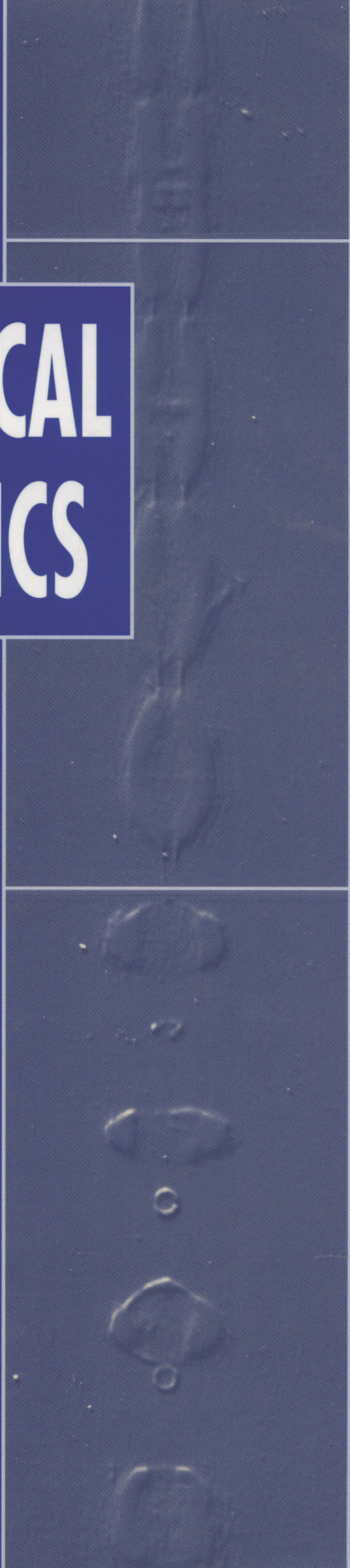


Second Edition

PHYSICOCHEMICAL HYDRODYNAMICS

An Introduction

Ronald F. Probstein



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Physicochemical Hydrodynamics

An Introduction
Second Edition

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江苏工业学院图书馆
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 WILEY-
INTERSCIENCE

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication Data is available.

ISBN 0-471-45830-9

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

This book is dedicated with affection to my wife
Irène, whose courage, good humor, and patience
have been an inspiration to me.

Preface to the Paperback Edition

It has been less than ten years since the Second Edition of this book was published. Despite the many advances that have taken place in this period because of the book's emphasis on rational theory and fundamentals it remains fresh and current to the many fields of application of PCH, including: mechanical, chemical, and environmental engineering, and materials science and biotechnology. In the period since its publication new fields have emerged that rely in whole or in part on the foundations of PCH with the material in the book forming the bases for characterizing the particular application. Two important fields in this category are microfluidics and fluid aspects of nanotechnology. The original edition is unaltered except for the correction of a few typographical errors. Many thanks are due to Bob Esposito and his associates at Wiley who agreed to bring out the book in a less expensive edition.

Ronald F. Probst

*Cambridge, Massachusetts
January, 2003*

Preface to the Second Edition

The field of physicochemical hydrodynamics has received much increased attention since the first edition. This has necessitated some revisions and updating. In addition, comments from both students and practitioners suggested that a number of topics not included should be added or topics not treated in sufficient depth should be expanded. The material essentially follows the same outline as the first edition with some topics added through appended sections along with a new chapter on rheology and concentrated suspensions. Among the new topics included are hydrodynamic chromatography, chemical reactions in electrokinetics, and surface tension induced convection. Problems have been added to complement the new material. Suggestions or answers for the problems generally are not included, but a solutions manual is available from the publisher for course instructors to aid in tailoring assigned problems.

The principles followed in the writing were the same as outlined in the original preface except that the field of rheology is now included. This preface is repeated here as given in the first edition.

In the preparation of this volume, I once more acknowledge my gratitude to Mehmet Z. Sengun and R. Edwin Hicks both of whom again provided invaluable comments which have been incorporated in the text. Thanks are also due to Howard Brenner for his discussions and comments. In so far as the book is based on the first edition, the acknowledgments still apply and to that extent are repeated here essentially unchanged.

Preface to the First Edition

Physicochemical hydrodynamics was first set out as a discipline by the late Benjamin Levich in his classic book of the same name. The subject, which deals with the interaction between fluid flow and physical, chemical, and biochemical processes, forms a well-connected body of study, albeit a highly interdisciplinary one. It has applications in many areas of science and technology and is a rapidly expanding field. The aim of this textbook is to provide an introduction to the subject, which I shall refer to here by its acronym PCH.

