

Physicochemical Hydrodynamics

An Introduction
Second Edition

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Second Edition

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

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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.

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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. Probstein

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

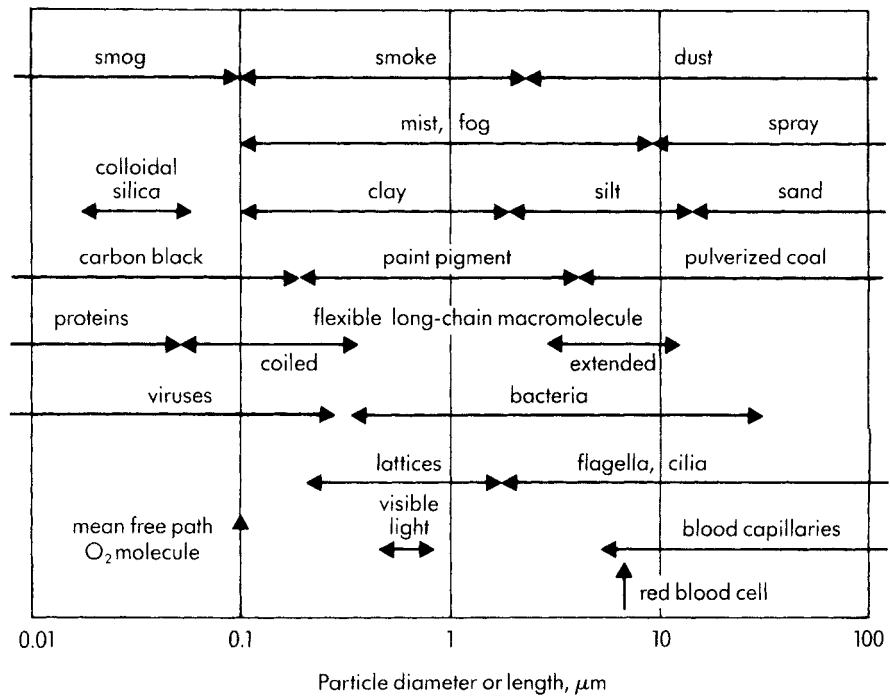


Figure 1.3.1 Some particles of interest and their characteristic sizes (after Batchelor 1976).

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.

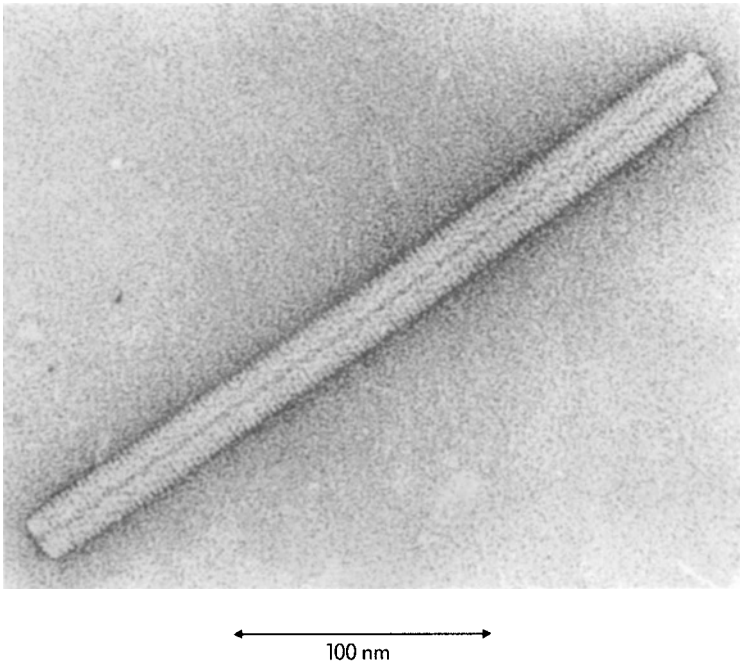


Figure 1.3.3 Electron micrograph of tobacco mosaic virus particle. [Courtesy of Prof. Emeritus Robley C. Williams, Virus Laboratory and Dept. of Molecular Biology, Univ. of California, Berkeley.]

