RHEOLOGY
PRINCIPLES, MEASUREMENTS, AND APPLICATIONS

CHRISTOPHER W. MACOSKO

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Principles, Measurements, and Applications

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RHEOLOGY

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Even the mountains flowed before the Lord.

From the song of Deborah after her victory over the Philistines, Judges 5:5, translated by M. Reiner (*Physics Today*, January 1964, p. 62).

The Soudan Iron Formation exposed in Tower-Soudan State Park near Tower, Minnesota. This rock was originally deposited as horizontal layers of iron-rich sediments at the bottom of a sea. Deposition took place more than a billion years ago, in the Precambrian era of geologic time. Subsequent metamorphism, deformation, and tilting of the rocks have produced the complex structures shown. (Photo by A.G. Frederickson, University of Minnesota.)

DEDICATION

A.M.D.G.

This book has been written in the spirit that energized far greater scientists. Some of them express that spirit in the following quotations.

"This most beautiful system of the sun, planets and comets could only proceed from the counsel and dominion of an intelligent and powerful Being."

Isaac Newton

"Think what God has determined to do to all those who submit themselves to His righteousness and are willing to receive His gift."

James C. Maxwell
June 23, 1864

"In the distance tower still higher peaks, which will yield to those who ascend them still wider prospects, and deepen the feeling whose truth is emphasized by every advance in science, that 'Great are the works of the Lord' ".

J.J. Thomson,
Nature, 81, 257 (1909).

PREFACE

Today a number of industrial and academic researchers would like to use rheology to help solve particular problems. They really don't want to become full-time rheologists, but they need rheological measurements to help them characterize a new material, analyze a non-Newtonian flow problem, or design a plastic part. I hope this book will meet that need. A number of sophisticated instruments are available now for making rheological measurements. My goal is to help readers select the proper type of test for their applications, to interpret the results, and even to determine whether or not rheological measurements can help to solve a particular problem.

One of the difficult barriers between much of the rheology literature and those who would at least like to make its acquaintance, if not embrace it, is the *tensor.* That monster of the double subscript has turned back many a curious seeker of rheological wisdom. To avoid tensors, several applied rheology books have been written in only one dimension. This can make the barrier seem even higher by avoiding even a glimpse of it. Furthermore, the one-dimensional approach precludes presentation of a number of useful, simplifying concepts.

I have tried to expose the tensor monster as really quite a friendly and useful little man-made invention for transforming vectors. It greatly simplifies notation and makes the three-dimensional approach to rheology practical. I have tried to make the incorporation of tensors as simple and physical as possible. Second-order tensors, Cartesian coordinates, and a minimum of tensor manipulations are adequate to explain the basic principles of rheology and to give a number of useful constitutive equations. With what is presented in the first four chapters, students will be able to read and use the current rheological literature. For curvilinear coordinates and detailed development of constitutive equations, several good texts are available and are cited where appropriate.

Who should read this book, and how should it be used? For the seasoned rheologist or mechanicist, the table of contents should serve as a helpful guide. These investigators may wish to skim over the *first section* but perhaps will find its discussion of *constitutive relations* and material functions with the inclusion of both solids and liquids helpful and concise. I have found these four chapters on constitutive relations a very useful introduction to rheology for first- and second-year engineering graduate students. I have also used portions in a senior course in polymer processing. The rubbery solid examples are particularly helpful for later development of such processes as thermoforming and blow molding. There are a number of worked examples which students report are helpful, especially if they attempt to do them before reading the solutions. There are additional exercises at the end of each chapter. Solutions to many of these are found at the end of the text.

