# David A. Edwards Howard Brenner Darsh T. Wasan

# Interfacial Transport Processes and Rheology



Butterworth-Heinemann Series in Chemical Engineering

# **Interfacial Transport Processes and Rheology**

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# David A. Edwards

Department of Chemical Engineering Massachusetts Institute of Technology

# Howard Brenner

Department of Chemical Engineering Massachusetts Institute of Technology

# Darsh T. Wasan

Department of Chemical Engineering Illinois Institute of Technology

Butterworth-Heinemann

Boston London Oxford Singapore Sydney Toronto Wellington

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# Preface

This textbook is designed to provide the theory, methods of measurement, and principal applications of the expanding field of interfacial hydrodynamics. It is intended to serve the research needs of both academic and industrial scientists, including chemical or mechanical engineers, material and surface scientists, physical chemists, chemical- and bio-physicists, rheologists, physico-chemical hydrodynamicists, and applied mathematicians (especially those with interests in viscous fluid mechanics and continuum mechanics). As a textbook it provides material for a one- or two-semester graduate-level course in interfacial transport processes. It may also be noted that, while separate practical and theoretical subdivisions of material have been introduced, a kind of cross emphasis is often stressed: (i) to the academic scientist, of the importance of understanding major *applications* of interfacial transport; and (ii) to the industrial scientist, of the importance of understanding major applications the underlying *theory*.

#### Organization of the Textbook

This textbook is divided into two major parts.

Part I: Part I strictly considers the "macroscale" view of fluid interfaces, whereby the latter appear as two-dimensional, singular surfaces, as is the classical idealization. The interface is furthermore regarded in this portion of the text as being *material* in nature, referring to the class of interfacial problems for which no *net* interphase transfer of mass across the interface occurs at any point (or else is sufficiently small to be negligible in its consequences). This mass-transfer restriction does not prevent applications of the resulting theory to the purely *diffusive* transport of solute species across the (material) interface (as such diffusive transport is necessarily measured relative to the mass-average velocity), and is probably applicable to most, though certainly not all, practical cases of interphase transport. As discussed below in the subsection on *Classroom Instruction*, the first segment of the book can usefully serve as an introduction to the general subject of interfacial transport processes, adequate for a one-semester course at the graduate level. Part I is divided into chapters respectively emphasizing the theoretical (Chapters 2 to 5), experimental (Chapters 6 to 9), and applied (Chapters 10 to 14) aspects of interfacial rheology. With the exception of the theoretical portion of this material, which develops an

overall physicomathematical structure of interfacial transport processes that begins in Chapter 3 and concludes with Chapter 5, the chapters comprising this portion of the book largely stand alone. As such, they may be read out of sequence, as befits the interests of the reader or instructor.

One of the primary advantages of Part I pertains to the needs and interests of the industrial researcher, who is presumably concerned primarily with the experimental and applications chapters. He or she possesses the opportunity in Part I to acquire from Chapters 1 and 2 a simple theoretical background sufficient for reading those later chapters pertaining to experimental measurements and applications.

The theoretician will be primarily interested in Chapters 3 to 5 of Part I. These introductory chapters may be considered a prerequisite to the more rigorous theoretical chapters of Part II.

**Part II:** Part II begins with Chapter 15, and concerns the more detailed "microscale" view of a fluid interface, whereby the interface is recognized to be not a singular surface across which discontinuities may occur, but rather is seen to be a thin, diffuse (i.e. continuous), three-dimensional transition zone (characterized by steep spatial physicochemical inhomogeneities) between otherwise relatively homogeneous "bulk"-fluid phases. A Gibbsian *surface-excess* formalism is employed in the context of a rigorous (matched asymptotic expansion) micro-continuum theory with the purpose of 'deriving' the macro-interfacial theory of Part I (Chapters 3 to 5) from the more fundamental microscale perspective. In contrast with Part I, the interface is now no longer necessarily regarded as being material. Rather, the more general case of *nonmaterial* interfaces is treated.

