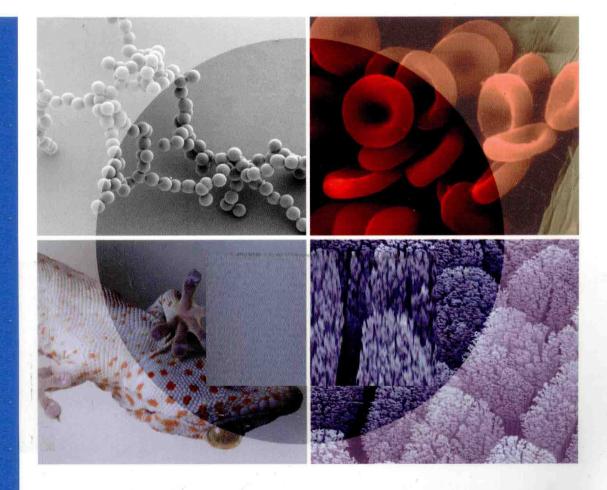
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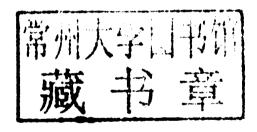


# Surface and Interfacial Forces



Hans-Jürgen Butt and Michael Kappl

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### Description of Cover-illustration:

Top left: Scanning electron micrograph of clusters of silica particles deposited onto a silicon wafer. The particles have a diameter of 1.9 µm and resemble an example of how surface force can dominate the behavior of small scale systems. Even though these structures look fragile, shaking such a sample could not deform them, since inertial forces will be smaller than the van der Waals forces between these particles. Top right: Scanning electron micrograph of red blood cells (courtesy of John Minarcik, Department of Laboratory Medicine & Pathology, University of Alberta). Bottom left: Photograph of a Tokay gecko (Gekko gecko) adhering to a glass plate. Bottom right: Scanning electron micrograph of the fine structure of the gecko foot. Each gecko toe consists of hundred thousands of small keratin hairs called setae. Each seta is further divided into several hundred subunits, the so-called spatulae with a diameter of about 200 nm. This structure allows the gecko to form intimate contact with surfaces and utilize van der Waals and capillary forces to adhere to surfaces. Both gecko images were kindly provided by S. Gorb, Max

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## Preface

Two decades have passed since the book by Jacob Israelachvili "Intermolecular and Surface Forces" appeared. During this period, our knowledge on interfacial forces has significantly, improved partially due to new experimental tools and improved simulation capabilities. For example, the invention of scanning probe microscopy and the development of optical methods allow us to look at surface forces in much more detail.

Surface forces are relevant in a number of technologies, in particular eco-efficient technologies, for a sustained growth in the face of unbridled exploitation of natural resources, a growing world population, and the expected climate change. For example, a good understanding of particle dispersion is a prerequisite to improve mineral processing and adapt it to the increasing exploitation of raw materials. Food industry, facing a growing demand for healthy food, relies on a good understanding of the stability of emulsions and thus of the interaction of oil drops in water or oily liquids in water. The same is true for oil recovery and waste water treatment. The synthesis of polymers in aqueous emulsions allows an environment-friendly production; again, a good knowledge of the forces that keep the particles dispersed is required.

The number of papers published in journals on colloid and interface science has increased by about seven times during the past 20 years. We suppose that this increase is correlated with an increasing number of active researchers in the field. One reason for this increase is certainly the growth in the world population, the fact that a larger proportion of the world population takes part in the technological progress. Another reason is that several technologies rely more and more on processes at the small scale. One example is the increasing relevance of microand nanotechnology, including lab-on-chip technology, microfluids, and biochips. Objects in the micro- and nanoworld are dominated by surface effects rather than gravitation or inertia.

These developments motivated us to write this textbook. It is a general introduction to surface and interfacial forces. Though a basic knowledge of colloid and interface science is helpful, it is not essential because all important concepts have been explained. Certainly, no advanced level of mathematics is required. Looking

Surface and Interfacial Forces. Hans-Jürgen Butt and Michael Kappl Copyright © 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 978-3-527-40849-8 through the pages of this book, you will see a substantial number of equations. Please do not be scared! We preferred to explicitly give all transformations rather than writing "as can easily be seen" and stating the result.