Emphasis is on rational theory and its consequences, with the purpose of showing the underlying unity of PCH, in which diverse phenomena can be described in physically and mathematically similar ways. The magic of this unity is shown in the similar manner in which solutes concentrate in a flow containing chemically reacting surfaces, reverse osmosis membranes, and electrodialysis membranes or the similarity of particle motions in sedimentation, centrifugation, ultrafiltration, and electrophoresis. Experimental results, numerical solutions, and reference to topics not covered are noted where they serve to illustrate a concept, result, or limitation of what has been presented. Empiricism is not eschewed, but only limited use is made of it and then only when it contributes to a better understanding of an idea or phenomenon.

The book is an outgrowth of a graduate course that I have taught for a number of years at M.I.T. under the joint sponsorship of the mechanical and chemical engineering departments. Like the course, the text is directed toward graduate students in these fields, as well as in materials science, environmental engineering, and biotechnology. An undergraduate course in fluid dynamics and a knowledge of the fundamentals of physical chemistry together with a course in advanced calculus provide sufficient prerequisites for most of the material presented. An effort has been made to include the necessary fundamentals to make the book self-contained. But because of my bias toward the "hydrodynamic" aspect, there undoubtedly has crept in the presumption of a greater knowledge of this area than of the physical-chemical ones.

The subject is a broad one, and since the aim has been to present the fundamentals, it has been necessary to limit the material covered by selecting examples that illustrate the unity of PCH and at the same time put forward its

essentials. Consequently, a number of fields, including turbulence, rheology, natural convection, and compressible flows, have been omitted. Numerical methods or formal asymptotic matching procedures are also not included. There is no doubt as to the importance of high-speed computation in PCH, but, consistent with providing an introduction to the fundamentals, the book lets the student first taste the essence of PCH in the form of simple analytical solutions rather than be satiated on a banquet of detailed numerical results.

Problems, which are so important a part of a student's learning experience, are included at the end of each chapter. The problems are ordered following the sequence in which the material is set out. Some of the problems call for numerical answers where it was felt it would be helpful to the student's "feel" for the magnitudes involved. With minor exceptions, SI units are used throughout. The questions range in difficulty, with most requiring an analytic development, but with some asking only for a descriptive answer. All are intended to illustrate the ideas presented, though often the solution goes beyond the explicit discussion in the book, with the answer constituting a generalization or extension of the text material.

Every effort has been made to acknowledge the work of others. However, for pedagogical reasons reference may sometimes be to a recognized text, review, or general reference rather than to the original source, but the person to whom the work is attributed is made clear. On the other hand, the reader is sometimes referred to an early original work where it was felt the examination of the source itself was most illuminating.

Ronald F. Probststein

Acknowledgments for the First Edition

It is with deep appreciation that I gratefully acknowledge the assistance of Mehmet Z. Sengun, who carefully read the manuscript chapter by chapter as it was being prepared for publication, offered important constructive suggestions, and corrected many of the inevitable errors that appear in a textbook of this kind. In addition, I also want to express my gratitude to him for the many excellent problems he contributed. A special note of thanks and appreciation is due R. Edwin Hicks, who read the manuscript and provided numerous valuable comments and corrections which have been incorporated into the text. I wish also to thank C. Ross Ethier for contributing several of the problems and Eric Herbolzheimer, who provided me with an unpublished manuscript.

I acknowledge with gratitude the important contribution of the Bernard M. Gordon Engineering Curriculum Development Fund at M.I.T., which enabled me to be relieved of my teaching duties for a year that I might complete this book more rapidly. Thanks are due David N. Wormley, Chairman of the Mechanical Engineering Department, and Gerald L. Wilson, Dean of Engineering, who were instrumental in bringing this about.

A special note of appreciation is due Virginia Brambilla for her capable handling of many of the secretarial details, and to Robert H. Dano, who expertly prepared all of the figures.

R.F.P.