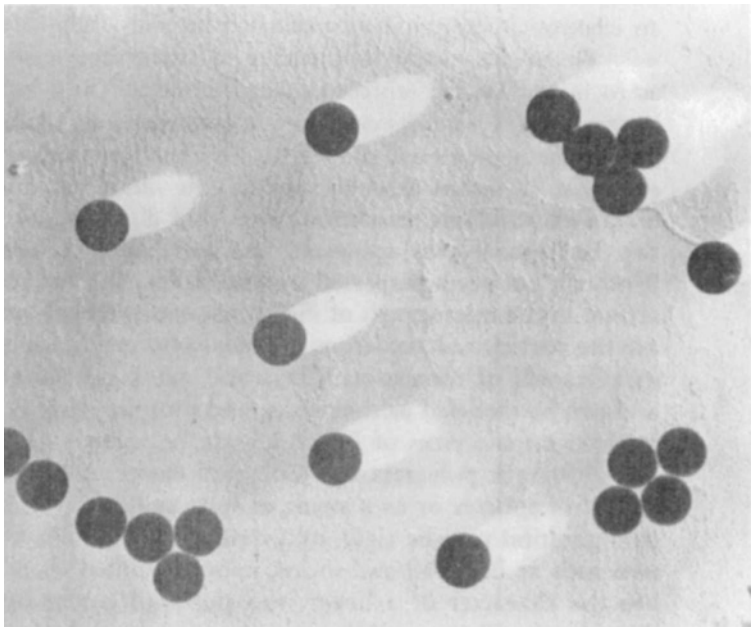


Figure 1.3.4 Electron micrograph of shadowed 300 nm diameter polystyrene latex particles. [Courtesy of Olga Shaffer, Emulsion Polymers Institute, Lehigh University.]

The individual particles of which we have spoken seem, in many cases, amenable to a relatively simple geometric description. In solution, however, particles may floc or aggregate due to random particle-particle and particle-floc collisions, and generally complex shapes arise that belie the much simpler shape of the original particle. Figure 1.3.5 from Weitz & Oliveria (1984) shows in two-dimensional projection an irreversible aggregate of uniform-size, spherical gold particles with diameter 15 nm.

The treelike cluster in Fig. 1.3.5 is one of a general class of shapes named *fractals* by Mandelbrot (1982). A fractal is a shape whose regularities and irregularities are statistical and whose statistical properties are identical at all scales, that is, scale-invariant under a change of length scale. From Fig. 1.3.5 it may be seen that associated with the cluster are open spaces with scales extending down from that of the cluster to that of a single particle. There is no characteristic length scale for the open spaces or other geometrical features between their extremes, indicating dilation symmetry. If a sphere of radius r is

