S.-H. Chen / R. Rajagopalan
Editors

Micellar Solutions and Microemulsions

Structure, Dynamics, and Statistical Thermodynamics

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Preface

During the last decade there has been a renewed interest in research on supramolecular assemblies in solutions, such as micelles and microemulsions, not only because of their extensive applications in industries dealing with catalysts, detergency, biotechnology, and enhanced oil recovery, but also due to the development of new and more powerful experimental and theoretical tools for probing the microscopic behavior of these systems. Prominent among the array of the newly available experimental techniques are photon correlation spectroscopy, small-angle neutron and X-ray scattering, and neutron spin-echo and nuclear magnetic resonance spectroscopies. On the theoretical side, the traditionally emphasized thermodynamic approach to the study of the phase behavior of self-assembled systems in solutions is gradually being replaced by statistical mechanical studies of semi-microscopic and microscopic models of the assemblies. Since the statistical mechanical approach demands as its starting point the microscopic structural information of the self-assembled system, the experimental determination of the structures of micelles and microemulsions becomes of paramount interest. In this regard the scattering techniques mentioned above have played an important role in recent years and will continue to do so in the future. In applying the scattering techniques to the supramolecular species in solution, one cannot often regard the solution to be ideal. This is because the inter-aggregate interaction is often long-ranged since it is coulombic in nature and the interparticle correlations are thus appreciable. Even if the aggregates are charge-neutral, there are other forces such as the van der Waals force and the solvation forces, which are sufficiently important for the thermodynamics of dense colloidal solutions. Thus the fundamental task of the statistical mechanical theories is to elucidate these basic interactions and to use them as a starting point for the development of the statistical mechanical models. This monograph discusses these fundamental issues.

Part One of the book, which contains eight chapters, deals with basic interactions, statistical mechanics, and computer simulation, and Part Two, which contains another eight chapters, gives selected applications of statistical thermodynamics to the phase behavior, critical phenomena, structure, interface tension, and transport properties of micellar solutions and microemulsions. In both parts, experimental and theoretical chapters are intermingled with each other. The choice of the subject matter is of course determined by the timeliness of the topics and the taste of the editors.

