John C. Slattery

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Springer-Verlag

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With 185 Illustrations

Springer-Verlag
New York Berlin Heidelberg
London Paris Tokyo Hong Kong

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Library of Congress Cataloging-in-Publication Data
Slattery, John Charles, 1932–
Interfacial transport phenomena / John C. Slatery.
p. cm.
Includes bibliographical references and index.
ISBN 0-387-97387-7 (alk. paper). — ISBN 3-540-97387-7 (alk. paper)
1. Transport theory. 2. Surfaces (Physics) 3. Energy transport. 4. Mass transfer. 5. Heat—Transmission. 6. Entropy. I. Title.
QC175.2.S59 1990
530.1'38—dc20
90-10123
CIP

Printed on acid-free paper.

Camera-ready copy prepared by the author using Egg Bookmaker Interface.
Printed and bound by: Edwards Brothers, Inc., Ann Arbor, Michigan.
Printed in the United States of America.

9 8 7 6 5 4 3 2 1

ISBN 0-387-97387-7 Springer-Verlag New York Berlin Heidelberg
ISBN 3-540-97387-7 Springer-Verlag Berlin Heidelberg New York

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Preface

Transport phenomena is used here to describe momentum, energy, mass, and entropy transfer (Bird *et al.* 1960, 1980). It includes thermodynamics, a special case of which is thermo*statics*. *Interfacial transport phenomena* refers to momentum, energy, mass, and entropy transfer within the immediate neighborhood of a phase interface, including the thermodynamics of the interface.

In terms of qualitative physical observations, this is a very old field. Pliny the Elder (Gaius Plinius Secundus, 23-79 A.D.; Pliny 1938) described divers who released small quantities of oil from their mouths, in order to damp capillary ripples on the ocean surface and in this way provide more uniform lighting for their work. Similar stories were retold by Benjamin Franklin, who conducted experiments of his own in England (Van Doren 1938).

In terms of analysis, this is a generally young field. Surface thermostatics developed relatively early, starting with Gibbs (1948) and continuing with important contributions by many others (see Chapter 5). Derjaguin and Landau (1941) and Verwey and Overbeek (1948) indicated how London-van der Waals and electrostatic double-layer forces were to be incorporated in continuum mechanics, now often referred to as DLVO theory. But prior to 1960, there were relatively few notable papers concerned with the analysis of dynamic systems. Two stand out in my mind. Boussinesq (1913) recognized the surface stress tensor and proposed the constitutive equation that we now refer to as the Boussinesq surface fluid model (Sec. 2.2.2). Unfortunately, he did not carry out an experiment in which the effects of the interfacial viscosities could be clearly recognized. While many studies of the surface viscosities followed, the corresponding data analyses were not convincing. Brown et al. (1953) appear to have been the first to demonstrate how the interfacial shear viscosity could be measured in a limit where the viscous effects in the adjacent phases could be neglected with respect to those in the interface (Sec. 3.4.1).

More recently, interest in analysis has begun to flourish within this area. Since many people have made important contributions, the best that I can do briefly is to indicate a few papers that have had particular meaning for me. Scriven (1960) restated the Boussinesq surface fluid model in a form more convenient for analysis. Burton and Mannheimer (1967; Osborne 1968; Mannheimer and Schechter 1968, 1970; Pintar *et al.* 1971) analyzed and demonstrated the deep channel surface viscometer, which is still the recommended technique for measuring relatively small surface shear viscosities (Exercise 3.4.1-3 and Sec. 3.5.1). Dussan V. and Davis (1974), through both analysis and experiment, pointed out with unusual clarity the contradictions to be reconciled in describing a moving common line (Secs. 1.2.9 through 1.2.11 and 1.3.9). By analyzing a thin film, Israelachvili (1985) derived an expression for interfacial tension that is in excellent agreement with experimental measurements, demonstrating that continuum mechanics can be usefully extended to regions having molecular dimensions (Exercise 4.1.4-3).

With the appearance of these papers, there were also questions. Were the surface viscosities real physical parameters or were they artifacts of the manner in which the surface viscometer was analyzed? Was the measured value of the surface shear viscosity consequently dependent upon the viscometer used to measure it? Was the introduction of the surface stress tensor consistent with some general view of continuum mechanics? Could the effects of the surface viscosities be observed in any situations judged to be of practical importance? Was there really slip in the neighborhood of a moving common line? Was it possible to successfully apply continuum mechanics to the very thin films within the neighborhood of a common line? In trying to answer questions like these for my students, I decided to prepare this book.

