
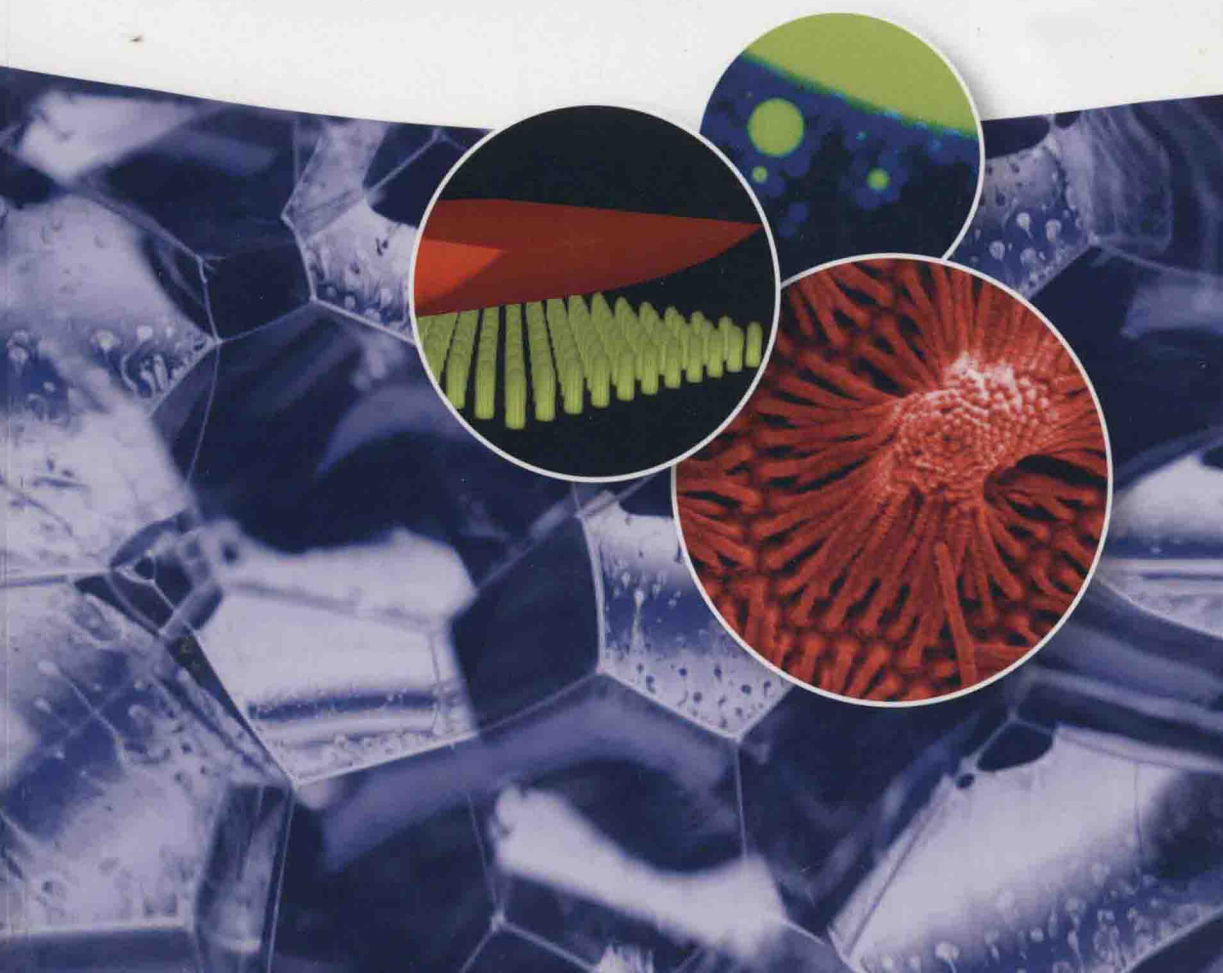


Hans-Jürgen Butt, Karlheinz Graf, Michael Kappl



Physics and Chemistry of Interfaces

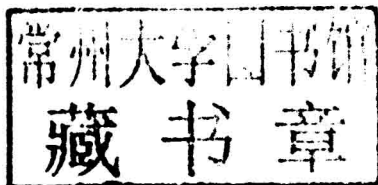
Third, Revised and Enlarged Edition



Hans-Jürgen Butt, Karlheinz Graf, and Michael Kappl

Physics and Chemistry of Interfaces

Third, Revised and Enlarged Edition



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Preface

This textbook serves as a general introduction to surface and interface science. It focuses on basic concepts rather than specific details, on understanding rather than on learning facts. The most important techniques and methods are introduced. The book reflects that interfacial science is a diverse and interdisciplinary field of research. Several classic scientific or engineering disciplines are involved. It contains basic science and applied topics such as wetting, friction, and lubrication. Many textbooks concentrate on certain aspects of surface science such as techniques involving ultrahigh vacuum or classic “wet” colloid chemistry. We tried to include all aspects because we feel that for a good understanding of interfaces, a comprehensive introduction is helpful.

Our manuscript is based on lectures given at the universities of Siegen and Mainz. It addresses advanced students of engineering, chemistry, physics, biology, and related subjects and scientists in academia or industry who are not yet specialists in surface science but desire solid background knowledge of the subject. The level is introductory for scientists and engineers who have a basic knowledge of the natural sciences and mathematics. Certainly an advanced level of mathematics is not required.

When looking through the pages of this book you will see a substantial number of equations. Please do not be scared! We preferred to give all transformations explicitly rather than writing “as can easily be seen” and stating the result. Chapter 3 is the only exception; to appreciate that chapter, a basic knowledge of thermodynamics is required. However, you can skip it and still be able to follow most of the rest of the book. If you do decide to skip it, please at least read and try to gain an intuitive grasp of surface excess (Section 3.2) and the Gibbs adsorption equation (Section 3.5.2).

