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Yan Zeng

Colloidal Dispersions Under Slit-Pore Confinement

Doctoral Thesis accepted by
Technical University of Berlin, Germany

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Author
Dr. Yan Zeng
North Carolina State University
Raleigh, NC
USA

Supervisor
Prof. Regine von Klitzing
Fakultät II/Institut für Chemie
Technische Universität Berlin
Berlin
Germany

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To my family

Supervisor's Foreword

Interactions between colloidal particles address a fundamental topic related to the aim of stabilizing macroscopic colloidal dispersions like foams, emulsions, and suspensions. Due to ongoing miniaturization in many technologies, the structuring of colloidal particles under confinement is attracting more and more attention in research nowadays.

In her thesis, Yan Zeng produced the confinement in a Colloidal Probe AFM between a silica microsphere and a planar silicon wafer presenting a slit-pore geometry. Measuring the force through complex fluids like silica suspensions and micellar solutions leads to oscillatory force curves, also called as structural forces due to a layerwise expulsion of the particles. The resulting characteristic of two parameters (particle distance and correlations length) are in very good agreement with the ones obtained from respective scattering data (SAXS) of the bulk phase. There is a fundamental difference between the distance of neutral particles (micelles of nonionic surfactants) and charged particles (negatively charged silica particles)—Neutral particles can be pressed in contact under confinement, while charged particles are pressed out of the slitpore before coming into contact. The distance between the charged nanoparticles scales with the concentration c with $c^{-1/3}$ and not with (diameter of particle + 2 $\times$ Debye length) as often mentioned in literature. The scaling behavior is very robust against changes in parameters like ionic strength and particle size. The correlation length scales with (radius of particle + Debye length).

One focus of the thesis was the separation between the confinement effect itself and the effect of the properties of the confining surfaces. Therefore, the silicon wafer was coated with polyelectrolytes or it was replaced by the fluid interface of an air bubble. Both the particle distance and the correlation length remain constant, and only the interaction strength is affected by the surface roughness, surface potential, and/or surface elasticity.

This thesis is an excellent example for a successful collaboration between theoreticians and experimentalists. The group of Sabine Klapp at TU Berlin showed that the experimental data can be reproduced by Monte Carlo simulations and with a DLVO-like model. Yan Zeng showed that the wavelength of the force

oscillation for the asymptotic distance regime is identical with one of the pair correlation function of the volume phase. This was predicted by density functional theory long ago, but had not been confirmed before experimentally. In the thesis of Yan Zeng this fundamental prediction is verified for the first time for a real colloidal system.

Berlin, September 2012 Regine von Klitzing

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Thank you.

Contents

Abbreviations and Symbols[1]

A	Amplitude of the oscillatory structural force
c	Weight percentage of silica nanoparticles
c_s	Molar concentration of surfactant
CMC	Critical micelle concentration
d	Thickness of layers in a layer-by-layer coated polymeric film
d	Micelle diameter
F	Force
F/R	Normalized force measured by AFM
F_{Ta}	Hydrodynamic force
$g(r)$	Bulk pair correlation function
h	Separation between AFM colloidal probe and the substrate
I_{max}	Maximum scattering intensity in arbitrary units
I_{tot}	Total ionic strength
I_{salt}	Ionic strength of added salt
k_b	Stiffness of deformable surface
k_c	AFM cantilever spring constant
K	Conductivity
κ^{-1}	Debye length
κ_W^{-1}	Debye length including the wall-counterions
N	Number of layers in a layer-by-layer coated polymeric film
$P_{\max}$	Height of the first maximum of the solvation pressure
q_{max}	Momentum transfer in the position of maximum scattering
q^{-1}	Dimensionless correlation length of micelle
Δq	Full width at half maximum of the structure peak
R	Radius of the AFM colloidal probe
R	Radius of the silica nanoparticle
$2(R + \kappa^{-1})$	Effective particle diameter
R_{RMS}	Root mean square roughness

[1] Non-essential and empirical parameters are not included.

t^{-1}	Decay length of electrostatic repulsive force
u	Scanning velocity
w_0	Dimensionless interaction strength of micelle
ΔX	Change in the nominal separation
Z	Valency of charged particle
$\tilde{Z}$	Effective valency of charged particle
Z_c	AFM cantilever deflection
ζ	Zeta-potential
ψ_S	Surface potential of confining wall
ϕ	Volume fraction
δ	Deformation
θ_f	Phase shift in the oscillatory force (solvation force) curve
θ	Contact angle
η	Viscosity
λ	Wavelength
λ_f	Wavelength in confinement
λ_b	Wavelength in bulk
$2\pi/\omega$	Dimensionless wavelength of micelle
ρ	Particle number density
ρ_c	Number density of counterions
ρ_p	Mass density of silica particle
ρ_s	Mass density of solution
σ	Diameter of the silica nanoparticle
γ	Surface tension
τ	Relaxation time
ξ	Correlation length
ξ_f	Correlation length in confinement
ξ_b	Correlation length in bulk
AFM	Atomic force microscope/microscopy
Brij 35	Polyoxyethylene lauryl ether
C_{16}TAB	Hexadecyltrimethylammonium bromide
β-$C_{12}G_2$	β-dodecylmaltoside
CP-AFM	Colloidal probe atomic force microscope/microscopy
DLVO	Derjaguin-Landau-Verwey-Overbeek
GCMC	Grand canonical Monte Carlo
HA	Hyaluronic acid
HNC	Hypernetted chain
HS 40	Silica particle suspensions with diameter of 16 nm
InvOLS	Deflection inverse optical lever sensitivity
MC	Monte Carlo
PAA	Poly(acrylic acid)
PAH	Poly(allylamine hydrochloride)
PEI	Polyethylenimin
PSS	Poly(sodium 4-styrenesulfonate)

SAXS	Small angle X-ray scattering
SDS	Sodium dodecyl sulfate
SM 30	Silica particle suspensions with diameter of 11 nm
Tween 20	Polyoxyethylene sorbitan monolaurate
TFPB	Thin film pressure balance
TMA 34	Silica particle suspensions with diameter of 26 nm