In Chapter 1, Chen and Sheu discuss the method of analysis of small-angle neutron scattering data when the inter-aggregate interaction is significant, such as in charged micellar solutions or in charged globular protein solutions. For these solutions the dominant interaction is the repulsive double-layer interaction. The interparticle structure factor in this case can be calculated analytically by a generalized one-component macroion (GOCM) theory using the generalized Derjaguin–Landau–Verwey–Overbeek (DLVO) interaction. A detailed derivation of the generalized DLVO interaction using a standard liquid-state theory formalism is given in this chapter. In Chapter 2, Lozada-Cassou and Henderson have developed a liquid-theoretic method for calculating the force between two flat interacting electrical double layers. This new method can be regarded as an extension of the well-known Poisson–Boltzmann (PB) theory and predicts that the electrostatic interaction between colloidal parts can, under certain conditions, be attractive. In Chapter 3, Jönsson and Wennerström use computer simulation techniques to study the electrical double layer with respect to both equilibrium and transport properties. This method can be used to test and complement the results obtained from the conventional use of the Poisson–Boltzmann equation. For a system with high surface charge densities and divalent counterions, the PB approach predicts a repulsive interaction between overlapping double layers, with the Monte Carlo simulations show a net attraction due to the strong ion–ion correlation effects. Rossky, Murthy, and Bacquet describe, in Chapter 4, a series of integral equation calculations and Monte Carlo computer simulations of ion distributions around rod-like polyelectrolytes such as DNA in aqueous solutions. The results of the two methods agree in general for both monovalent and divalent counterions but are sufficiently different from those of the PB equation, especially in the case of divalent counterions. The calculations also show the range of validity of the popular phenomenological charge-condensation model. The present status of the experimental studies of solvation forces, namely, the forces arising from the structural rearrangement of the solvent molecules near surfaces, is reviewed in Chapter 5 by Horn and Ninham. In the classical DLVO theory of colloidal stability, there are only the repulsive double-layer force and the attractive van der Waals interaction. The discovery of solvation forces is more recent and their origin less certain. Horn and Ninham discuss the circumstances under which the solvation forces can be expected to be significant. In recent years, Israelachvili and coworkers have made direct measurements of forces between two mica plates immersed in liquids at very close separations. These solvation forces arise when the plates are separated by a gap of the order of the diameter of the liquid molecules. The origin of such forces is examined in Chapter 6 by Wertheim, Blum, and Bratko using a model system consisting of hard spheres confined between two plates. Because of the simple geometry of their system, Wertheim, Blum, and Bratko have been able to carry out some rigorous statistical mechanical calculations of the density profile between the plates. The results are compared with exact profiles generated by Monte Carlo simulations. For high densities, oscillatory profiles similar to those obtained experimentally are seen. In Chapter 7, Hirtzel and Rajagopalan review the use of some of the standard Monto Carlo and Brownian dynamics simulation techniques, with a focus on their use in determining the interparticle structure and thermodynamic and transport properties of colloidal dispersions. These are powerful techniques for carrying out exact statistical mechanical calculations of complex fluids and are becoming popular in the studies of supramolecular systems. This chapter is written specifically in a tutorial style accessible to graduate students entering this field. Since scattering experiments also measure, besides the particle structure of colloids, the interparticle structure factor, which is intimately related to the thermodynamic properties of the solution, theoretical calculation of the structure factors for given interparticle interaction potentials becomes important. Although the GOCM discussed in Chapter 1 is suitable for calculating the structure factor of monodispersed charge-stabilized systems, there are some difficulties in applying it to very polydispersed systems. Fortunately, it is possible to carry out an analytical calculation of the structure factor for polydispersed hard-sphere systems in the Percus–Yevick approximation. Vrij and de Kruif present a detailed exposition of such a calculation in Chapter 8. Many of the analytical results summarized in this chapter are not available in the published literature. We hope that this formalism will find good use in the future by those doing scattering experiments.

Part Two of the book begins with a review by Safran, in Chapter 9, of a phenomenological theory for the structure and phase behavior of dilute three-component microemulsions. Microemulsions in this region are likely to have globular structures such as spherical, cylindrical, or lamellar. This phenomenological theory starts with an appropriate expression for the free energy of the system in terms of a few characteristic parameters such as the spontaneous curvature and the bending constant of the surfactant terms film and then adds to it the mean-field interaction and the entropy terms. It is rather remarkable that this simple theory is able to predict a fairly realistic structure of the aggregates and the phase transitions from one structure to the other as observed in experiments. Another type of mean-field theory is formulated in Chapter 10, by Blankschtein, Thurston, Fisch, and Benedek, for two-component surfactant-water systems by taking into account the monomer–micellar association chemical equilibrium. This theory is successful in accounting for the micellar–micellar phase separation phenomena often found in zwitter-ionic and nonionic micellar solutions much like the well-known Flory–Huggins theory for polymer solutions. In Chapter 11, Taupin, Auvray, and di Meglio review an extensive series of theoretical and experimental work by a French group on five-component microemulsions in the region of the phase diagram where the structure is bicontinuous. Small-angle X-ray and neutron scattering experiments are used to show, for the first time, that the surfactant film has a low rigidity constant when a cosurfactant is present and has, on the average, zero mean curvature in the bicontinuous microemulsions. Chapter 12, by Langevin, goes on to discuss the theory and experiments on the characteristic properties of ultralow interfacial tension in five-component microemulsions in the droplet and bicontinuous phases. Understanding of the ultralow surface tensions between a microemulsion and water-rich or oil-rich phases is vital for industrial applications of microemulsions. In Chapter 13, Huang, Kotlarchyk, and Chen describe a microemulsion-to-microemulsion phase separation phenomenon in an AOT/water/alkane three-component microemulsion system. This popular system behaves like a typical binary fluid mixture showing a lower consolute point, when the molar ratio of water-to-AOT is kept constant. Thus, one can apply the well-developed theory of static and dynamic phenomena quite successfully. In Chapter 14, Roux and Bellocq continue the exploration of critical phenomena in another ternary microemulsion system composed of SDS/water/pentanol from the point of view of identifying a new field variable. For both the AOT-based and SDS-based ternary microemulsion systems the critical phenomena have been demonstrated to belong to an Ising-like universality class. Light scattering and neutron scattering investigations of a five-component microemulsion follow in Chapter 15, by Chang, Billman, Licklider, and Kaler. The microstructure of these microemulsions is identified to be droplets at low volume fractions of water or oil, while microemulsions with comparable water and oil volume fractions are shown to have bicontinuous structures. In the last chapter, Kim and Dozier discuss the measurements of transport properties, such as the self-diffusion coefficient, mutual diffusion coefficient, and electrical conductivity of the AOT-based ternary microemulsions. In particular, a striking electrical percolation threshold, both in temperature and in volume fraction, is found. The conductivity is shown to have a power-law behavior below and above the percolation threshold.