The development of topics provided in Chapters 15 to 17 will be seen to parallel that provided in Chapters 3 to 5. A derivation of interfacial transport equations is supplied in the first three chapters of Part II for nonmaterial interfaces. Each of the nonmaterial relations derived in Part II are shown to reduce to its material counterpart in Part I in circumstances wherein the interface is restricted to being material, albeit with greatly enhanced insight into the physical nature of the purely phenomenological equations of Part I.

Finally, Chapter 18 provides an extension of the generic matchedasymptotic, surface-excess formalism of Chapter 15 to the case of threephase contact lines. However, only the equilibrium case is considered, thus excluding "line-excess" transport phenomena from consideration in this book.

Part II is intended for students and/or researchers interested in a rigorous (though potentially rewarding) theoretical understanding of interfacial transport processes. It seeks to introduce some of the many fruitful avenues of theoretical research currently open to further investigation in the field, as well as to identify new research areas, e.g. rheological equations of state for nonmaterial interfaces, sources of 'non-Newtonian' interfacial rheological behavior for material interfaces, and "line rheology", to name a few such areas.

#### **Classroom Instruction**

A one-semester graduate-level course entitled Interfacial Transport *Processes* was taught during the fall of 1990 in the Chemical Engineering Department at the Massachusetts Institute of Technology (and once again during the spring of 1991 in the Mechanical Engineering Department at the Technion—Israel Institute of Technology) by one of us (D.A.E.) based upon a preliminary version of this text. The first few weeks of the semester began with a brief overview of Chapters 1 and 2; this was followed by a review of basic tensor analysis and the differential geometry of surfaces, employing Appendices A and B and §3.2 of Chapter 3. The remaining portion of the first half of the semester was devoted to a study of the basic theory underlying interfacial transport processes and interfacial rheology, as embodied in Chapters 3 to 5. The second half of the course covered the experimental and applications chapters (6 to 14). The advanced material of Part II was considered only briefly, owing primarily to lack of time in a onesemester introductory course; special attention was given to the kinematics of nonmaterial interfaces, utilizing various examples in Parts I and II pertaining to the kinematics of a nonmaterial spherical gas bubble or droplet interface. Selected homework problems taken from the *Questions* appearing at the end of each chapter were assigned each week, and a 'take-home' midterm and final examination was required of the students.

A possible alternative layout of an interfacial transport processes course would involve two semesters, with the first semester focusing solely upon the purely theoretical material of Chapters 3 to 5 and 15 to 18. As envisioned by the authors, roughly the first half of the semester would be devoted to a consideration of the material provided in Appendices A and B together with Chapters 3 to 5, with the remaining classroom time in the first semester being used for the study of the advanced material of Chapters 15 to 18 (of Part II). The second semester of the course would concentrate upon the measurement (6 to 9) and applications (10 to 14) chapters of the text. (This second semester course could be offered independently of the first by substituting the formal theoretical material covered in the above-described first-semester course with a relatively brief, initial consideration of the less demanding theoretical material of Chapters 1 and 2.) This second semester course would most profitably be taught with the aid of pertinent classroom demonstrations and, ideally, student access to laboratory experiments.

Solutions to the *Questions* appearing at the end of each chapter have been prepared in the form of a *Solutions Manual*. Intended as an aid to those either presenting this material in the classroom or using it for self study, this manual is available from the publisher, *Butterworth-Heinemann*, 80 Montvale Avenue, Stoneham, Massachusetts 02180. Requests should be on official letterheads and over the signature of either a member of a university faculty or the industrial or governmental equivalent.

