Particles at Fluid Interfaces and Membranes

Attachment of Colloid Particles and Proteins to Interfaces and Formation of Two-Dimensional Arrays

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Preface

In the small world of micrometer to nanometer scale many natural and industrial processes include attachment of colloid particles (solid spheres, liquid droplets, gas bubbles or protein macromolecules) to fluid interfaces and their confinement in liquid films. This may lead to the appearance of lateral interactions between particles at interfaces, or between inclusions in phospholipid membranes, followed eventually by the formation of two-dimensional ordered arrays. The present book is devoted to the description of such processes, their consecutive stages, and to the investigation of the underlying physico-chemical mechanisms.

For each specific theme the physical background is first given, that is the available experimental facts and their interpretation in terms of relatively simple theoretical models are presented. Further, the interested reader may find a more detailed theoretical description and review of the related literature.

The first six chapters give a concise but informative introduction to the basic knowledge in surface and colloid science, which includes both traditional concepts and some recent results.

Chapters 1 and 2 are devoted to the basic theory of capillarity, kinetics of surfactant adsorption, shapes of axisymmetric fluid interfaces, contact angles and line tension.

Chapters 3 and 4 present a generalization of the theory of capillarity to the case, in which the variation of the interfacial (membrane) curvature contributes to the total energy of the system. Phenomenological and molecular approaches to the description of the interfacial bending moment, the curvature elastic moduli and the spontaneous curvature are presented. The generalized Laplace equation, which accounts for the latter effects, is derived and applied to determine the configurations of free and adherent biological cells; a convenient computational procedure is proposed.

Chapters 5 and 6 are focused on the role of thin liquid films and hydrodynamic factors in the attachment of solid and fluid particles to an interface. The particles stick or rebound depending on whether repulsive or attractive surface forces prevail in the liquid film. Surface forces of various physical nature are presented and their relative importance is discussed. In addition, we consider the hydrodynamic interactions of a colloidal particle with an interface (or another particle), which are due to flows in the surrounding viscous liquid. Factors and mechanisms for detachment of oil drops from a solid surface are discussed in relation to washing.

Chapters 7 to 10 are devoted to the theoretical foundation of various kinds of capillary forces. When two particles are attached to the same interface (membrane), capillary interactions, mediated by the interface or membrane, may appear between them. Two major kinds of capillary interactions are described: (i) capillary *immersion* force related to the surface wettability and the particle confinement into a liquid film (Chapter 7), (ii) capillary *flotation* force originating from interfacial deformations due to particle weight (Chapter 8). Special attention is paid to the theory of capillary immersion forces between particles entrapped in *spherical* liquid films (Chapter 9). A generalization of the theory of immersion forces allows one to describe membrane-mediated interactions between *protein inclusions* into a lipid bilayer (Chapter 10).

Chapter 11 is devoted to the theory of the capillary bridges and the capillary-bridge forces, whose importance has been recognized in phenomena like consolidation of granules and soils, wetting of powders, capillary condensation, long-range hydrophobic attraction, bridging in the atomic-force-microscope measurements, etc. The treatment is similar for *liquid-in-gas* and *gas-in-liquid* bridges. The nucleation of capillary bridges, which occurs when the distance between two surfaces is smaller than a certain limiting value, is also considered.

Chapter 12 considers solid particles, which have an irregular wetting perimeter upon attachment to a fluid interface. The undulated contact line induces interfacial deformations, which are theoretically found to engender a special lateral capillary force between the particles. Expressions for the dilatational and shear elastic moduli of such particulate adsorption monolayers are derived.

Chapter 13 describes how lateral capillary forces, facilitated by convective flows and some specific and non-specific interactions, can lead to the aggregation and ordering of various particles at fluid interfaces or in thin liquid films. Recent results on fabricating two-dimensional (2D) arrays from micrometer and sub-micrometer latex particles, as well as 2D crystals from proteins and protein complexes are reviewed. Special attention is paid to the methods for producing ordered 2D arrays in relation to their physical mechanisms and driving forces. A review and discussion is given about the various applications of *particulate* 2D arrays in optics, optoelectronics, nano-lithography, microcontact printing, catalytic films and solar cells, as well as the use of *protein* 2D crystals for immunosensors and isoporous ultrafiltration membranes, etc.

Chapter 14 presents applied aspects of the particle-surface interaction in *antifoaming* and *defoaming*. Three different mechanisms of antifoaming action are described: spreading mechanism, bridging-dewetting and bridging-stretching mechanism. All of them involve as a necessary step the entering of an antifoam particle at the air-water interface, which is equivalent to rupture of the asymmetric particle-water-air film. Consequently, the stability of the latter liquid film is a key factor for control of foaminess.

The audience of the book is determined by the circle of readers who are interested in systems, processes and phenomena related to attachment, interactions and ordering of particles at interfaces and lipid membranes. Examples for such systems, processes and phenomena are: formation of 2D ordered arrays of particulates and proteins with various applications: from optics and microelectronics to molecular biology and cell morphology;

antifoaming and defoaming action of solid particles and/or oil drops in house-hold and personal-care detergency, as well as in separation processes; stabilization of emulsions by solid particles with application in food and petroleum industries; interactions between particulates in paint films; micro-manipulation of biological cells in liquid films, etc.