This book is written both as a guide for those preparing for active research in transport phenomena and as a reference for those currently working in the area. The emphasis is upon achieving understanding starting from the fundamental postulates. The dominant theme is the translation of physical problems into mathematical terms.

I normally introduce my students to this book after they have completed the first semester of lectures from my first book (Slattery 1981). The text is self-contained, but I would prefer to see the reader already conversant with analogous discussions for single phases. Although I have lectured from this text here at Texas A & M, it is written with the intention of being sufficiently complete to be used for self-study. This is the manner in which most of my students have employed the text as it was being written. All of the exercises have answers. Where appropriate, the reader is led through an exercise, since the objective is not to test his comprehension of the preceding text. The exercises are used as a literary device to transmit information relevant to the text without overwhelming the reader with additional details.

In many respects this book was a group effort. Many colleagues have influenced and directed my thinking through conversations, by listening to their talks at meetings, and by reading their papers. While I have not been able to provide complete answers to all of their questions, I have been able to finish this book only through the continued probing, encouragement, and active help of my students. Jing-Den Chen and M. Sami Selim offered

comments on portions of the final manuscript. My wife Bea and Brenda Wilson cheerfully typed and retyped through many revisions over many years, never questioning whether the book would finally be completed. The final manuscript was prepared by Cheri Sandlin, with assistance from Ruth Heeremans and Izora Brown. Alfred Li provided invaluable help and support through the long months of proof reading, correcting the final manuscript, and preparing indices. The Peregrine Falcon Company made available a test copy of *THE EGG BOOKMAKER INTERFACE* (The Peregrine Falcon Co., P. O. Box 8155, Newport Beach, CA 92658-8155), in which the camera-ready copy was typed. David Adelson further modified this test copy, permitting me to use boldface greek, boldface script, boldface brackets (for jumps at interfaces), and boldface parentheses (for jumps at common lines). Joel Meyer and Peter Weiss prepared the final forms of the figures. Stephen H. Davis shared with me the original photographs from his work with Elizabeth B. Dussan in Sec. 1.2.9. Richard Williams and the David Sarnoff Research Center provided both the previously published and the previously unpublished photographs from his work that also appear in Sec. 1.2.9. My friends and colleagues at Northwestern University, where most of this book was written between 1972 and 1989, gave me their patience and encouragement. Thanks to you all.

College Station, Texas
July 10, 1990

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Contents

1
Kinematics and conservation of mass

This chapter as well as appendix A may be thought of as introductory for the main story that I have to tell. In appendix A, I introduce the mathematical language that we shall be using in describing phenomena at phase interfaces. In this chapter, I describe how the motions of real multiphase materials can be represented using the continuum point of view. To bring out the principal ideas as clearly as possible, I have chosen to confine my attention in these first chapters either to a material composed of a single species or to a material in which there are no concentration gradients. The conditions under which these results are applicable to multicomponent materials will be clear later.

There are two basic models for real materials: the particulate or molecular model and the continuum model. We all agree that the most realistically detailed picture of the world around us requires that materials be composed of atoms and molecules. In this picture, mass is distributed discontinuously throughout space; mass is associated with protons, neutrons, and electrons, which are separated by relatively large voids. In contrast, the continuum model requires that mass be distributed continuously through space.

The continuum model is less realistic than the particulate model, but far simpler. Experience has shown that for many purposes the more accurate details of the particulate model are not necessary. To our sight and touch, mass appears to be continuously distributed throughout the water which we drink and the air which we breathe. Our senses suggest that there is a large discontinuity in density across the static surface defined by our desk top or the moving and deforming surface of the ocean. The problem may be analogous in some ways to the study of traffic patterns on an expressway: the speed and spacing of the automobiles are important, but we probably should not worry about their details of construction or the clothing worn by the drivers.

The distinction between the particulate and continuum models should be maintained. In the context of a continuum representation, one sometimes hears a statement to the effect that a region is large enough to contain many molecules ... but small enough to represent a point in space ...