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1 Introduction

1.1 Physicochemical Hydrodynamics

Physicochemical hydrodynamics may be broadly defined as dealing with fluid flow effects on physical, chemical, and biochemical processes and with the converse effects of physical, chemical, and biochemical forces on fluid flows. The interplay between the hydrodynamics and physics or chemistry, including biochemistry, may be *local* or *global*. When it is local, the principal features of the flow may be obtained without a knowledge of the physical or chemical phenomena, and the state of the flow fixes the physical and chemical behavior. When it is global, the physicochemical phenomena control the nature of the entire flow. So far as the fluid mechanics is concerned, the local effects may be considered a class of *weak interactions*, and the global ones a class of *strong interactions*. An explosion is a strong interaction since the energy release associated with the chemical reaction defines the flow. The electroosmotic flow through fine charged capillaries, such as in porous soils, is a strong interaction since the electric field defines the flow. On the other hand, the interaction of a fluid flow with a corrosion reaction at a pipe surface is a weak one since the corrosion will not affect the bulk flow. Similarly, the exothermic chemical reaction in a flow where the reacting components are dilute would only result in a small energy release and would not generally affect the bulk flow.

A distinctive characteristic of physicochemical hydrodynamics is the commonality of behaviors underlying many seemingly diverse phenomena. The commonality is brought about by two factors: (1) the similar character of the continuum, linear constitutive transport relations for mass, heat, and charge; (2) the similarity or, frequently, the identity of boundary conditions for chemical, electrochemical, and biochemical reactions; mass, charge, and heat transfer; and phase change. Throughout the book we shall attempt to exploit the behavioral similarities of these different physical and chemical phenomena.

1.2 Fluid and Flow Approximations

In our treatment of single-component or multicomponent flows of fixed composition, as well as multicomponent flows of species that are reacting, we regard the fluid as a single continuum phase that is continuously and indefinitely divisible. This ensures that all macroscopic physical, chemical, and thermodynamic quantities, such as momentum, energy, density, and temperature, are finite and uniformly distributed over any infinitesimally small volume, and enables a meaning to be attached to the value of the quantity "at a point." The basis of this *continuum approximation* lies in the assumption that the characteristic macroscopic flow scale is large compared with the molecular length scale characterizing the structure of the fluid.

The subject matter will frequently be concerned with situations where the fluid contains a dispersed phase that cannot be considered a component—for example, macromolecules, rigid particles, or droplets. In these cases the continuum approximation is assumed to hold within the suspending fluid and the dispersed phase. The concentration of the rigid or fluid dispersed phase will encompass both dilute and concentrated suspensions.

Although the continuum approximation disregards the molecular nature of the fluid, we shall have recourse to this structure when considering the origin of nonequilibrium, viscous, diffusive, and interfacial effects.

The word *hydrodynamics* is used in the title of this book rather than the more general term *fluid mechanics*, partly because of convention but also to indicate that the fluids we deal with are generally held to be "incompressible" liquids rather than gases. Insofar as the fluids are regarded as continuous, the distinction between liquids and gases is not fundamental with respect to the dynamics, provided compressibility may be neglected. A gas is much less dense and much more compressible than a liquid so long as it is not too close to or above the critical temperature at which it can be liquefied. As a consequence, pressure variations in a gas flow are associated with much larger density changes than in the flow of a liquid. However, the density in a flowing compressible gas can be regarded as essentially constant if the changes in pressure are small. The behavior of a gas flow with small pressure changes is essentially the same as that of an "incompressible" liquid flow. For a single-phase fluid in the absence of temperature gradients, the criterion for *constant-density* flow translates into the *Mach number*, equal to the ratio of the characteristic flow speed to the speed of sound in the fluid, and being small compared to unity.

A word of caution is necessary since the characterization "incompressible" is conventionally interpreted as synonymous with "constant density." However, from our remarks a low-speed flow of, say, air may be regarded a constant-density flow despite the fact that air is a highly compressible fluid. On the other hand, a solution of saltwater subjected to a centrifugal force field in an ultracentrifuge develops a strong density gradient, and the solution, though incompressible, can hardly be considered of constant density.

The fluids we will examine are *real fluids* in that they are characterized by their ability to support shear stresses; as such they are *viscous*. More generally, real fluids support viscous effects, usually termed *transport effects* in the physicochemical literature. These include diffusion of mass, heat, and charge.

Transport effects together with nonequilibrium effects, such as finite-rate chemical reactions and phase changes, have their roots in the molecular behavior of the fluid and are dissipative. *Dissipative phenomena* are associated with thermodynamic irreversibility and an increase in global entropy.