In preparing this volume our primary intention was to assemble a set of coherent, up-to-date articles written by some of the most active researchers to cover the present status of progress in statistical mechanical theories of colloidal, micellar, and microemulsion systems. This monograph has turned out to be an exciting collection of original articles, accurately reflecting the direction of current developments in the field. This would not have been possible without the cooperation of all the authors, and we would like to express our sincere gratitude for their efforts and patience.

This monograph is intended for graduate students and professional scientists and engineers who wish to have an overview of the present status of the fundamental issues in the field of micellar solutions and microemulsions.

To facilitate the readers' understanding of the material included in this book, the following three references are recommended:

- J.N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 1985.
- C. Tanford, *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd Ed., Wiley, New York, 1980.
- J.-P. Hansen and I.R. McDonald, *Theory of Simple Liquids*, 2nd Ed., Academic Press, New York, 1986.

Israelachvili's book presents a good introduction to the various forces relevant to colloidal solutions. Tanford's book explores the thermodynamic principles of self-assembly of amphiphilic molecules in aqueous media. The book by Hansen and McDonald presents a detailed treatment of integral equation theories of liquids.

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Part One Basic Interactions, Statistical Mechanics, and Computer Simulations

1

Interparticle Correlations in Concentrated Charged Colloidal Solutions—Theory and Experiment

S.-H. CHEN and E.Y. SHEU

We present a liquid theoretic approach to analyses of small-angle scattering data when the interparticle correlations effect is important. In particular, the one-component macroion (OCM) theory for calculating the interparticle structure factor is shown to be an appropriate theory for analyses of small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) data on dilute-charged colloidal solutions. A detailed derivation of a generalized one-component macroion (GOCM) theory is given. The GOCM theory extends the range of validity of OCM theory to higher concentrations. The result of GOCM theory indicates that the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) double-layer interaction should be interpreted as the potential of mean force in the dilute concentration limit. Two examples, a series of moderately concentrated cytochrome-C protein solutions and sodium dodecyl sulfate micellar solutions, are used to illustrate the applicability of GOCM theory.

I. Introduction

During the last decade, various experiments using light scattering, both static and dynamic [1], small-angle neutron scattering (SANS) as well as small-angle X-ray scattering (SAXS) on polystyrene latex spheres [2,3], ionic micelles [4,5], and hydrophilic proteins [5] in aqueous solutions, have identified a pronounced correlation peak in the scattering intensity distributions. The position of the correlation peak is generally located at the $|\mathbf{Q}|$ value ($\mathbf{Q}$ is the scattering vector) approximately equal to 2π times the reciprocal of the mean interparticle separation distance. This experimental fact implies that there exists significant local ordering around a given macroion in the electrostatically stabilized colloidal suspensions due to their strong mutual electrostatic interactions, even at very low particle volume fraction. Since this electrostatic interaction is screened by the available counterions, which keep the solution neutral as a whole, the macroion–macroion interaction in this case is dominated by the double-layer repulsive