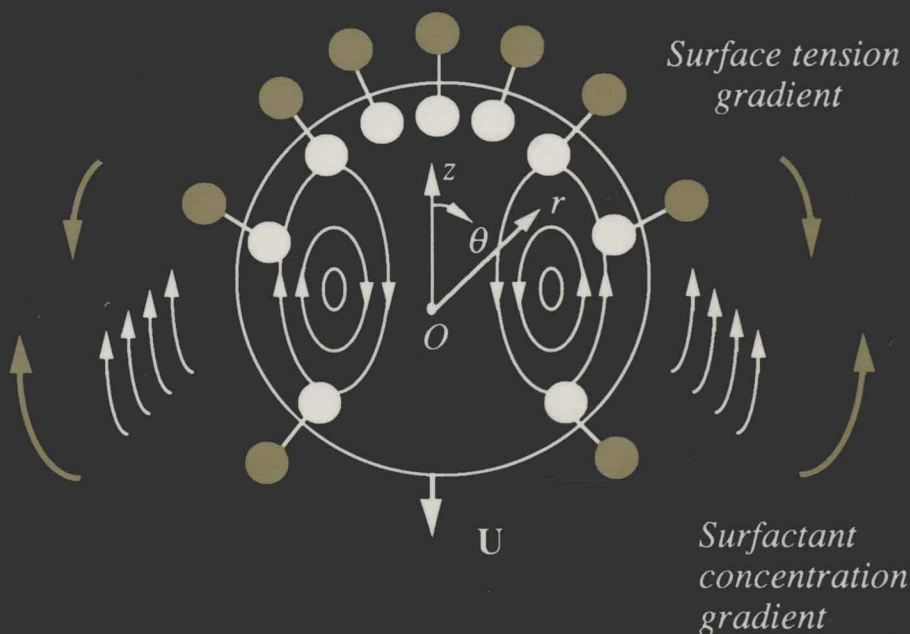


Interfacial Transport Processes and Rheology

David A. Edwards
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Butterworth-Heinemann Series in Chemical Engineering

Interfacial Transport Processes and Rheology

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Butterworth-Heinemann

Boston London Oxford Singapore Sydney Toronto Wellington

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Library of Congress Cataloging-in-Publication Data

Edwards, David A., 1961-

Interfacial transport processes and rheology / David A. Edwards, Howard Brenner, Darsh T. Wasan.

p. cm. — (Butterworth-Heinemann series in chemical engineering)

Includes bibliographical references and index.

ISBN 0-7506-9185-9

1. Surface chemistry. 2. Rheology 3. Transport theory.

I. Brenner, Howard. II. Wasan, D.T. III. Title. IV. Series

QD506.E38 1991

541.3'3—dc20

91-24665

CIP

British Library Cataloguing in Publication Data

Edwards, David A.

Interfacial transport processes and rheology.

I. Title II. Brenner, Howard

III. Wasan, Darsh T.

531.11

ISBN 0-7506-9185-9

Butterworth-Heinemann
80 Montvale Avenue
Stonham, MA 02180

10 9 8 7 6 5 4 3 2 1

Printed in the United States of America

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 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 matched-asymptotic, surface-excess formalism of Chapter 15 to the case of three-phase 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 one-semester 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.

H.B. was aided in the writing of this book by a grant from the *Bernard H. Gordon Engineering Curriculum Development Fund* at MIT, and he is grateful for the encouragement implicit in such an award. He would also like to acknowledge the research support that he and his students have received from the Office of Basic Energy Sciences of the Department of Energy, the Army Research Office, and the National Science Foundation. Such support contributed both directly and indirectly to the writing of this book. Lastly, H.B. would like to acknowledge the award of sabbatical leave grants to him during the academic year 1988–89 in the form of a Fellowship from the John Simon Guggenheim Memorial Foundation and a Chevron Visiting Professorship from the Department of Chemical Engineering of the California Institute of Technology. The hospitality displayed to him at Caltech was valuable in furthering the goals embodied in this book.

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

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PART I

INTERFACIAL RHEOLOGY: BASIC THEORY, MEASUREMENTS & APPLICATIONS