Viscous flows may be classified into the limiting regimes of laminar and turbulent flows. In *laminar flow* the motion is regular and the fluid moves as if it were layered, with each layer having a different velocity. On the other hand, *turbulent flow* exhibits an irregular and chaotic behavior, though there may be some persistence of order present. In forced convection, the motion is laminar or turbulent, depending on whether the Reynolds number is respectively small or large compared with a critical value (the *Reynolds number* is defined as the characteristic flow speed multiplied by the characteristic flow length divided by the fluid kinematic viscosity). The numerator in the dimensionless ratio characterizes the flow and measures momentum transport by convection, whereas the denominator characterizes the fluid and measures momentum transport by diffusion.

The important practical features of turbulence are the sharply increased rates of transfer and mixing compared with molecular diffusion. Although a fundamental understanding of turbulence remains elusive, there are nevertheless many technical and engineering problems that can be handled by empirical and phenomenological modeling, examples of which include the mixing length and eddy diffusivity concepts. Because our aim is to display phenomena that arise from the interplay between physical chemistry and flow, we shall restrict our considerations to laminar flow, for which there is a rational and well-defined theory at least for Newtonian fluids. Another reason for this choice is that many of the important problems in physicochemical hydrodynamics are concerned with flow systems of small scale, so the Reynolds numbers are low and the motions are laminar. Examples are fluid systems involving macromolecules and particles, porous media and capillaries, and significant interfacial forces.

We shall also examine laminar flows for non-Newtonian fluids, where the stress is not linear in the rate of strain. Such flows, which fall under the science of rheology, encompass a spectrum of materials from elastic fluids at one end to Newtonian fluids at the other. Included are polymeric fluids and suspensions, both of which play an important role in physicochemical hydrodynamics.

In the spirit of our restriction to the laminar regime, we shall only briefly touch on *natural convection*—that is, flows produced by buoyancy forces acting on fluids in which there are density differences. A common example is buoyant motion in a gravitational field where the density difference arises from heat exchange. Even in weakly buoyant motions generated by small density differences, turbulence is ubiquitous. We shall, however, consider convection induced by surface tension gradients.

1.3 Particle and Pore Geometry

Throughout the book we shall frequently deal with suspensions of small “particles,” including macromolecules, colloids, cells, and flocs. The geometry of these particles is important for defining their interactions with the fluid

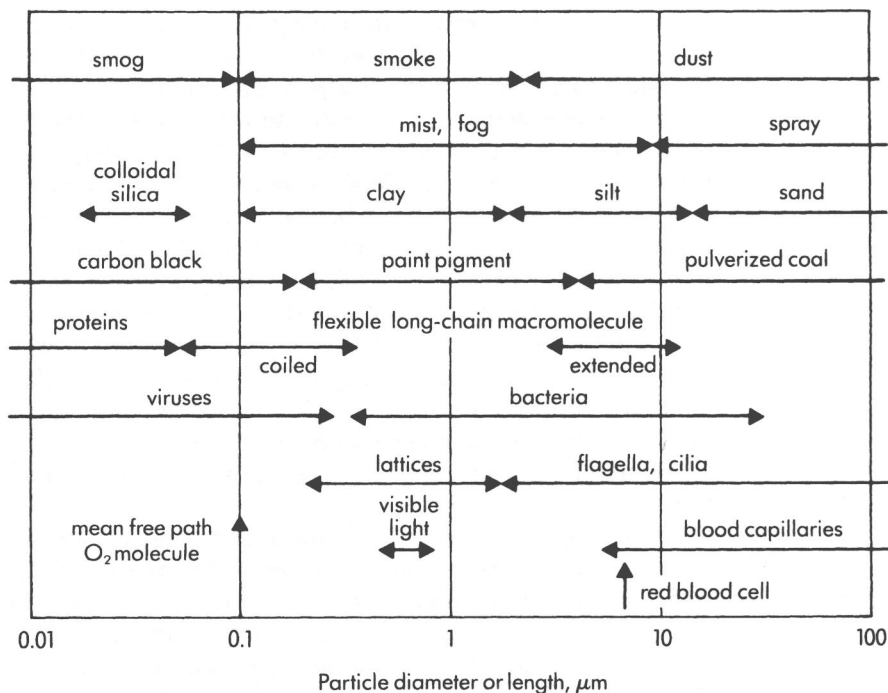


Figure 1.3.1 Some particles of interest and their characteristic sizes (after Batchelor 1976).

system. Often their shapes are complex, and nonrigid particles may differ in configuration under static and dynamic conditions and in different environments. Figure 1.3.1 shows some of the particles of interest and their characteristic sizes.