#### Contributors to this Textbook

As the quotations preceding each chapter and numerous references throughout this book attest, many researchers have contributed to the early and more recent developments defining the field of interfacial transport processes, some long before it was possible to reconcile their efforts as belonging to an identifiable field of science. Our contribution has largely been one of identifying, collecting, selecting, correlating and finally reconciling pertinent subject material drawn from the prior research efforts of others, to whom much of the credit for the existence of this book must be acknowledged. Many of their names appear in the bibliography at the end of this book. However, since this book has been cast as a textbook rather than as a research monograph, no attempt has been made to provide an exhaustively comprehensive bibliography. Thus, many researchers will have been overlooked, and to these individuals we express our regrets that the restricted scope of our book did not allow explicit identification of their contributions.

In addition to these indirect contributors to the book, a number of individuals have contributed more directly, and we wish to acknowledge them. The evolution of the material in Chapters 15 to 17 of Part II deserves special comment in this regard. The original research culminating in Part II of this book, begun in the late 1970's (Brenner 1979, and Brenner & Leal 1982), was later continued and extended by Li Ting—then a graduate student at the Illinois Institute of Technology with D.T. Wasan in collaboration with H. Brenner. Dr. Ting's early efforts are summarized in his PhD thesis (Ting 1984); his later postdoctoral efforts at MIT contributed immeasurably to the developments outlined in Part II. The doctoral thesis of Dr. Gretchen M. Mavrovouniotis (1989) provides the most recent form of the matched asymptotic, surface-excess transport theory to have appeared in the published literature prior to that outlined in Chapters 15 to 17. Developments subsequent to her thesis owe to the collaborative efforts of D.A. Edwards and H. Brenner.

The authors would like to acknowledge the hospitality of the Department of Chemical Engineering at MIT. Their cooperation in allowing us to develop and teach a new graduate course in *Interfacial Transport Processes* during the Fall 1990 semester afforded an opportunity to fine tune earlier drafts of this book. Moreover, the many questions and helpful suggestions of the graduate and post-graduate students who attended this course contributed greatly to the quality and internal consistency of the text. The authors particularly wish to thank Fuquan Gao, Dave Otis, Chunhai Wang and Alejandro Mendoza-Blanco, each of whose enthusiastic input provided important encouragement during the latter stages of the writing of the book. The *Interfacial and Colloid Phenomena* course taught at IIT in the Fall of 1990 by D.T.W. was also extremely beneficial.

D.A.E. wishes to thank the members of the Faculty of Mechanical Engineering at the Technion, and in particular Dr. Michael Shapiro, for their genuine hospitality and intellectual support during his two periods of residence (1987–89 and Spring, 1991) in their department. Their assistance in permitting the offering of an *Interfacial Transport Processes* course during his second stay in the department proved of value both in the development of a solutions manual to the text and in accomplishing last-minute textual corrections (of which latter efforts Tal Hocherman and Michael Shlyafstein were of particular assistance). Many friends have been made in Haifa,

Jerusalem and Boston, and their support has been of inestimable value; the memories are especially warm and dear of the love, idealism and courage of Miky.

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D.T.W., who was assisted by grants from the National Science Foundation and the Department of Energy, wishes to express his indebtedness to Professor Robert Schechter for his original interest and collaboration in the early stages of this project. The outline that was cowritten by Robert Schechter and Darsh Wasan in March of 1984 provided an early conceptual nucleus for the book, and proved of particular value in the development of the material in Chapters 7 and 9, where there appears frequent reference to the important research publications of Professor Schechter and his collaborators.

May 26, 1991

D.A. Edwards H. Brenner D. T. Wasan This page intentionally left blank

# PART I

# INTERFACIAL RHEOLOGY: BASIC THEORY, MEASUREMENTS & APPLICATIONS

# ][

"We live in a world of three dimensions. We measure their length, breadth and thickness. The position of a point can be described by three coordinates, x, y and z. We can not escape from the inside of a spherical surface except by passing through it, but if we are standing in a circle on a surface we escape by stepping over it.

"It is amusing to try to imagine a fourth dimension. We can reason that if we could travel into it, we could escape from the inside of a sphere without going through its surface.