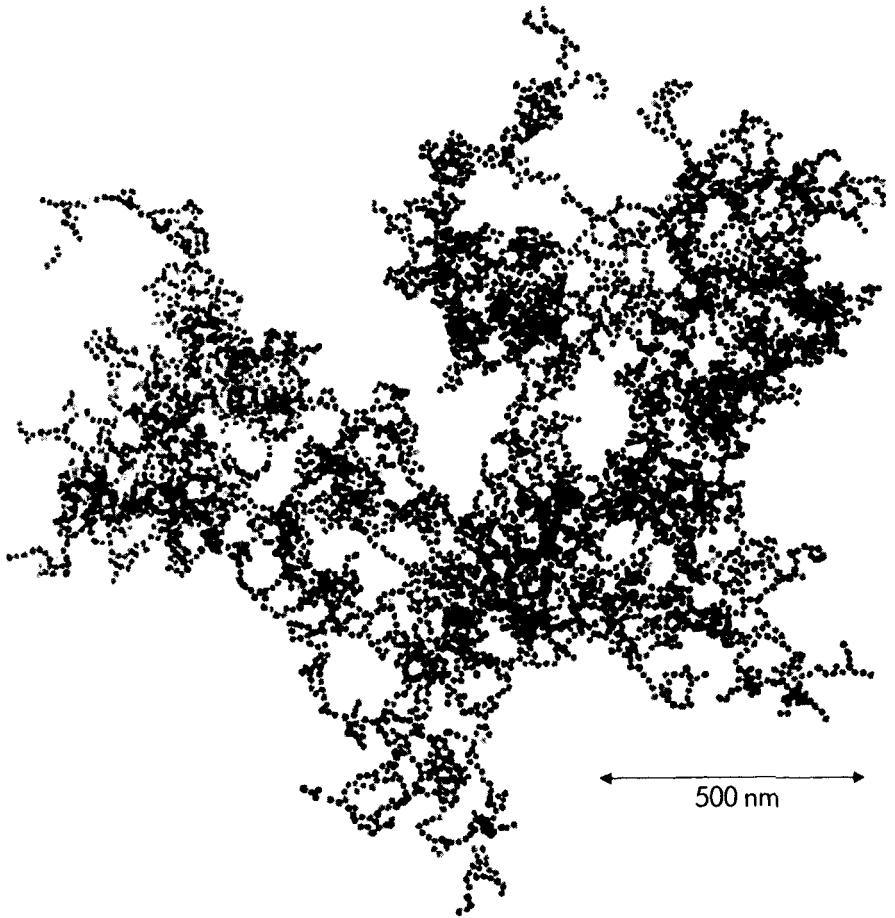


Figure 1.3.5 Electron micrograph of irreversible aggregate formed in suspension of spherical gold particles with diameter 15 nm. [Courtesy of Dr. David A. Weitz. From Weitz, D.A. & Oliveria, M. 1984. Fractal structures formed by kinetic aggregation of aqueous gold colloids. *Phys. Rev. Letters* 52, 1433–1436. With permission.]

drawn around an arbitrary point on the cluster and the number of particles N is counted, it is found that $N(r) \sim (r)^{1.75}$ for r ranging from about the particle size to the cluster size (Weitz & Oliveria 1984). It is argued theoretically that the hydrodynamic interactions of the cluster in a low-speed, inertia free flow (low Reynolds number flow) are as if the cluster were a hard sphere of radius a spanning the cluster (Witten & Cates 1986). Such behavior provides some justification for the approach of representing even irregularly shaped particles by regular geometrical shapes.

An additional point regarding particle suspensions is that we shall generally assume the dispersion to be *monodisperse*; that is, the particles are all the same. Most suspensions are *polydisperse*, with the particles characterized by a distribution of sizes and shapes. When we do not account for the polydispersity specifically, we will assume that the particular property being determined can be defined by an appropriate average over the particle system as, for example, number, mass, or volume average.

Closely related to the geometrical representation of particles is the representation of porous media (Adler 1992). In the text we will have frequent occasion to be concerned with porous media, examples of which are packed beds of particles, soils, sedimentary rock, gels, membranes, and many biological systems. The characteristic sizes of the channels or interstices in such media may range from several molecular diameters in synthetic, reverse osmosis membranes to sizes characteristic of the particles making up a packed bed or a natural medium. Porous media are generally heterogeneous and characterized by three-dimensional random networks. They often exhibit a fractal nature, as in geophysical environments, such as sedimentary rocks, and in biological environments, such as the lung and capillary systems.

Consistent with our approach to particle geometry, we shall assume the porous media with which we deal to be homogeneous. Moreover, we will model the media by simple geometrical means such as bundles or assemblages of straight capillaries or beds of discrete geometrically defined particles, such as spheres or cylinders. It is generally assumed that appropriate averages can be defined for a real porous media that enable the simplified models to be representative.

References

- ADLER, P.M. 1992. *Porous Media: Geometry and Transports*. Boston: Butterworth-Heinemann.
- BATCHELOR, G.K. 1976. Developments in microhydrodynamics. In *Theoretical and Applied Mechanics* (ed. W.T. Koiter), pp. 33–55. Amsterdam: North Holland.
- MANDELBROT, B.B. 1982. *The Fractal Geometry of Nature*. San Francisco: W.H. Freeman.
- PERUTZ, M.F. 1964. The hemoglobin molecule. *Sci. Amer.* **211**(5), 64–76.
- STRYER, L. 1988. *Biochemistry*, 3rd edn. New York: W.H. Freeman.
- WEITZ, D.A. & OLIVERIA, M. 1984. Fractal structures formed by kinetic aggregation of aqueous gold colloids. *Phys. Rev. Letters* **52**, 1433–1436.
- WITTEN, T.A. & CATES, M.E. 1986. Tenuous structures from disorderly growth processes. *Science* **232**, 1607–1612.

2 Transport in Fluids

2.1 Phenomenological Models

The principles of conservation of momentum, energy, mass, and charge are used to define the state of a real-fluid system quantitatively. The conservation laws are applied, with the assumption that the fluid is a continuum. The conservation equations expressing these laws are, by themselves, insufficient to uniquely define the system, and statements on the material behavior are also required. Such statements are termed *constitutive relations*, examples of which are Newton's law that the stress in a fluid is proportional to the rate of strain, Fourier's law that the heat transfer rate is proportional to the temperature gradient, Fick's law that mass transfer is proportional to the concentration gradient, and Ohm's law that the current in a conducting medium is proportional to the applied electric field.