A number of problems with solutions are included to enable for self-study. Unless noted otherwise, the temperature was assumed to be 25 °C. At the end of each chapter the most important equations, facts, and phenomena are summarized.

One of the main problems with writing a textbook is trying to limit its content. We tried hard to keep the volume within the scope of one advanced course lasting roughly 15 weeks, two days per week. Unfortunately, this meant cutting short or leaving out altogether certain topics. Statistical mechanics, heterogeneous catalysis, and polymers at surfaces are issues that could be expanded.

This book no doubt contains errors. Even after several readings by various people, this is unavoidable. If you find any mistakes, please let us know about them by snail mail (Max-Planck-Institute for Polymer Research, Ackermannweg, 55128 Mainz, Germany) or e-mail (butt@mpip-mainz.mpg.de) so that they can be corrected and do not confuse more readers.

We are indebted to several people who helped us in collecting information and preparing and critically reading the manuscript. In particular we would like to thank E. Backus, K. Beneke, T. Blake, J. Blum, M. Böhm, E. Bonaccorso, P. Broekmann, R. de Hoogh, M. Deserno, W. Drenckhan, J. Elliott, G. Ertl, R. Förch, S. Geiter, G. Glasser, G. Gompper, M. Grunze, J. Gutmann, L. Heim, M. Hietischold, M. Hillebrand, T. Jenkins, X. Jiang, U. Jonas, J. Krägel, R. Jordan, Krüss GmbH, J. Laven, I. Lieberwirth, G. Liger-Belair, C. Lorenz, M. Lösche, S. Ludwig, E. Meyer, R. Miller, A. Müller, P. Müller-Buschbaum, T. Nagel, D. Quéré, J. Rabe, H. Schäfer, J. Schreiber, M. Stamm, M. Steinhart, C. Stubenrauch, G. Subklew, F. Thielmann, J. Tomas, K. Vasilev, D. Vollmer, R. von Klitzing, K. Wandelt, B. Wenclawiak, R. Wepf, R. Wiesendanger, J. Winterlein, G. de With, J. Wölk, D.Y. Yoon, M. Zharnikov, and U. Zimmermann.