A number of problems with solutions are included to allow private studies. If not mentioned otherwise, the temperature is assumed to be 25 °C. At the end of each chapter, the most important equations, facts, and phenomena are summarized.

This book certainly contains errors. Even after proofreading by different people independently, this is unavoidable. If you find any error, please write us a letter (Max Planck Institute for Polymer Research, Ackermannweg, 55128 Mainz, Germany) or an e-mail (butt@mpip-mainz.mpg.de) so that we can correct it and do not confuse more readers.

We are indebted to several people who helped us collect information, prepare, and critically read this manuscript. In particular, we would like to thank Maria D'Acunzi, Günter Auernhammer, Clemens Bechinger, Elmar Bonaccurso, Derek Y.C. Chan, Vince Craig, Raymond Dagastine, Markus Deserno, Georg Floudas, Stanislav Gorb, Karina Grundke, Vagelis Harmandaris, Manfred J. Hampe, Manfred Heuberger, Katharina Hocke, Roger Horn, Naoyuki Ishida, Gunnar Kircher, Reinhard Miller, Maren Müller, Martin Oettel, Sandra Ritz, Tim Salditt, Tanja Schilling, Doris Vollmer, and Xuehua Zhang.

Mainz, August 2009

Hans-Jürgen Butt and Michael Kappl

# Symbols and Abbreviations

Many symbols are not unique for a certain physical quantity but are used two or even three times. We use the symbols as they are usually used in the relevant literature. Since the scope of this book includes many disciplines and thus different scientific communities, multiple usage of symbols is unavoidable. In molecular chemistry and physics, for instance,  $\mu$  is the dipole moment while in engineering  $\mu$  symbolizes the coefficient of friction.

```
contact radius (m), activity (mol/L)
а
             Molecular radius (m)
a_0
A
             Area (m<sup>2</sup>)
A_{\mathsf{H}}
             Hamaker constant (I)
             Slip length, distance between grafting sites (m)
h
             Number concentration (number of molecules per m<sup>3</sup>) or amount
C
             concentration (mol m<sup>-3</sup>, or mol l^{-1} = M), mean cosine of contact angles
             Concentration in mass per unit volume (kg m<sup>-3</sup>)
c_{\rm m}
             Center-to-center distance between two spheres (m)
d_{cc}
D
             Distance (m)
D_d
             Diffusion coefficient (m<sup>2</sup> s<sup>-1</sup>)
D_0
             Interatomic spacing used to calculate adhesion (m), typically 1.7 A
Ď
             Dimensionless normalized distance
             Electric field strength (V m<sup>-1</sup>), Young's modulus (Pa), surface
E
             elasticity (N m<sup>-1</sup>)
E^*
             Reduced Young's modulus (Pa)
F_{adh}
             Adhesion force (N)
F_{\rm F}
             Friction force (N)
F_1
             Load (N)
             Force per unit area (N m<sup>-2</sup>)
             Different kinds of dimensionless correction functions
G
             Gibbs energy (J)
G_{\rm m},~G_{\rm m}^0
             Molar Gibbs energy and standard molar Gibbs energy (J mol<sup>-1</sup>)
Н
             Enthalpy (I)
h
             Height of a liquid with respect to a reference level (m), Planck constant,
             film thickness (m)
```

