

INTERFACE SCIENCE AND TECHNOLOGY

Particles at Interfaces

Interactions, Deposition, Structure

Zbigniew Adamczyk



Particles at Interfaces: Interactions, Deposition, Structure

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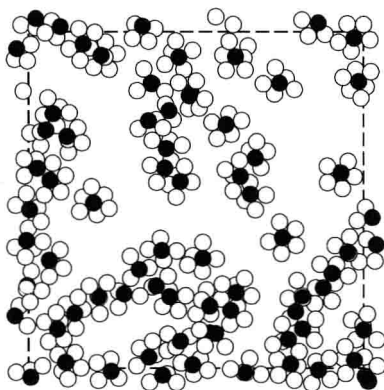
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To Maria...

Preface

Colloid science, once merely a collection of disconnected facts and observations, matured at the beginning of the 20th century to become a quantitative branch of knowledge.

Undoubtedly, one of the milestones on this road was the mathematical theory of Brownian motion, formulated by Einstein in 1905–1906 and independently at the same time by Smoluchowski, who used kinetic, rather than statistical arguments. This theory, combined with Perrin's precise observations involving latex particles, furnished decisive proof of the existence of molecules, an existence still denied in those days by the phenomenological school of Mach and Ostwald. The humble lesson this theory has to teach us is that no matter how long a Brownian object is observed, one can never predict where its next movement in time will be. The only things that can be known with a defined uncertainty are the time- or ensemble-averaged quantities, for example the distance traveled by the particle after a long time. Philosophically speaking, there are definite limits to our knowledge of the behavior of any system. One can, therefore, construct no more than approximate models of reality, while its true nature remains undisclosed. In this respect, the Brownian motion theory had far reaching consequences, pioneering the contemporary fuzzy-logic way of thinking.

The next major steps in quantifying colloid science were the theory of electrokinetic phenomena, in particular electrophoresis, developed by Smoluchowski in 1903, and the theory of fast coagulation which he elaborated in 1916. Both theories have been successfully used until now to determine the zeta potential of particles and predicting colloid system stability. The range of applicability of the theory of coagulation can be significantly extended by considering the actual profile of particle interaction energy. This profile is derived from another fundamental theory, summarized in

Vervey and Overbeek's book published in 1948, referred to as the DLVO theory (an acronym comprised of the names Derjaguin, Landau, Vervey and Overbeek). The main assumption in formulating the theory was the additivity principle of the electrostatic and van der Waals interactions. Additionally, useful expressions for the double-layer interaction energy between particles were derived using the Poisson–Boltzmann equation, which describes the charge screening effect.

Because of computational limitations, the DLVO theory could not be combined with hydrodynamics and statistical theories concerning particle populations. However, with the advent of the modern computer it became feasible to solve particle transport equations, precisely incorporated long-range hydrodynamic and short-range specific (surface) interactions. A major advancement was achieved in this field in the 1970s and 1980s when particle transport problems were solved for flows of practical interest and interface geometries, such as spherical and cylindrical ones. Further progress was attained in the 1990s when increasing computer efficiency enabled one to perform Monte Carlo or Brownian dynamic simulations, which mimicked real systems more closely. In this way, important clues were gained on the mechanisms of irreversible processes, e.g., the adsorption of particles on interfaces. *Ab initio* type simulations performed for large particle populations enabled one to determine both the kinetics of particle deposition, the structure and the jamming coverage of particle monolayers of various shape.

Yet despite the rapid progress in this field, there are few if any books devoted entirely to the subject of particle transport, deposition and structuring on boundary surfaces. This book attempts to fill this gap by presenting recent developments in this growing field. Combining traditional theories of electrostatics, hydrodynamics and transport with new approaches in a harmonious whole is the major aim of this book. The need for such theoretical reference data obtained for well-defined particle systems and transport conditions is vital in view of the complexity of the problems, which have been studied recently. They involve concentrated systems of polydisperse and non-spherical particles, as well as bio-particles such as DNA fragments, proteins, viruses, bacteria, cells, polymers, etc. These particles are of complex structure and undergo transformations under the action of surface forces. Particle mono- and multilayers are often formed on heterogeneous surfaces, covered by specifically or non-specifically binding sites. There is a possibility that the results can be misinterpreted because the monolayers are usually dried before microscope examination, which disturbs their struc-

ture. Even using the *in situ* AFM methods (with the tapping mode), one may produce some tip-induced artifacts. The situation is especially critical with the subtle problem of protein adsorption, requiring the most refined experimental approaches.

The book, which provides one with readily accessible reference data and equations for estimating basic effects, is mainly addressed to students and young scientists. Consequently, most approaches are of a phenomenological nature, enabling one to derive concrete expressions, which describe the basic physics of the problem under consideration. To facilitate access to the information contained in the book most of the relevant formulae and results are compiled in tables, accompanied with appropriate diagrams. The math is limited to the necessary minimum with emphasis on the physics of the phenomena, defining why they occur and what the kinetics of the processes and the practical implications are. Accordingly, the book, which represents the first part of the saga, is meant as a kind of physical foundation. The next volume will be devoted to experiments and applications. I hope that with such an approach the book, which is also meant to be self-contained, proves user-friendly and will save a good deal of the student's time.