"In the special theory of relativity, Einstein has given us reason for looking upon time as a kind of imaginary fourth dimension which differs from any of the ordinary dimensions of space much as

the number one differs from the imaginary number  $\sqrt{-1}$ .

"In the general theory of relativity, there are suggestions that the effect of gravitation is to warp four-dimensional space-time in a fifth dimension, very much as we have to warp a map of Europe to make it fit onto a globe representing the earth.

"Poincaré in an interesting book, 'Science and Hypothesis,' attempted in 1903 to trace the probable development of science on the earth if it had happened that the earth's atmosphere, like that of Venus, had been perpetually cloudy. Without the ability to observe the stars and sun, mankind would have persisted for long in a belief that the earth is flat. If a pioneer among scientists had made the statement that the surface of the earth has no edge or boundary but yet has a limited area, he would have been disbelieved; for these two statements seemed contradictory to those who believed in a flat earth....

"Many of you perhaps have seen the little book entitled 'Flatland,' written in 1885 by an author who gives the name A. Square, but who is said to be Edwin A. Abbott.... I propose to tell you of a real two-dimensional world in which phenomena occur that are analogous to those described in 'Flatland.""

Irving Langmuir (1936)

# **CHAPTER 1**

# Interfacial Rheology and Its Applications

Interfacial rheology, or 'interfacial hydrodynamics', is the field of science that studies the response of mobile interfaces to deformation. First encounters with this field most frequently occur through the study of conventional bulk-phase hydrodynamics, where the need arises at a so-called 'free surface' to specify an appropriate boundary condition upon the normal component of the bulk-phase stress tensor. This boundary condition generally introduces *two-dimensional* tensile forces, as well as viscous and elastic forces, which, aside from their localized action upon a two-dimensional, non-Euclidean, moving and deforming surface, are quite analogous to comparable three-dimensional hydrodynamic forces in bulk-phase fluids. Through the science of interfacial rheology one seeks *inter alia* to determine: (i) the shape of a dynamic free fluid interface; (ii) the nature of interfacial response to deformation; and (iii) the quantitative influence that interfacial stress imparts upon hydrodynamic motion in contiguous fluid phases.

Textbooks concerned with classical hydrodynamics (Lamb 1945, Landau & Lifshitz 1960, Bird *et al.* 1960, Batchelor 1967, Slattery 1981) often omit an explicit consideration of interfacial rheology; rather, they view the normal stress boundary condition at a free fluid interface as a continuity condition imposed upon the normal component of the fluid stress tensor, *modulo* a possible discontinuity arising at a curved interface due to (a homogeneous) interfacial tension. The justification for this first-level hydrodynamic approach to fluid interfaces is that a precise knowledge of the normal stress boundary condition is often unnecessary for a basic understanding of the bulk-fluid motion. Hence, if the fluid surface-tovolume ratio, or *specific surface*, is small for the particular system considered (as is most often the case for introductory-level fluid flow problems), a rigorous formulation of the normal stress condition at fluid boundaries is generally unnecessary. In circumstances for which the fluid system under study possesses a *large* specific surface, as occurs with many fluid-fluid *colloidal dispersions* (e.g. single bubbles, bubbly liquids, emulsions, and foams), interfacial rheological knowledge may prove indispensable for understanding bulk hydrodynamic behavior; this is illustrated, for example, in processes of dynamic phase mixing, either induced or enhanced through the mechanism of interfacial turbulence. A common feature of many colloidal systems is the presence of molecular or macromolecular *surfactants* at the fluid interface; these adsorbed species tend not only to stabilize the interface in a dispersed state, but also to introduce additional interfacial stresses beyond that stress already contributed by a homogeneous interfacial tension.