In Part I of the book we only use the simplest deformations, primarily simple shear and uniaxial elongation, to develop the important constitutive equations. In Part II the text describes *rheometers*, which can measure the material functions described in Chapters 1 through 4. How can the assumed kinematics actually be achieved in the laboratory? This rheometry material can serve the experienced rheologist as a useful reference to the techniques presently available. Each of the major test geometries is described with the working equations, assumptions, corrections, and limitations summarized in convenient tables. Both shear and extensional rheometers are described. Design principles for measuring stress and strain in the various rheometers should prove helpful to the new user as well as to those trying to build or modify instruments. The important and growing application of optical methods in rheology is also described.

The reader who is primarily interested in using rheology to help solve a specific and immediate problem can go directly to a chapter of interest in Part III of the book on *applications of rheology*. These chapters are fairly self-contained. The reader can go back to the *constitutive equation* chapters as necessary for more background or to the appropriate rheometer section to learn more about a particular test method. These chapters are not complete discussions of the application of rheology to suspensions and polymeric liquids; indeed an entire book could be, and some cases has been, written on each one. However, useful principles and many relevant examples are given in each area.

ACKNOWLEDGMENTS

This text has grown out of a variety of teaching and consulting efforts. I have used part of the material for the past several years in a course on polymer processing at the University of Minnesota and nearly all of it in my graduate course, Principles and Applications of Rheology. Much of my appreciation for the needs of the industrial rheologist has come from teaching a number of short courses on rheological measurements at Minnesota and for the Society of Rheology and Society of Plastics Engineers. The University of Minnesota summer short course has been taught for nearly 20 years with over 800 attendees. Many of the examples, the topics, and the comparisons of rheological methods included here were motivated by questions from short course students. Video tapes of this course which follows this text closely are available. My consulting work, particularly with Rheometrics, Inc., has provided me the opportunity to evaluate many rheometer designs, test techniques, and data analysis methods, and fortunately my contacts have not been shy about sharing some of their most difficult rheological problems. I hope that the book's approach and content have benefited from this combination of academic and industrial applications of rheology.

As indicated in the Contents, two of the chapters were written by my colleagues at the University of Minnesota, Tim Lodge and Matt Tirrell. With Skip Scriven, we have taught the Rheological Measurements short course at Minnesota together for several years. Their contributions of these chapters and their encouragement and suggestions on the rest of the book have been a great help. Ron Larson, a Minnesota alumnus and distinguished member of the technical staff at ATT Bell Labs, contributed Chapter 4 on nonlinear viscoelasticity. We are fortunate to have this expert contribution, a distillation of key ideas from his recent book in this area. I collaborated with Jan Mewis of the Katholieke Universiteit Leuven in Belgium on Chapter 10 on suspensions. Jan's expertise and experience in concentrated suspensions is greatly appreciated. Robert Secor, now of 3M, prepared Appendix A to Chapter 3, concerned with fitting linear viscoelastic spectra, during his graduate studies here. Mahesh Padmanabhan was very helpful in preparation of much of the final version, particularly in writing and editing parts of Chapters 6 and 7 as well as in preparing the index.

This manuscript has evolved over a number of years, and so many people have read and contributed that it would be impossible to acknowledge them all. My present and past students have been particularly helpful in proofreading and making up examples. In addition, my colleagues Gordon Beavers and Roger Fosdick read early versions of Chapters 1 and 2 carefully and made helpful suggestions.

A major part of the research and writing of the second section on rheometry was accomplished while I was a guest of Martin

Laun in the Polymer Physics Laboratory, Central Research of BASF in Ludwigshafen, West Germany. The opportunity to discuss and present this work with Laun and his co-workers greatly benefited the writing. Extensive use of their data throughout this book is a small acknowledgment of their large contribution to the field of rheology.

A grant from the Center for Interfacial Engineering has been very helpful in preparing the manuscript. Julie Murphy supervised this challenging activity and was ably assisted by Bev Hochradel, Yoav Dori, Brynne Macosko, and Sang Le. The VCH editorial and production staff, particularly Camille Pecoul, did a fine job. I apologize in advance for any errors which we all missed and welcome corrections from careful readers.

Chris Macosko
August 1993

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