Mainz, June 2012

Hans-Jürgen Butt, Karlheinz Graf, and Michael Kappl

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1

Introduction

An *interface* is an area that separates two phases from each other. If we consider the solid, liquid, and gas phases, we immediately get three combinations of interfaces: solid–liquid, solid–gas, and liquid–gas interfaces. The term *surface* is often used synonymously with interface, although interface is preferred to indicate 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 and a solid surface. Surface is used for a condensed phase in contact with a gas or vacuum. 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 co-exist with an isotropic phase. Solid–solid interfaces separate two solid phases. They are important for the mechanical behavior of solid materials such as concrete. Gas–gas interfaces do not exist because gases mix.

Often interfaces and colloids are discussed together. *Colloid* is an abbreviated synonym for colloidal system. Colloidal systems are disperse systems where one phase has dimensions on the order of 1 nm to 1 μm (Figure 1.1). The word *colloid* comes from the Greek word for glue and was first used in 1861 by Thomas Graham.¹⁾ He used the word to refer to materials that seemed to dissolve but were unable to penetrate membranes 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 dispersion can be formed. Most have important applications and have special names (Table 1.1). While there are only five types of interfaces, we can distinguish ten types of disperse systems because we must discriminate between the continuous, dispersing (external) phase and the dispersed (inner) phase. In some cases this distinction is obvious. Nobody will, for instance, confuse fog with foam, although in both cases a liquid and a gas are involved. In other cases the distinction between continuous and inner phase 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.

1) Thomas Graham, 1805–1869; British chemist, professor in Glasgow and London.

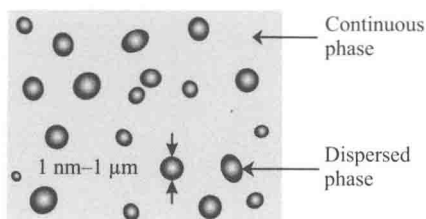


Figure 1.1 Schematic of a dispersion.

Table 1.1 Types of dispersion.

Continuous phase	Dispersed phase	Term	Example
Gas	Liquid	Aerosol	Clouds, fog, smog, hairspray
	Solid	Aerosol	Smoke, dust, pollen
Liquid	Gas	Foam	Lather, whipped cream, foam on beer
	Liquid	Emulsion	Milk
	Solid	Suspension	Ink, muddy water, dispersion paint
Solid	Gas	Porous solids	
		Foam	Styrofoam, soufflé
	Liquid	Solid emulsion	Butter
	Solid	Solid suspension	Concrete

Colloids and interfaces are closely related. This is a direct consequence of the enormous specific surface area of colloids. More precisely, their interface-to-volume ratio is so large that their behavior is determined mainly by interfacial properties. Gravity and inertia are negligible in the majority of cases. For this reason colloidal systems are often dominated by interfacial effects rather than bulk properties. This is also why interfacial science serves as the basis for nanoscience and technology; many inventions in this field originate from surface science.

The behavior of a colloidal system is governed by thermal fluctuation, and colloidal particles move due to Brownian motion. This distinguishes them from granular matter, a material composed of macroscopic elements. The constituents of granular matter must be large enough so that they are not subject to thermal motion. Usually the structure of granular matter depends on its history; it is generally far from being in thermodynamic equilibrium, and gravitation plays a significant role.

Example 1.1

A granular system that is dominated by surface effects is shown in Figure 1.2. A scanning electron microscope (SEM) image shows aggregates of SiO_2 particles (diameter $0.9\ \mu\text{m}$). These particles were blown as dust into a chamber filled with gas. While sedimenting, they formed fractal aggregates due to attractive van der Waals forces, and collected on the bottom. These aggregates are stable for weeks or