This textbook is concerned with the theory, measurement, and practical significance of various interfacial transport processes, with the primary emphasis of Part I focused upon the rheological aspects of fluid interfaces possessing a relatively large specific surface. The chapters comprising Part I of this book are devoted respectively to theory (Chapters 2 to 5), measurement (Chapters 6 to 9), and applications (Chapters 10 to 14). The more theoretical of these chapters (specifically Chapters 3 to 5) employ vector-dyadic notation, together with frequent use of differential geometry, knowledge of which is unnecessary for those readers interested primarily in the measurement and applications chapters of Part I. Accordingly, Chapters 1 and 2 are designed to provide a rheological background sufficient to the task.

This introductory chapter begins with a brief discussion of the historical development of interfacial rheology, followed by descriptive overviews of the nature and practical significance of (i) surfactants, (ii) colloidal dispersions for which the specific surface may be large, and (iii) current engineering processes wherein interfacial rheology may play a significant role.

#### 1.1 Historical Review

Only in recent years has "interfacial rheology", as a unique field of study, achieved a cohesive identity comparable to that existing in the more conventional fields of bulk-phase transport processes. Prior to several key experimental and theoretical observations in the 1950's and early 1960's, the term "interfacial (or 'surface') rheology" had been employed mostly in reference to experimental studies devoted to qualitatively elucidating the rigidity and viscoelasticity of adsorbed monolayers at fluid interfaces (Mouquin & Rideal 1927, Tschoegl 1958, Davies & Rideal 1963, Biswas & Haydon 1963, Joly 1964). Simultaneously, however, there developed other areas of interfacial research that were often of greater scientific interest, relating to observations of bubble and fluid droplet motion, fluid instabilities, thermocapillary migration, interfacial turbulence, the behavior of thin liquid films, coalescence phenomena, etc., variously engaging the attention of leading scientists [Thompson (Lord Kelvin) 1855, Plateau 1869, Rayleigh 1878, Gibbs 1957], often at early stages of their careers. [Thus, for example, the first publications of the youthful Einstein (1901) and Bohr (1909) dealt with interfacial phenomena.]

Until recently, such dynamic interfacial phenomena were often viewed in an independent, *ad hoc* context, often appearing under the heading of 'special topics' within the more established disciplines of hydrodynamics or hydrodynamic stability analysis. For this reason, the phenomena themselves, despite their surprisingly widespread applications, have remained obscure, or perhaps worse — misunderstood, by many scientists and engineers. As discussed in the brief historical review below, these dynamic interfacial phenomena may now be viewed within the context of modern interfacial rheology.

#### Interfacial Rheology Prior to 1960: The Early Period

It seems plausible that a spherical fluid droplet should settle more rapidly under the influence of gravity than would a comparable solid sphere, since fluid tends to 'slip' at a droplet interface (by establishing an internal circulation), whereas the 'no-slip' condition prevails at a solid surface. Such were the theoretical predictions of Rybczynski (1911) and Hadamard (1911), who generalized Stokes' (1851a) (low-Reynolds number) solution for the settling velocity of a solid sphere to the case of a spherical fluid droplet. However, experiments (Lebedev 1916, Silvey 1916) performed shortly thereafter revealed that fluid droplets of sufficiently small radius settled as if they were solid spheres, obeying Stokes' original formula.

Boussinesq (1913a), in an attempt to resolve this discrepancy between theory and experiment, postulated the existence of a 'surface viscosity', conceived as the two-dimensional equivalent of the conventional threedimensional viscosity possessed by bulk-fluid phases. Owing to viscous interfacial frictional resistance, this surface viscosity would be expected to 'solidify' the fluid interface by diminishing its mobility, and to scale in such a manner as to become of increasing importance with decreasing droplet radius, all other things being equal. Surface viscosity was not altogether a new concept even then, for Plateau (1869) had earlier suggested such a possibility upon observing the difference between the damping of a needle within a surfactant-adsorbed gas-liquid surface and its comparable damping when submerged within the bulk liquid. Later, Plateau (1871) related the existence of surface viscosity to the stability of foam systems.

