Physicochemical Hydrodynamics: An Introduction

By Ronald F. Probstein, John Wiley and Sons, New York, 2nd ed., 1994, 400 pp., $69.95.

Physicochemical hydrodynamics is the study of the interaction between the flow of liquids and physical, chemical and biochemical processes. These interactions occur typically because of the complex nature of the fluid, which might be a suspension of interacting particles or a solution of ions in the presence of an electric field. They also occur because the flow is strongly impacted by interfacial effects. Examples of these types of phenomena are ubiquitous in chemical engineering and are becoming increasingly more important. They include many separation processes, such as reverse osmosis and ultrafiltration, centrifugation, gel chromatography and electrophoresis. Other examples are the surface tension effects that are significant in coating flows and in droplet deformation and breakup. In this, the second edition of *Physicochemical Hydrodynamics: An Introduction*, all of these topics and more are covered, as they were in the first edition. In addition, new sections have been included on hydrodynamic chromatography, chemical reactions in electroosmosis through soils, and Bénard convection cells, plus a new chapter has been added on rheology and concentrated suspensions.

One might expect this diverse list of topics to be the subject of several volumes, rather than a single book. However, emphasis here must be placed on the second half of the title of Probstein's work. The author's intent is clearly to *introduce* a representative sample of problems to graduate students in chemical and mechanical engineering and related areas, and to subject those problems to simple analytic analyses, rather than to present an exhaustive survey. The details and complexities of formal asymptotic matching procedures and numerical methods are avoided. Although this avoidance, together with the broad range of topics covered, clearly limits the level of rigor possible in the derivations, it does keep the focus on development of the reader's physical, intuitive understanding of problems. Where appropriate, references to other texts or to articles in the literature are provided for the benefit of those who desire a more rigorous treatment of various examples.

The framework that provides unity to this text which covers so many diverse phenomena lies in the continuum theories that are used in the analyses. The constitutive and conservation equations that are used to derive these fundamental theories of transport of heat, mass, momentum and charge are presented in Chapters 2 and 3, Chapter 1 being a short introduction. Although the coverage is brief compared to some other texts (for example, L. G. Leal's *Laminar Flow and Convective Transport Processes*, Butterworth-Heinemann, 1992; J. S. Newman's *Electrochemical Systems*, Prentice-Hall, 1991), these chapters provide a useful background for subject matter that is by its very nature interdisciplinary. What to some students might seem a short review could to others be their first introduction to a topic, providing them with the essentials needed to move forward while at the same time prompting further reading in some of the well-known texts listed as references. These first three chapters conclude with a section on scaling or dimensional analysis of the governing equations, which contains a nice summary of the dimensionless groups that arise in the problems to follow, as well as their physical interpretations.

The succeeding four chapters are arranged in a logical progression in order of increasing complexity, with the first two dealing with uncharged systems and the latter two with charged systems. In Chapter 4, properties of solutions of uncharged molecules are discussed, including such problems as mass-transfer boundary layers in laminar flow through channels with reacting walls, reverse osmosis, Taylor-Aris dispersion in tubes, and gel chromatography. Solutions of uncharged macromolecules and particles that are large compared to the surrounding solvent molecules are treated in Chapter 5. This chapter can conveniently be separated into two parts, one dealing with fundamental properties of suspensions and the other with suspension-processing operations. A fundamental discussion of macromolecules and particulates in liquids necessarily involves the field of microhydrodynamics, or the fluid mechanics of suspensions of small, sometimes Brownian solutes for which inertia is usually negligible. The mathematical detail of this field is avoided here by quoting some key results for spherical and spheroidal particles and referencing the well-known works of Happel and Brenner (1983) (*Low Reynolds Number Hydrodynamics*, Martinus Nijhoff) and Kim and Karrila (1991) (*Microhydrodynamics*, Butterworth-Heinemann). There follows a good discussion of Brownian motion, along with derivations of the Stokes-Einstein equation both by the original, "thermodynamic force" argument of Einstein and by using the Langevin equation. The first half of Chapter 5 concludes with a presentation of Einstein's derivation of the viscosity of a dilute suspension by viscous dissipation arguments. In the second half of Chapter 5, a series of suspension-processing operations are discussed. These include sedimentation, analytic and preparative ultracentrifugation, ultrafiltration and hydrodynamic chromatography. The discussions of sedimentation and centrifugation are particularly strong, and include a description of enhanced settling in inclined tubes, an insightful explanation of the workings of an analytic ultracentrifuge, and a review of related techniques such as density-gradient centrifugation.

