Mechanics of Non-Newtonian Fluids

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BY

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PREFACE

This is a book about fluid mechanics. In contrast to the usual books on that subject, the present volume is an exposition of the mechanics of non-Newtonian fluids, such as polymer melts, polymer solutions, and suspensions. More than 10 years ago, when the first notes were compiled, I was convinced that a need existed for a book which could be used to prepare beginning graduate students for reading current literature associated with the flow of rheologically complex materials. An intervening decade of teaching and research in the subject of non-Newtonian fluid mechanics has sharpened my own interest and knowledge, and it is hoped that the fruits of this experience will, in some measure, be passed on to the reader.

Although needs of beginning graduate students have been a primary motivation for this volume, its contents are intended for all research engineers who wish to learn the fundamentals governing flow of polymer melts, polymer solutions, and suspensions. The book is for people in research because one will not find an extensive treatment of the process technology of non-Newtonian fluids. That is not to say, however, that the subject has been approached as a mathematical exercise, free of real fluids and real fluid mechanical phenomena. Hence the book is also addressed to those with an engineering outlook—students and practitioners, academicians and industrial research people—who wish to learn what it is, at this writing, that we know about non-Newtonian fluids.

I have said that process technology is not covered in detail. Nevertheless, it is hoped that most readers will have an interest in the technology of rheologically complex fluids. It is my belief that a fundamental appreciation of the problems of technology requires firm grounding in the mathematical and physical language that describes mechanics of non-Newtonian fluids, i.e., in rheology. A comprehensive exposition of rheology requires a somewhat higher level of mathematical notation than is necessary for classical fluid mechanics. This fact has been accepted at the outset, and two full chapters are devoted to development of vectors and tensors. Their inclusion means that the volume should be essentially self-contained for one who is familiar with undergraduate-level fluid mechanics or transport phenomena.

Following an introduction and the mathematical developments of Chapters 2 and 3, Chapter 4 is a concise statement of the conservation equations of continuum mechanics. The next two chapters contain principles relating to description of deformation and of constitutive equations. These chapters draw heavily from the work of Truesdell and Noll.

In Chapter 7 one finally reaches the stage where a fluid model can be discussed. Noll's concept of the simple fluid is developed.

Chapter 8 is a discussion of means for measurement of the viscometric functions noted in Chapter 7.

Simple-fluid behavior in some prototype nonviscometric flows is treated in Chapter 9.

To this point the book has concentrated on continuum behavior. In Chapter 10 more specialized constitutive equations, including those which have been developed from elementary discrete models and lead to linear viscoelasticity, are discussed.

Principles enunciated in earlier chapters are used to generalize some of these linear models in Chapter 11. Several choices are available for development of constitutive equations which account for nonlinear behavior. It is possible to explain the subject with a single formalism. On the other hand, one can emphasize the multiplicity of approaches that have been used in the important research literature. The culmination of the latter course would be an encyclopedic listing of all constitutive equations which have enjoyed some measure of success. A middle ground has been followed in Chapter 11 in hopes that the reader will clearly see the fundamental concepts which permeate all of the "systems", and will also become familiar with several approaches to the subject, so that papers developed from an Oldroyd, Noll–Coleman, or Rivlin formalism will all be accessible.

Chapter 12 is a wide-ranging description of fluid mechanical phenomena exhibited by non-Newtonian materials. It is especially true in this chapter that selection from an almost limitless supply of examples and points of view represents a combination of the author's biased interests and his feeling of responsibility for some degree of balance.

The book concludes with an introduction to the subject of suspension rheology. Suspension models are particularly useful as a conceptual aid to the fluid mechanist because one can show, through application of classical fluid mechanics on a microscale, a rigorous physical basis for bulk phenomena. Many of the bulk phenomena predicted from suspension theory also occur with polymer melts and solutions. Although the fundamental physics of the latter is surely different in detail from that governing a suspension, suspensions do have useful modeling properties and are therefore included.

Non-Newtonian fluid mechanics is a quantitative subject and, as is also true of classical fluid mechanics, cannot be learned passively and without practice at theorem proving and problem solving. To this end, a few problems have been suggested at the end of most chapters. In early portions of the book these tend to be amplification or verification of derivations in the text. In later chapters, numerical problems dealing with viscometry and design have been included. It is anticipated that these problems will be supplemented as needed.

It is a challenge to write about a subject that is active. However, the day must come when an author decides to put his material into print without yet another revision to include recent work. I believe that the main ideas of this book have an importance sufficient to transcend the inevitable new theories and experiments which will appear in the literature between the time of writing and the time of publication.

It would be impossible to acknowledge all of those who have contributed to the creation of this volume. Thoughtful suggestions have consistently come from numerous Princeton graduate students. I would be remiss, however, to neglect this opportunity to record the critical reading of an early manuscript by Professor Martin Feinberg, and the great help in matters pedagogical and editorial provided by Dr. Andrew Kraynik.

Colleagues here and elsewhere have been gracious in responding to my requests for critiques of various chapters, and many of them will, I hope, recognize improvements prompted by their suggestions. Professor Roger Tanner's thorough review of all but the last chapter has resulted in a great many changes. He provided a timely voice of conscience against the author's urge to call the manuscript "finished".

Mrs. Loretta Leach has labored with patience, effectiveness, and even temperament far beyond that to be expected from a typist faced with the bewildering array of symbols appearing here.