Boussinesq (1913b) used his theory of surface viscosity to derive an analytical expression for the settling velocity of a spherical fluid droplet. A 'hardening' of the fluid interface with decreasing radius was indeed predicted, such that for a sufficiently small radius the droplet would behave as a solid sphere, consistent with experiment.

For many years the Boussinesq solution, based upon his surface viscosity postulate, was accepted as the explanation for the anomalous droplet settling-velocity results, encouraging the development of a plethora of instruments for measuring 'surface viscosity', as well as other rheological properties of a fluid interface [see the review by Joly (1964)].

Meanwhile, Rayleigh (1916) was working to establish a quantitative theory of 'Bénard instability', offering circumstantial evidence that the cellular circulation patterns observed by Bénard (1901) in shallow pools of liquid heated from below arise via instabilities created by buoyancy-driven convection. While this explanation of Bénard instability was accepted at the time, subsequent experiments (Low & Brunt 1925) pointed to untenable discrepancies between Rayleigh's theory and the observations of Bénard. Block (1956), who made the crucial observation that instabilities occur also for thin fluid layers heated from *above*, postulated that spatial nonuniformities in surface tension were responsible for the instabilities. This was later confirmed by the analysis of Pearson (1958).

The basic physical process by which a surface-tension gradient produces convection in the bulk phase became known (Marangoni 1871) as the 'Marangoni effect' [though Thompson (Lord Kelvin) (1855), was, in fact, first to observe this phenomenon], referring generally to surface tension variations caused by local inhomogeneities in either surface temperature or surfactant concentration.

Examples of the Marangoni effect in Nature were by then recognized in phenomena such as the formation of droplets (or 'tears') of strong wine on the sides of a wine glass (Thompson 1855, Loewenthal 1931), camphor dance (Bikerman 1958), and crystal climbing (Bikerman 1958), while an additional application to dynamic interfacial processes was soon established by the experiments of Young *et al.* (1959), who showed that gas bubbles could be prevented from gravitationally rising through a fluid by the imposition of a uniform vertical temperature gradient. This constitutes an example of the phenomenon known as 'thermocapillarity'.

Reopening the controversy surrounding the Rybczynski-Hadamard formula for the settling velocity of a fluid droplet, Levich (1962) voiced the opinion that the explanation lay not, as Boussinesq suggested, in the existence of a surface viscosity, but rather in the Marangoni effect. Frumkin & Levich (1947) postulated that the anomalous experimental results revealing that fluid droplets settle as solid spheres were, in fact, due to the presence of surface-active agents, which were swept to the rear of the droplet as it settled. The surface concentration gradients and concomitant interfacialtension gradients thereby created were thus now assumed to be the agencies responsible for retarding the settling velocity. Experimental findings were soon reported (Gorodetskaya 1949) as qualitatively justifying Levich's theory.

As both effects were understood to arise from the presence of surfaceactive agents, the controversy over "surface viscosity effect" vs "surfacetension gradient effect" was regarded as being nontrivial. This controversy was further rekindled as interest developed in the classical problem of wave damping by surface-active agents.

Ever since early observations indicated that oil spread over the surface of the sea causes a damping of ripples [Pliny the Elder, in Book 2 of his *Natural History*, noted that divers found damping of waves by this mechanism useful for improved underwater vision, whose observations were later expanded upon by Benjamin Franklin (1773)], researchers have sought to explain this practically useful phenomenon. Whereas Thompson (Lord Kelvin) (1871) was the first theoretician to consider the capillary wave problem in an inviscid medium, it was not until the studies of Levich (1941) and Lamb (1945) that the damping effect of a thin liquid film or surfactant monolayer at the fluid surface was explained through the existence of inhomogeneities in surface tension, i.e. as resulting from the Marangoni effect.