The constitutive equations to be adopted are defined empirically, though the coefficients in these equations (viscosity coefficient, heat conduction coefficient, etc.) may be determined at the molecular level. Often, however, these coefficients are determined empirically from the phenomena themselves, though the molecular picture may provide a basis for the interpretation of the data. It is for this reason that the description of the fluid state based on a continuum model and concepts is termed a *phenomenological description or model*.

Sometimes when dealing with a fluid that contains a dispersed particle phase that cannot be considered a component, we treat the suspension fluid as a continuum with a constitutive relation that is modified because of the presence of the particles. An example to be discussed in Chapter 5 is Einstein's modification of the Newtonian viscosity coefficient in dilute colloidal suspensions due to hydrodynamic interactions from the suspended particles. As with molecular motions, the modified coefficient may be determined from measurements of the phenomenon itself by using results from analyses of the particle behavior in the fluid as a guide. These ideas are further expanded upon in Chapter 9 where the behaviors of concentrated suspensions of colloidal and non-colloidal particles are examined.

From physical experience we know that a flow of energy or matter can be set up in a conducting system whenever there is a spatial gradient of a state variable, for example, temperature, pressure, or voltage. All fluxes will vanish under conditions of *spatial homogeneity* where the spatial gradients of all state variables are zero. Irreversible thermodynamics provides a more specific statement. Recall that an *intensive thermodynamic property* is independent of the mass or size of the system, the converse holding for an *extensive property*. Thus, the transport of fluxes (that is, the rates of flow per unit cross-sectional area of energy and matter in a conducting or transporting medium) are determined by the nature of the transporting medium and its local intensive thermodynamic state and by the local gradients in the natural intensive properties.

The phenomenological or constitutive equations describe the manner in which the fluxes depend upon the spatial gradients of the intensive properties. In what follows we shall discuss the momentum flux, which is related to velocity gradient by fluid viscosity; heat flux, which is related to temperature gradient by fluid thermal conductivity; mass flux, which is related to concentration gradient by the fluid diffusivity; and current density, which is related to electrostatic potential gradient by specific conductivity. The fluxes of mass, heat, and charge are all vector quantities, and their transport characteristics are quite similar and often analogous. Momentum flux or stress, however, is a second-order tensor, and except when there is only a single component of stress, similarities in transport behavior to the other quantities are often limited. This may be interpreted as a consequence of the fact that the components of a vector transform like the coordinates themselves, whereas the components of a second-order tensor transform like the squares of the coordinates.

2.2 Viscosity and Momentum Transport

The real fluids we consider can support shear stresses and are viscous. We emphasize this again because real-fluid effects per se are identified with dissipation. However, dissipation may arise in a fluid not only because of viscous and other transport effects but also because of nonequilibrium effects associated with finite-rate reactions. Nonequilibrium effects can be present in an inviscid fluid, that is, a fluid unable to support shear stresses. The distinction between nonequilibrium effects, on the one hand, and transport effects, on the other, is based on the concept of spatial homogeneity. Transport effects, like viscosity, are defined as dissipative effects that depend inherently upon spatial gradients. A nonequilibrium effect is defined as a dissipative effect that is present with spatial homogeneity, with the proviso that the fluid density can change with time (Hayes & Probstein 1966).

Newton's law of viscosity states that there is a linear relation between the shear stresses and rates of strain. Let us first examine this law for the case of simple shear where there is only one strain component. For explicitness consider the planar Couette problem of a steady shear flow generated by the parallel motion of one infinite plate at a constant speed U with respect to a second fixed infinite plate, the plates being separated by a small distance h with the pressure p constant throughout the fluid (Fig. 2.2.1). The role of boundary conditions in