K	Spring constant (N m <sup>-1</sup> )
K <sub>c</sub>	Spring constant (N m ) Spring constant of AFM cantilever (N m <sup>-1</sup> )
$k_{\rm c}$	Bending modulus of a membrane (J)
	Segment elasticity (N m <sup>-1</sup> )
$k_{\rm s}$	
L	Center-to-center distance between two spherical particles (m)
$L_{\rm c}$	Contour length of a polymer chain (m)
$L_0$	Thickness of an undisturbed polymer brush (m)
$l_{\rm r}$	Length of repeat unit in a polymer (m)
$l_{\rm s}$	Segment length of polymer chain also called Kuhn length (m)
M	Torque (N m)
$M_{ m w}$	Molar mass (kg mol <sup><math>-1</math></sup> )
$M_{ m r}$	Molar mass of repeat unit of a polymer (kg mol <sup>-1</sup> )
m	Mass (kg), molecular mass (kg per molecule)
N	Number of molecules (dimensionless or mol), number of segments in a
	linear polymer chain
n	Refractive index, integer number
P	Pressure (Pa)
$P_{\rm c}$	Capillary pressure caused by the curvature of an interface (Pa)
$P^{V}$	Equilibrium vapor pressure of a vapor in contact with a liquid with a
D	curved surface (Pa)
$P_0$	Equilibrium vapor pressure of a vapor in contact with a liquid having a
0	planar surface (Pa)
Q R	Electric charge (A s), heat (J), quality factor of a resonator
	Gas constant  Padii of aphorical particles (m)
$R_1, R_2$ $R^*$	Radii of spherical particles (m)
	reduced radius (m) Radius of gyration of a polymer (m)
$R_{ m g}$	Radius of a spherical particle (m)
$R_{\rm p}$	
$R_0$	Size of a polymer chain (m)
r	Radius (m), radial coordinate in cylindrical or spherical coordinates Radius of a bubble, a capillary, and a drop, respectively (m)
$r_{\rm b}, r_{\rm c}, r_{\rm d}$	Two principal radii of curvature of a liquid (m)
$r_1, r_2$ $S$	Entropy (J K <sup>-1</sup> ), number of adsorption binding sites per unit area (mol
5	$m^{-2}$ ), spreading coefficient (N m <sup>-1</sup> )
T	Temperature (K)
$T_{\Theta}$	Theta temperature (K)
t	Time (s)
U	Internal energy (J), applied or measured electric potential (V)
$\overline{V}$	Volume (m <sup>3</sup> ) or free energy of interaction between two molecules or
•	particles (J)
$V_{ m m}$	Molar volume (m <sup>3</sup> mol <sup>-1</sup> )
ν	Velocity (m s <sup>-1</sup> ), excluded volume parameter (m <sup>3</sup> )
$\nu_0$	Sliding or rolling velocity (m s <sup>-1</sup> )
$V^{A}$	Free energy for the interaction between two surfaces per unit area (J $\mathrm{m}^{-2}$ )
$W_{ m adh}$	adhesion energy per unit are a (J/m²)
essent.	Oc. 1. Met 1

```
Cartesian coordinates (m), reduced electric potential, and the reduced
x, y, z
             distance y = x/(2L_0)
Z
             Valency of an ion
             Polarizability (C m^2 V^{-1}), factor defined by Eq. (4.23)
α
             Surface tension (N m<sup>-1</sup>). Specifically, \gamma_L, \gamma_S and \gamma_{SL} are the surface
γ
             tensions of a liquid-vapor, a solid and solid-liquid interface, respectively
\gamma^{s}
             Surface energy of a solid (J)
Ϋ́
             Shear rate (s<sup>-1</sup>)
             Grafting density of polymer (mol m<sup>-2</sup> or m<sup>-2</sup>)
Γ
            Thickness of the hydration layer (m), indentation (m)
δ
             Relative permittivity
3
             Zeta potential (V)
ς
             Viscosity (Pa s)
η
Θ
             Contact angle (deg)
             Inverse Debye length (m^{-1}) (Eqs. (4.8) and (4.11))
×
             Capillary constant (m) (Eq. (5.7))
N.
λ
             Decay length or wavelength of light (m)
             Characteristic length scale, critical wavelength of fluctuations (m)
\lambda_c
             Debye length (m)
\lambda_{D}
             = \gamma V_{\rm m}/RT, Kelvin length (m)
\lambda_{K}
             penetration depth of evanescent wave (m)
\lambda_{ev}
             Chemical potential (J mol<sup>-2</sup>), dipole moment (C m), friction coefficient
u
             Dimensionless coefficient of kinetic and static friction, respectively
\mu_{k}, \mu_{s}
             Coefficient of rolling friction (m)
\mu_r
            Tabor parameter
\mu_T
             Maugis parameter
\mu_{M}
             Frequency (Hz), Poisson ratio (dimensionless)
ν
П
             Disjoining pressure (Pa)
             Mass density (kg m^{-3})
0
             Number density of molecules next to a wall (molecules per m<sup>3</sup>)
Q_0
             Molecular density (molecules per m<sup>3</sup>)
Qn
             Electric charge density (C m<sup>-3</sup>)
00
             Volume fraction
             Surface charge density (C m<sup>-2</sup>)
σ
             Surface area per molecule (m<sup>2</sup>)
\sigma_A
ξ
             Coordinate in the gap between two half-spaces (m)
```