Consequently, the book could be a useful reading for university and industrial scientists, lecturers, graduate and post-graduate students in chemical physics, surface and colloid science, biophysics, protein engineering and cell biology.

Prehistory. An essential portion of this book, Chapters 7−10 and 13, summarizes results and research developments stemming from the Nagayama Protein Array Project (October 1990 − September 1995), which was a part of the program "Exploratory Research for Advanced Technology" (ERATO) of the Japanese Research and Development Corporation (presently Japan Science and Technology Corporation). The major goal of this project was formulated as follows: Based on the molecular assembly of proteins, to fabricate macroscopic structures (2D protein arrays), which could be useful in human practice. The Laboratory of Thermodynamics and Physicochemical Hydrodynamics (presently lab. of Chemical Physics and Engineering) from the University of Sofia, Bulgaria, was involved in this project with the task to investigate the mechanism of 2D structuring in comparative experiments with colloid particles and protein macromolecules. These joint studies revealed the role of the capillary immersion forces and convective fluxes of evaporating solvent in the 2D ordering. In the course of this project it became clear that the knowledge of surface and colloid science was a useful background for the studies on 2D crystallization of proteins. For that reason, in 1992 one of the authors of this book (K. Nagayama) invited the other author (P. Kralchevsky) to come to Tsukuba and to deliver a course of lectures for the project team-members entitled: "Interfacial Phenomena and Dispersions: toward Understanding of Protein and Colloid Arrays". In fact, this course gave a preliminary selection and systematization of the material included in the introductory chapters of this book (Chapters 1 to 6). Later, after the end of the project, the authors came to the idea to prepare a book, which is to summarize and present the accumulated results, together with the underlying physicochemical background. In the course of work, the scope of the book was broadened to a wider audience, and the material was updated with more recent results. The major part of the book was written during an 8-month stay of P. Kralchevsky in the laboratory of K. Nagayama in the National Institute for Physiological Sciences in Okazaki, Japan (September 1998 − April 1999). The present book resulted from a further upgrade, polishing and updating of the text.

Acknowledgments. The authors are indebted to the Editor of this series, Dr. Habil. Reinhard Miller, and to Prof. Ivan B. Ivanov for their moral support and encouragement of the work on the book, as well as to Profs. Krassimir Danov and Nikolai Denkov for their expert reading and discussion of Chapters 1 and 14, respectively. We are also much indebted to our associates, Dr. Radostin Danev and Ms. Mariana Paraskova, for their invaluable help in preparing the numerous figures. Last but not least, we would like to acknowledge the important scientific contributions of our colleagues, team-members of the Nagayama Protein Array project, whose co-authored studies have served as a basis for a considerable part of this book. Their names are as follows. *From Japan*: Drs. Hideyuki Yoshimura, Shigeru Endo, Junichi Higo, Tetsuya Miwa, Eiki Adachi and Mariko Yamaki; *From Bulgaria*: Drs. Nikolai Denkov, Orlin Velev, Ceco Dushkin, Anthony Dimitrov, Theodor Gurkov and Vesselin Paunov.

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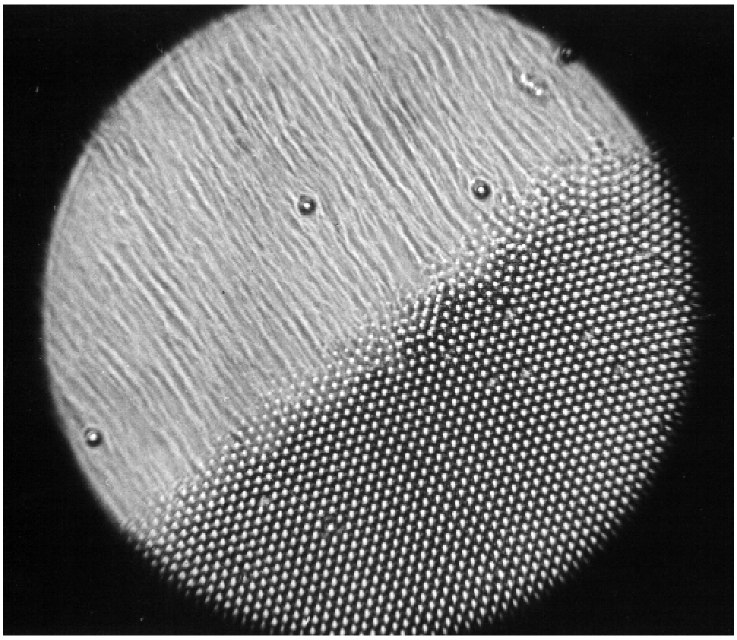

Photograph of the process of 2D array formation from latex particles, 1.7 μm in diameter, under the action of the capillary immersion force and an evaporation-driven convective flux of water (see Chapter 13); the tracks of particles moving toward the ordered phase are seen; from N.D. Denkov, O.D. Velev, P.A. Kralchevsky, I.B. Ivanov, H. Yoshimura, K. Nagayama, Langmuir 8 (1992) 3183.

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