On a personal note, I would like to express my thanks to the various persons who shaped my scientific carrier giving invaluable advice, providing inspiration and motivation in moments of despair.

Looking back to my PhD times I must mention Professor Andrzej Pomianowski, a true scientific father of mine, who taught me that passion is the key when dealing with science, art and related subjects. It was he who first introduced me to the realm of colloids, to the many fascinating phenomena occurring when two interfaces come into intimate contact, foaming and lubrication to name just a couple.

Two friends of mine in those good old days were of invaluable help to me: Tadeusz Dąbroś, with whom I carried out innumerable discussions on the surface of tennis courts, and Jan Czarnecki, who gave me an intense course in the elegant formulation of thoughts. He also convinced me, with a little help of Newtonian liquids, that social activities can be treated as extended science, too.

Then, as a young Post Doc fellow in Montreal, I met another brilliant person, a man of enormous vitality. He opened my eyes to the nuances of scientific reality, taught me that there is industry and practical problems to be solved. Most lessons took place on squash courts where we also practiced elastic two-body collisions, rather painful to Theo van de Ven, just to mention his broken glasses.

Returning to Cracow, I had the chance to collaborate with Piotr Warszyński, first my student, then, quite unexpectedly, my boss. Over the last 20 years we have discussed a myriad of subjects, exchanging thousands of words... one way. Most, of what I have learned of hydrodynamics is to Peter's credit. With Peter my run of good luck still continues. Thanks to him it was proved unequivocally that I am quite an influential partner, as I managed to damage a bone of his over the distance of about 20 m, i.e., the length of a tennis court. Although Peter recovered after a couple of weeks, he became considerably more careful in contact with me.

There are many others to whom I am very indebted, mostly to the members of my and related groups: Basia Jachimska, Kasia Jaszczołt, Marta Kolasińska, Kazimierz Małysa, Aneta Michna, Basia Siwek, Lilianna Szyk-Warszyńska and Maria Zembala. They helped me enormously by providing fascinating experimental results, carrying out numerous discussions, supplying relevant literature, doing artwork and assisting in other technical matters. They suffered a lot for over a year when the book was *in statu nascendi* and I was unable to properly appreciate their hard work.

I am also very thankful to Jakub Barbasz and Paweł Weroński who masterminded the numerical simulations and provided me in emergencies with the required graphs. A significant part of Paweł Weroński's PhD thesis, especially the unpublished results concerning the unoriented adsorption of spheroidal particles, has been exploited in Chapter 5. Jakub Barbasz and Małgorzata Nattich were also kind enough to critically revise the manuscript and in checking the numerical calculations. Another bright person who helped me a lot was Piotr Wandzilak, who performed the linguistic corrections of the manuscript, also giving invaluable advices and suggestions. The list could go on since there were more people who helped me in finishing this project, often suffering from my negligence. My deepest apologies to all of you.

Last but not least there are two very special persons to whom I am indebted eternally: Marta Krasowska and Ela Porebska, true angels who were destined to Earth. Not only have they done all the tedious technical things, patiently dealing with endless corrections and revisions, but also generously offered sustained inspiration and motivation. If you like the look of the book, it is only because they loved what they were doing.

Zbigniew Adamczyk

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Chapter 1

Significance of Particle Deposition

Effective attachment of particles to surfaces, involving transport, adsorption and adhesion steps, is important for many practical processes such as water and waste water filtration, electroflotation, separation of toner and ink particles, coating formation, paper making, xerography, production of magnetic tapes, catalysis, colloid lithography, protein and cell separation (affinity chromatography), food emulsion and foam stabilization, immobilization of enzymes, immunological assays, etc.

Controlled assembly of colloid particles into organized structures has potential applications in the production of nano- and microstructured materials of desired functionality, such as biocompatible coatings. Ordered arrays of colloid particles, for example silver particles, are exploited as narrow-band optical filters; they can be used as optical switches, photonic band gap materials, waveguides and other electrooptical and magneto-optical devices.

An emerging field of application of particle deposition is the “colloid bar coding” technique, which can encode libraries of millions of compounds using a few fluorescent dyes.

In other processes, such as membrane filtration, biofouling of membranes and artificial organs, flotation (slime coating formation) and production of microelectronic or optical devices, particle adsorption is highly undesirable.