We will generally consider macromolecules to represent the smallest dispersed phase not considered a component. A *macromolecule* is a large molecule composed of many small, simple chemical units called *structural units*. It may be either biological or synthetic. Biological macromolecules contain numerous structural units, in contrast to synthetic macromolecules. Sometimes all macromolecules are referred to as *polymers*, although a polymer may be distinguished as a macromolecule made up of repeating units. Polyethylene, for example, is a synthetic polymer built up from a single repeating unit, the ethylene group. It has a simple linear chain structure in which each structural unit is connected to two other structural units.

A *protein* is a biological macromolecule composed of amino acid residues of the 20 common amino acids, joined consecutively by peptide bonds. Hemoglobin, the oxygen-carrying protein in red blood cells, is nearly spherical, with a diameter of about 5 nm (Stryer 1988). A model of the hemoglobin molecule as deduced by Perutz (1964) from x-ray diffraction studies is shown in Fig. 1.3.2. The model is built up from blocks representing the electron density patterns at various levels in the molecule. A larger protein, one that is fundamental to the blood-clotting process, is fibrinogen, a long slender molecule with a length of

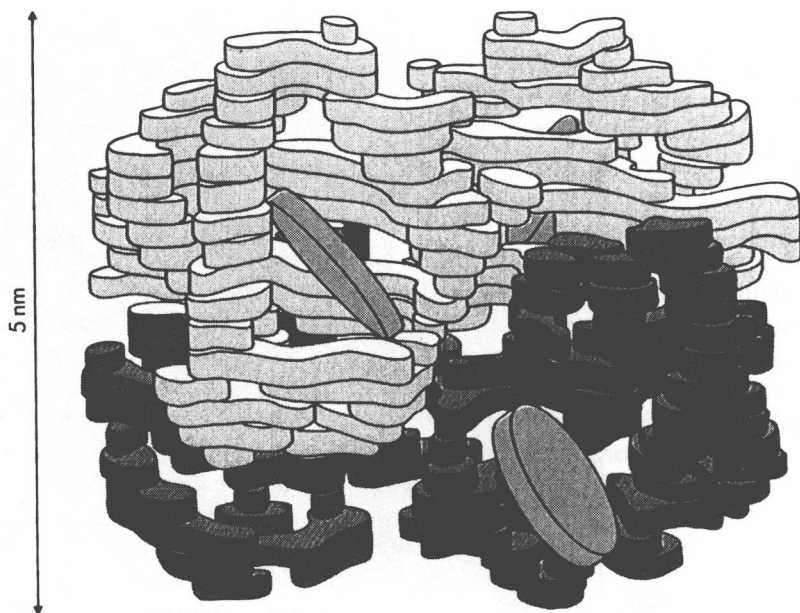


Figure 1.3.2 Model of hemoglobin deduced from x-ray diffraction studies. [After Perutz, M.F. 1964. The hemoglobin molecule. *Sci. Amer.* 211(5), 64–76. Copyright © 1964 by Scientific American, Inc. All rights reserved. With permission.]

about 50 nm (Stryer 1988). On a scale often an order of magnitude larger are viruses, which are very symmetric rigid macromolecules consisting of infectious nucleic acids surrounded by coats made up of protein subunits. Figure 1.3.3 is an electron micrograph of a tobacco mosaic virus of length about 300 nm.

Given the variety of particles and their diverse shapes, the question arises as to how they are represented or “modeled” in a rational treatment of their interactions in fluid systems. In our treatments we shall consider the particles to be regular geometrical shapes in the Euclidean sense. Thus particles will, for example, be represented by spheres (the model used most often), prolate and oblate ellipsoids of revolution, rods, and disks. Many protein macromolecules can be regarded as spherical, as, for example, hemoglobin in Fig. 1.3.2. Synthetic polymers dispersed in suspension, like the polystyrene latex particles shown in the micrograph of Fig. 1.3.4, are spherical or very nearly spherical, as are the particles of numerous colloidal systems. Many proteins can be regarded as ellipsoids of revolution. Clays and many crystalline materials are platelike and can be modeled as thin disks, and proteins such as fibrous collagen and the tobacco mosaic virus of Fig. 1.3.3 can be regarded as cylindrical rods.

Synthetic polymers and biological macromolecules are often modeled as a cluster of spheres or as a string of rods and spherical beads. The rod-and-bead configuration may be rigid, as a dumbbell, or flexible, where a bead connects to two rods as in a ball-and-socket joint or jointed chain. The protein fibrinogen has the character of a linear, rod-and-bead configuration with two rods and three beads. Most synthetic polymers and many biological macromolecules are flexible because of rotations about the chemical bonds.