For many years thereafter, studies of capillary (Brown 1940, Levich 1941, Hansen & Mann 1964, Lucassen & Hansen 1966) and longitudinal (Platikanov *et al.* 1966, Lucassen 1968, Lucassen & van den Tempel 1972, Garrett & Joos 1976, Maru & Wasan 1979, Ting *et al.* 1985) waves at fluid interfaces revealed that a surface viscous effect, if indeed present, would impart a damping influence identical to that caused by the Marangoni effect. As this synchronous behavior had also been observed earlier with falling droplets, the existence and/or importance of surface viscosity as a unique physical property of a fluid interface [in the sense that Plateau (1869) and Boussinesq (1913a) had seemingly intended] became a questionable issue, particularly were one to dismiss the (admittedly qualitative) experiments that had for many years been invoked to document the 'viscous' nature of adsorbed monolayers.

A novel phenomenon, commonly subsumed under the appellation 'interfacial turbulence', was initially observed experimentally in the thesis of Wei (1955). The basic phenomenon he sought to investigate concerned the spontaneous mixing that arises when two unequilibrated and immiscible fluids, at least one of which contains a solute that is soluble in both phases, are brought into mutual contact. The interfacial activity generated as the solute underwent interphase transport was observed to range between relatively minor rippling and twitching motions at the interface, to the creation of streams of liquid reaching into the second phase, such streamers breaking finally into dispersed emulsion droplets. The most intense activity was observed when contact of the phases occasioned a rapid, exothermic chemical reaction between two solutes in the neighborhood of the interface (Wei 1955, Sherwood & Wei 1957).

Once again, the Marangoni effect was soon shown to be the primary cause of interfacial turbulence (Sternling & Scriven 1959), though the theoretical analysis, which employed the original Boussinesq theory, demonstrated that interfacial viscosity effects were in this case clearly distinguishable from Marangoni effects. Thus, whereas the Marangoni effect was observed to *create* the instability, owing to solute inhomogeneities across the interface, the interfacial viscosity effect was observed to *damp* the interfacial instability.

The work by Sternling & Scriven (1959), together with Scriven's (1960) paper, wherein Boussinesq's theory was generalized to 'material' interfaces of arbitrary curvature, marked a turning point toward today's "modern" understanding of interfacial rheology.

#### Interfacial Rheology After 1960: The Modern Period

Since the work of Scriven (1960), consistent theoretical analyses of existing experimental devices have been developed to allow reproducible, quantitative measurements of interfacial rheological properties, such as interfacial viscosity and elasticity (this latter property being related to interfacial-tension gradients, i.e. Marangoni effects). These will be discussed in Chapters 6 to 9. Analyses of Bénard and Rayleigh instabilities, and interfacial turbulence, have both undergone further refinement, often with an explicit accounting of the generally unique contributions of interfacial-tension gradients and interfacial viscosities, as will be discussed in Chapter 10. Rational explanations for the similar influences of interfacial flows, such as surface wave propagation and the sedimentation of spherical droplets, have also been developed in the modern, post-1960 period, as will be discussed in Chapters 4 and 5.

The importance of interfacial rheology to the drainage and stability of thin liquid films has been established in recent years; moreover, through this single phenomenon, the importance of interfacial rheology to important industrial processes involving the dynamics of foams and emulsions has been identified. These topics will be addressed in Chapters 10 to 14.

Many novel theoretical developments have transpired since 1960. These are reviewed in Chapter 15, which initiates Part II of this text, the latter being concerned with the current state of these new theoretical developments.

Presently, interfacial rheology is understood to play a significant role in many natural and industrial processes involving dynamic fluid interfaces, particularly when the specific surface is large, and surfactants are adsorbed to the interface. In the remainder of Chapter 1, this basic physical context of interfacial rheology is further elaborated, as too are several current engineering applications.