Besides these practical applications, studies of colloid particle deposition, carried out using direct experimental methods, can furnish fundamental information on interactions between particles and interfaces, and between adsorbed and moving particles. This is a crucial issue for colloid science, biophysics and medicine, soil chemistry, etc. For example, the symmetry and local intensity of flows can be easily detected by performing deposition experiments and observing the density of particles on the surface with an optical microscope. This is illustrated in Fig. 1.1, showing micrographs of polystyrene latex particles adsorbed on a mica surface exposed to a stagnation point flow of radial symmetry [1] or to an oblique flow [2]. The

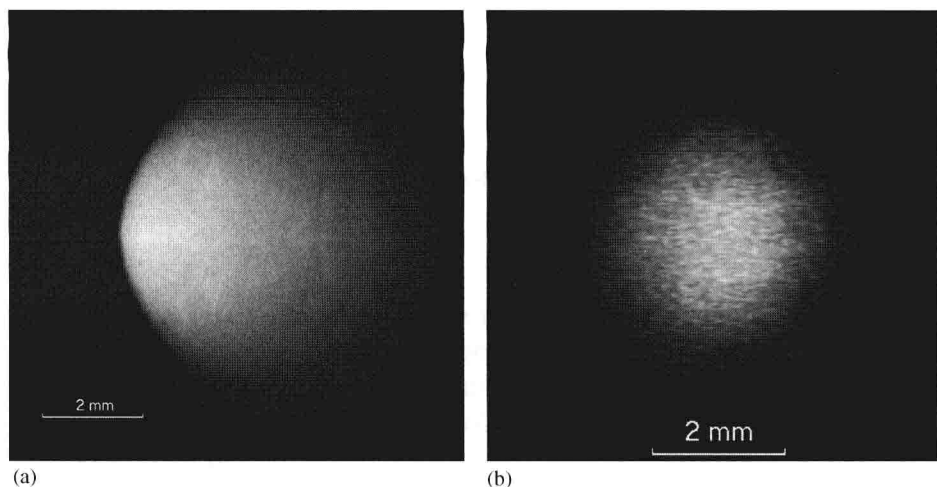


Fig. 1.1. (a) Flow pattern near a mica/electrolyte interface exposed to an oblique flow, visualized by adsorbed polystyrene latex particles. (b) Flow pattern near a mica/electrolyte interface exposed to a radial stagnation point flow, visualized by adsorbed polystyrene latex particles.

latter flow configuration enables microscopic observations for non-transparent substrates, e.g., metallic surfaces such as gold [3]. However, any quantitative information on the flow pattern can only be extracted from these measurements, if the theoretical predictions of local mass transfer rates are known; they are extensively discussed in Chapters 2 and 3.

Colloid adsorption can also be used to make visible various structures formed near interfaces by aggregating chains of polyelectrolytes, as seen in Fig. 1.2. In a similar way, colloidal particles of silver are used in the staining process to visualize nanosized particles of biological origin.

By measuring particle adsorption for model colloid systems, important information can be gained on the mechanisms and kinetics of molecular adsorption inaccessible for direct experimental studies. In this way the links between irreversible (colloid) and reversible (molecular) systems can be established. For example, by studying the particle distribution on surfaces in the limit of low coverage, when a gas-like phase is formed, one can derive important clues on the dynamic interactions between adsorbed and adsorbing particles, by inverting the Boltzmann distribution. This is illustrated in Fig. 1.3, showing a monolayer of polystyrene latex particles on mica [4] at dimensionless coverage $\Theta = 0.05$.

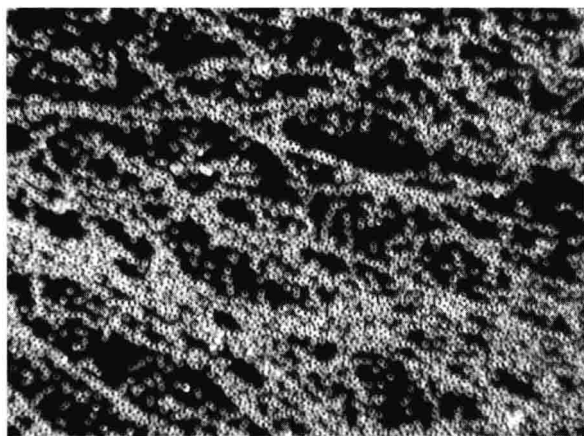


Fig. 1.2. Latex particles attached to polymer fibers formed at a mica/electrolyte interface.

As can be seen, the distribution of particles characterized in terms of the pair correlation function g is well reflected by the Boltzmann distribution. With increasing coverage (see Fig. 1.3.b), the structure of the colloid particle monolayer closely mimics a molecular liquid-phase structure, e.g., liquid argon at 130 K [5]. This fact suggests that colloid particle monolayers can be exploited as a useful reference system for studying fluctuation and structure formation phenomena occurring on a molecular scale, e.g., for proteins.

As a consequence, the possible structure of globular protein monolayers on solid substrates, for example, can be forecasted by using reference data collected for colloids. Experimental data for colloids can be transferred to molecular systems using appropriate theoretical background discussed in Chapters 4 and 5. One of the most efficient ways of obtaining structural data is the Monte-Carlo simulation, described in Chapter 5. Using this method, fascinating structures have been predicted in the case of particle adsorption on substrates bearing isolated adsorption centers of spherical shape. As seen in Fig. 1.4, flower-like structures appear because one adsorption center can coordinate on average 5.5 adsorbing particles [6]. Hence, such theoretical simulations suggest that it would be possible to produce clusters of targeted architecture, e.g., containing a prescribed number of particles. The coordination number can be regulated by changing the particle-to-site size ratio. Indeed, experimental results reported recently [7] seem to confirm this prediction. This is seen in Fig. 1.5, presenting micrographs of polystyrene latex