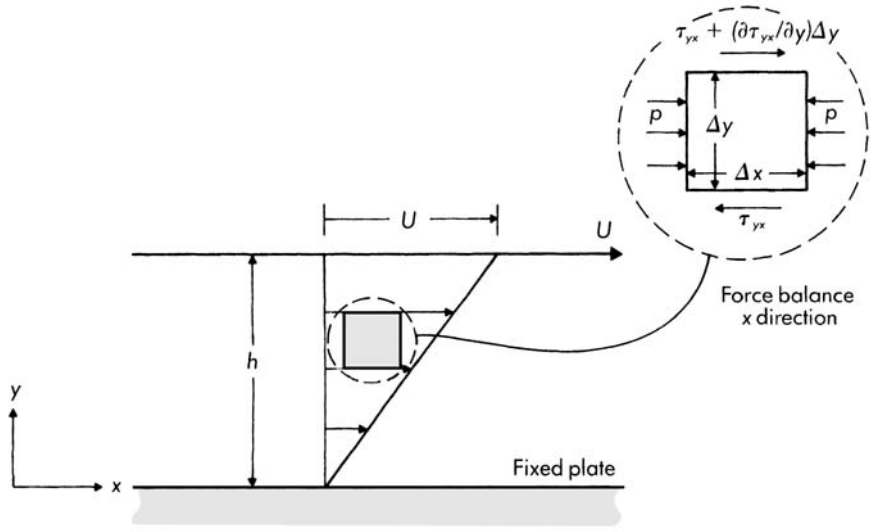


Figure 2.2.1 Shear flow between two parallel plates.

a viscous flow is critical, and we assume the *no-slip condition*—that is, the fluid “sticks” to both plates. A tangential force is required to maintain the motion of the moving plate, and this force must be in equilibrium with the frictional forces in the fluid.

A force balance for the shaded fluid element in Fig. 2.2.1 gives for the net force acting on the element in the x direction

$$\sum F_x = \left(\frac{\partial \tau_{yx}}{\partial y} \right) \Delta y \Delta x \quad (2.2.1)$$

Here, τ_{yx} is the shear stress exerted in the x direction on a fluid surface of constant y . By convention, on a positive y face the shear is positive in the positive x direction, and on a negative y face the shear is positive in the negative x direction.

From Newton’s second law

$$\frac{\sum F_x}{\text{Vol}} = \rho \frac{Du}{Dt} \quad (2.2.2)$$

where ρ is the mass density and D/Dt is the *material derivative* or rate of change of a physical quantity following a fluid element:

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u_i \frac{\partial}{\partial x_i} \quad (2.2.3)$$

The notation D/Dt is used to distinguish from the usual total time derivative.

For steady flow with the plates infinite in the x direction, $\partial/\partial t = 0$ and $\partial/\partial x = 0$. As a consequence, the velocity component parallel to the plates is $u = u(y)$ while the normal component $v = 0$. Hence, $Du/Dt = 0$, and

$$\frac{\sum F_x}{\text{Vol}} = \frac{\partial \tau_{yx}}{\partial y} = 0 \quad (2.2.4)$$

or, throughout the fluid,

$$\tau_{yx} = \text{constant} \quad (2.2.5)$$

For most fluids the shear stress is a unique function of the strain rate. The constitutive relation of Newton assumes the shear stress to be linear in the strain rate. In the Couette problem there is only the single strain-rate component du/dy and single stress component τ_{yx} , so the Newtonian viscosity law may be written

$$\tau_{yx} = \mu \frac{du}{dy} \quad (2.2.6)$$

The quantity μ is the viscosity coefficient of a *Newtonian fluid*—that is, a fluid that follows the Newtonian viscosity law. It is an intensive property and is generally a function of temperature and pressure, although under most conditions for simple fluids it is a function of temperature alone. All gases and most simple liquids closely approximate Newtonian fluids. Polymeric fluids and suspensions may not follow the Newtonian law, and when they do not they are termed *non-Newtonian fluids*. Non-Newtonian behavior falls under the science of rheology which will be discussed in Chapter 9.

In writing Newton's law of viscosity with a positive sign, we have followed the convention of applied mechanics that all stresses are positive. Chemical engineers use a negative sign in relating stress and strain rate in parallel with heat and mass transport where, for example, heat flux is proportional to the negative of the temperature gradient. The difference in convention is unimportant.

For Couette flow the shear force per unit area τ_{yx} is constant, and since it is proportional to the local velocity gradient, it follows that the velocity profile is linear. If the no-slip boundary condition is satisfied at both plates,

$$\frac{u}{U} = \frac{y}{h} \quad (2.2.7)$$

from which

$$\tau_{yx} = \mu \frac{U}{h} \quad (2.2.8)$$

Bird et al. (1960) point out that τ_{yx} has another interpretation. With reference to the Couette problem, in the neighborhood of the moving surface at $y = h$ the fluid acquires a certain amount of x momentum. This fluid, in turn, imparts some of its momentum to the adjacent layer of fluid, causing it to remain in motion in the x direction. Hence x momentum is transmitted to the fluid in the negative y direction. Consequently, τ_{yx} may be thought of as the