Matsubara angular frequencies (Hz)

 $\xi_{\rm m}$ 

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### 1

### Introduction

The topic of this book is forces acting between interfaces. There is no clear, unique definition of an interfacial force. One possible definition is as follows: Interfacial forces are those forces that originate at the interface. For example, electrostatic double-layer forces are caused by surface charges at the interface. Such a definition would, however, not include van der Waals forces. For van der Waals interaction, the surface atoms do not have a distinct role compared to the bulk atoms. Still, van der Waals forces substantially contribute to the interaction between small particles. One could define surface forces as all interactions that increase proportional to the interfacial area. Then, for certain geometries gravitation should also be included. Gravitation is, however, not described here. On the other hand, hydrodynamic interactions would be excluded because they depend on the specific shape of interacting interfaces and not only on the interfacial area.

We take a pragmatic approach and discuss all forces that are relevant in systems, that have a small characteristic length scale, and whose structure and dynamics are dominated by interfaces rather than gravitation and inertia. In this sense, this book is about the structure and dynamics of system with a small characteristic length scale. At this point we need to specify two terms: "Interface" and "characteristic length scale."

An interface is the area that separates two phases. If we consider the solid, liquid, and gas phases, we immediately get three combinations of interfaces: the solid–liquid, the solid–gas, and the liquid–gas interfaces. The term surface is often used synonymously, although interface is preferred for the boundary between two condensed phases and in cases where the two phases are named explicitly. For example, we talk about a solid–gas interface but a solid surface. Interfaces can also separate two immiscible liquids such as water and oil. These are called liquid–liquid interfaces. Interfaces may even separate two different phases within one component. In a liquid crystal, for example, an ordered phase may coexist with an isotropic phase. Solid–solid interfaces separate two solid phases. They are important for the mechanical behavior of solid materials. Gas–gas interfaces do not exist because gases mix.

Often interfaces and colloids are discussed together. Colloid is a synonym for colloidal system. Colloidal systems are disperse systems in which one phase has dimensions in the order of 1 nm to 1  $\mu$ m (Figure 1.1). The word "colloid" comes from

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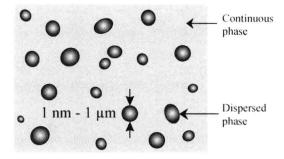


Figure 1.1 Schematic of a dispersion.

Table 1.1 Types of dispersions.

Continuous phase	Dispersed phase	Term	Examples
Gas	Liquid	Aerosol	Clouds, fog, smog, hairspray
	Solid	Aerosol	Smoke, dust, pollen
Liquid	Gas	Foam	Lather, whipped cream, foam on beer
	Liquid	Emulsion	Milk, skin creams
	Solid	Sol	Ink, muddy water, dispersion paint
Solid	Gas	Porous solids <sup>a)</sup>	Partially sintered or pressed powders
		Foam	Styrofoam, soufflés
	Liquid	Solid emulsion	Butter
	Solid	Solid suspension	Concrete

Porous solids have a bicontinuous structure while in a solid foam the gas phase is clearly a) dispersed.

the Greek word for glue and was used the first time in 1861 by Graham. 1) He applied it to materials that seemed to dissolve but were not able to penetrate a membrane, such as albumin, starch, and dextrin. A colloidal dispersion is a two-phase system that is uniform on the macroscopic but not on the microscopic scale. It consists of grains or droplets of one phase in a matrix of the other phase.

Different kinds of dispersions can be formed. Most of them have important applications and have special names (Table 1.1). While there are only 3 types of interfaces, we can distinguish 10 types of disperse systems because we have to discriminate between the continuous, dispersing (external) phase and the dispersed (inner) phase. In some cases, this distinction is obvious. Nobody will, for instance, mix up fog with a foam although in both cases a liquid and a gas are involved. In other cases, the distinction between continuous and inner phases cannot be made because both phases might form connected networks. Some emulsions for instance tend to form a bicontinuous phase, in which both phases form an interwoven network.

The characteristic length scale of a system can often be given intuitively. For example, for a spherical particle one would use the radius, for a thin film the thickness. For more complex systems, intuition, however, leads to ambiguous

<sup>1)</sup> Thomas Graham, 1805–1869. British chemist, professor in Glasgow and London.