaskowski, J., Miller, J. D. & Butt, H. J. "Attraction between hydrophobic surfaces studied by atomic force microscopy." *Int. J. Miner. Process.*, 72, 215-225, 2003.
- [7] Wallqvist, V., Claesson, P.M., Swerin, A., Östlund, C., Schoelkopf, J., Gane, P.A.C.. "Influence of Surface Topography on Adhesive and Long-Range Capillary Forces between Hydrophobic Surfaces in Water." *Langmuir*, 25, 9197-9207, 2009.
- [8] Tsai, P. S., Yang, Y. M. & Lee, Y. L. "Fabrication of hydrophobic surfaces by coupling of Langmuir-Blodgett deposition and a self-assembled monolayer." *Langmuir*, 22, 5660-5665, 2006.
- [9] Lee, Y. L., Du, Z. C., Lin, W. X. & Yang, Y. M. "Monolayer behavior of silica particles at air/water interface: A comparison between chemical and physical modifications of surface." *J. Colloid Interface Sci.*, 296, 233-241, 2006.
- [10] Sader, J. E., Chon, J. W. M. & Mulvaney, P. "Calibration of rectangular atomic force microscope cantilevers." *Review Of Scientific Instruments*, 70, 3967-3969, 1999.