#### **1.2 Surfactants**

Surface-active materials possess various names, such as detergent, wetting agent, emulsifier, demulsifier or dispersing agent, depending upon their function. Generally, they are large molecules (the classical surfactant molecule has a molecular weight of 200-2000) possessing a bipolar structure composed respectively of *hydrophobic* (water-'hating') and *hydrophilic* (water-'loving') segments, such molecules being 'attracted' to an interface separating aqueous and nonaqueous phases. This dual physicochemical nature causes the molecule to seek the bi-phase environment of the phase transition zone.

Fatty acids and alcohols are typical surfactant materials, serving as the active ingredient for many commercial products, including soaps, detergents, corrosion and rust inhibitors, dispersing agents, demulsifiers, germicides, and fungicides. The hydrocarbon "tail" of the fatty acid or alcohol is the *lypophilic* (oil-'loving') or hydrophobic part of the surfactant, and the polar

—COOH or —OH "head" the hydrophilic part (see Figure 1.2-1). Shortchain fatty acids and alcohols are generally soluble in the aqueous phase; however, by increasing the hydrocarbon chain length, or alternatively by reducing the polarity of the polar head groups (e.g. by the addition of electrolyte to the aqueous phase), these surfactants are ultimately rendered *insoluble*, and may form an *insoluble monolayer* at the fluid interface.

Aside from fatty acids and alcohols, the role of surface-active agents may also be played by polymeric molecules, proteins, and small solid particles (Schwartz *et al.* 1977).



Figure 1.2-1 Sodium dodecyl sulfate molecules are depicted adsorbed to a fluid interface, with their polar heads in the aqueous phase and their hydrophobic carbon tails in the nonaqueous phase.

Synthetic and natural polymers often exhibit a significant surfactant tendency, particularly when the hydrophobic and hydrophilic parts of the molecule are sufficiently separated, as with block and graph copolymers. Carboxylic polymers, sulfonated polymers, phenolic polymers and polyvinyl polymers constitute further examples of polymeric surfactant molecules.

Protein, a natural polymeric substance, is a linear polymer formed of amino acid groups connected by peptide linkages to form a polypeptide chain, and may be surface active by virtue of the existence of hydrophobic/hydrophilic segments. In a homogeneous bulk phase, proteins often assume a helical configuration; however, when adsorbed to an interface, this helical structure is destroyed as the molecule arranges itself according to its hydrophilic/hydrophobic constitution. In the process the protein is denatured (i.e. bonds are broken and the polypeptide chain altered) and hence may become insoluble in the aqueous phase. As a result, an insoluble monolayer is formed, which, when subject to deformation may exhibit peculiar gel-like interfacial rheological behavior.

Submicron solid particles may display surface activity owing to the intrinsic physicochemical hydrophobicity of their surfaces. This

hydrophobicity is manifested by a finite *three-phase equilibrium contact* angle at the solid/water/air (or oil) contact line (see Figure 1.2-2). The particle in the vicinity of the interface is then forced by the concomitant interfacial forces to adopt an equilibrium position at the interface, for which this contact angle requirement is met. This action of surfactancy is useful in the engineering process of ore flotation, as is discussed in §1.3.



Figure 1.2-2 A nonzero contact angle  $\theta$  is shown between an aqueous phase/air surface and a solid particle. It arises from the hydrophobicity of the particle surface. A completely hydrophilic particle exhibits a zero contact angle.

A surfactant is generally classified according to the polarity of its hydrophilic head; thus, the primary classifications are *anionic* (e.g. carboxylic acids, sulfuric esters and sulfonates), *nonionic* (e.g. polyethenoxy and polyhydroxy surfactants), or *cationic* (e.g. fatty nitriles and amines). Anionic surfactants are those most commonly encountered in practice.



**Figure 1.2-3** An exaggerated depiction of micelles within an aqueous solution. Each micelle is composed of individual ionic surfactants, which aggregate in such a way that the hydrophobic surfactant tails are sheltered within nonaqueous cores.