Chapters 6 and 7 deal with solutions of small and large *charged* species, respectively. Very little knowledge of electrochemistry is assumed of the reader, as Chapter 6 begins with a definition of an electrochemical cell, including definitions of *anode* and *cathode*. A basic discussion of the thermodynamics of electrochemical reactions and other considerations, such as overpotentials, is presented before the process operations of electrodialysis and ion exchange are covered. The chapter then concludes with three sections on electrical double layers and electroosmosis. The last of these three sections, which was not in the first edition, is an interesting description of how chemical reactions affect efforts to use electroosmosis to purge contaminants from soils, an area of active research for the author in recent years. Chapter 7 is devoted primarily to electrophoresis and electrophoretic separations, although there is a short section on sedimentation and streaming potentials. Here, the treatment of the problem of electrophoretic motion of a sphere in the limit of small double layers has been modified from the first edition, in which Smoluchowski's equation was derived without sufficient explanation. The modified derivation is a definite improvement over the original, although it is still less complete than those found elsewhere (for example, *Colloidal Dispersions* by W. B. Russel, D. A. Saville, and W. R. Schowalter, Cambridge University Press, 1989).

In Chapters 8, 9 and 10, the topics of suspension stability, rheology and surface tension are covered, respectively. Chapter 8 begins with an overview of DLVO theory, which is followed by a discussion of Smoluchowski's theory for collision rates in colloidal suspensions. The remainder of the chapter focuses on particle capture and filtration. Chapter 9, "Rheology and Concentrated Suspensions," is new and was written for the second edition. Of the four sections of this chapter, the first two deal with rheology generally, and the latter two with the particular rheology of monomodal- and bimodal-concentrated suspensions in the limit of high shear. Obviously, when covering topics as broad as these in one short chapter, only some of the most basic concepts and definitions can be included, and the comments above pertaining to the introductory nature of the text are once again applicable. Definitions of the shear-rate-dependent viscosity and the first and second normal stress differences are provided, along with the well-known Bingham and power-law models of generalized Newtonian fluids. There is also an informative discussion of the importance of relaxation times in the flow of polymer liquids. The sections on concentrated suspensions focus on the more influential of the many semiempirical models that are available for the high shear viscosity of those systems. Efforts to calculate the viscosity by rigorous theories and simulations are not discussed. Shear-induced migration, currently of great interest to the fluid mechanics community, is mentioned briefly but is not discussed. The final chapter, Chapter 10, covers several classic examples of the interaction between surface tension and fluid flow. These include capillary rise in tubes, dip coating, Raleigh's analysis of jet breakup, and thermocapillary migration in a shallow pan. The final section, which is new to the second edition, is a good discussion of buoyancy and Marangoni effects in the formation of hexagonal Bénard cells.

The wide variety of problems treated by the unified theoretical framework presented in this book make it a pleasure to read. Although the coverage could in places benefit from additional depth, it is thorough enough to identify the underlying physics governing many problems of physicochemical hydrodynamics. In addition, in most chapters there is a nice blend of fundamental scientific principles along with their application in analytic methods and in process operations. As an introductory text, this book should therefore be very useful to students in physical chemistry, chemical and mechanical engineering.

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Schrodinger Equations and Diffusion Theory

By Masao Nagasawa, Birkhauser Verlag, Berlin, 1993, 319 pp., $99.00.

This is a highly mathematical book that discusses in depth the equivalence between diffusion processes and Schrodinger's quantum mechanics. It is a desirable reference book for those interested in stochastic processes. Among chemical engineers, the book's audience will be limited to theorists and computer simulation experts who are interested in stochastic processes. This, however, does not imply that the book is not of relevance to the study of many problems of interest to chemical engineers. Transport of species through polymer membranes, acidic zeolites and other micro/mesoporous media, ion transport through solid polymer electrolytes used in lightweight batteries, nutrient transport in biological systems, and turbulent flows are examples of quintessential chemical engineering applications wherein an understanding of stochastic processes is important. This book does not discuss practical ways of analyzing these problems. It does, however, provide deep insight into the theoretical framework that underlies useful descriptions of these processes. Thus, the book will be of value to theorists and computer simulators.

The main benefit of this book for applied scientists stems from the comprehensive discussion of the many subtle issues associated with the equivalence between "imaginary time quantum mechanics" and diffusion processes. I particularly enjoyed Chapters 2–4 which contain beautiful (but mathematical) discussions of many important topics that include the Feynman-Kac formula, Kolmogoroff's representation, and the equivalence theorem. Chapter 6 also contains a good discussion of Feynman path integrals and how one defines a measure in this context. This discussion may also be of some use to polymer theorists.

The author's intended audience is probably not the applied science community. Even so, I believe that the book would be more beneficial to the engineering, physics and chemistry communities if more references to work were included, in which the underlying ideas discussed in the book are employed to study physical phenomena. An example would be the work on diffusion in disordered media that has revealed interesting physics of direct relevance to practical applications. In a similar vein, the book would have a wider audience if it contained some discussion of how to cast diffusion processes (and quantum mechanics) as field theories, because field-theoretic descriptions of diffusion processes can explore many phenomena of interest to the science and applied science communities. Except for the example on septation of *E-coli*, applied scientists will not find the examples in Chapter 9 very useful. My criticism of the book in this paragraph is perhaps somewhat unjustified since the author's intended audience probably included only the mathematics and applied mathematics communities.

In spite of its somewhat narrow focus, this book is an important addition to the literature on theory of stochastic processes. It will prove to be useful for theorists engaged in understanding various aspects of condensed matter phenomena that are of practical importance. I would recommend it highly to this community.

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