My family and friends have suffered the indignities and neglect known all too well to families and friends of authors.

Finally, there is the quiet room at 1836 and all that it connotes. Without it the book could not have been born.

Princeton, New Jersey
March 1976

W. R. SCHOWALTER

CONTENTS

CHAPTER 1

INTRODUCTION

1.1. WHAT THE WORDS MEAN

Those who are familiar with the subject know that the words *Fluid Mechanics* in a book title generally mean something less than that. How much less varies from volume to volume, but, in many instances, the term is understood to mean the mechanics of *Newtonian* fluids. A Newtonian fluid is one for which a linear relation exists between stress and the spatial variation of velocity. If changes in fluid density are not important, the constant of proportionality is the viscosity, a characteristic constant of the material at a given temperature and pressure. *Non-Newtonian fluid mechanics* is the mechanics of fluids for which the stress at a given temperature and pressure is *not* a linear function of the spatial variation of velocity.

Newtonian fluid mechanics underwent a transformation during the first half of this century. Primary causes for the transformation were the concept of a boundary layer, put forward by Prandtl in 1904 [1], and the development of the aircraft industry. The latter made it necessary for engineers to achieve an understanding of exterior flows of air past objects and to develop design procedures to deal with these flows. In contrast, non-Newtonian fluid mechanics has evolved more recently. To a large extent its origins are found in tests of polymeric materials by physical chemists who wished to relate the bulk-flow behavior of polymers to molecular structure. A driving force, not unlike that supplied earlier for Newtonian fluids by the infant aircraft industry, was provided by the commercial development of polymeric materials and the resulting need for rational design procedures and correlations. At this juncture, chemical engineers became substantially involved. They were largely responsible for integrating the discipline of classical fluid mechanics with the chemists' studies of stress response of polymeric systems under strain. Over the past 20 years this has led to a mechanics of non-Newtonian fluids, a subject which has developed largely outside the main avenues of activity in the field of Newtonian fluid mechanics.

Rheology, the study of flow of materials, includes classification of various types of non-Newtonian flow behavior. The classification is necessary because of the negative sense in which a non-Newtonian fluid is defined; that is to say, one must know what a fluid *is*, not what it is *not*, before useful equations describing the motion can be written. Rheologists seek to classify flow behavior in terms sufficiently specific to permit prediction of the flow behavior of real systems, but also sufficiently general to avoid useless subdivision and redundancy.

1.2. THE PERVASIVENESS OF NON-NEWTONIAN FLUIDS

Although non-Newtonian fluids were largely bypassed by those responsible for development of the applied science of fluid mechanics, fluids which exhibit rheological response vastly different from such Newtonian fluids as air or water are encountered daily. Non-Newtonian response is typically observed in concentrated suspensions and in high molecular-weight materials. One of the best opportunities to observe non-Newtonian behavior is found in the kitchen. Examples of non-Newtonian fluids include salad dressings, butter, whipped cream, and doughs. Anyone who has separated eggs is aware of the "strange" elastic and tensile properties of egg white. The resistance of egg white to stretching is characteristic of polymer solutions and melts and is a phenomenon important in, for example, the drawing of molten nylon filaments during the production of synthetic fiber.

Most biologically important fluids contain high molecular-weight components and are, therefore, non-Newtonian. The rheology of blood has received much study. Blood is rheologically complex on two counts: it is a suspension because erythrocytes with characteristic dimensions of several micrometers are present in excess of 40 vol%, and the suspending fluid itself exhibits non-Newtonian behavior because of the presence of high molecular-weight protein. The importance of rheological properties of other body fluids is now recognized. In particular, the rheological response of mucous in respiratory systems of both infants and adults is an important factor for proper respiratory behavior. The lubricating action of synovial fluid in joints is, likewise, strongly dependent on rheological properties.

Anyone who has played with that archetype of rheologically complex material, "silly putty", is aware that classical distinctions between solids and fluids are not always helpful. Indeed, non-Newtonian materials are often classified by the term "visco-elastic", indicating that they display both the properties of viscous fluids and elastic solids. Given this, the term non-Newtonian *fluid* mechanics is also open to interpretation, and, in Chapter 7, we shall state precisely what we mean by a fluid. The fact that certain materials, commonly thought of as solids, nevertheless exhibit flow properties usually associated with liquids, is also evident in geological phenomena: the motion of everything from sediment beds to mountain ranges is governed by rheological characteristics.

1.3. THE PERVERSENESS OF NON-NEWTONIAN FLUIDS

For the academician, non-Newtonian fluids offer a new challenge for description and understanding. Although we have seen that examples are commonplace, most of our intuition concerning the behavior of fluids is centered on Newtonian fluids. Those who have completed formal study of (Newtonian) fluid mechanics must sometimes ignore their intuition if they hope to predict non-Newtonian behavior. The subject is sufficiently new so that many "classical" flows of viscous fluids are still to be studied systematically. Those which have been examined have often revealed surprising new phenomena. We present a few examples below.

(i) Jet Stability

Stability of free and enclosed jets has engaged the attention of many great fluid mechanists, the analysis of Rayleigh being an excellent example. He showed that interfacial forces cause a free inviscid jet to be unstable when the characteristic wavelength of a disturbance on the jet surface exceeds the circumference of the jet. Subsequent work, experimental and theoretical, has led to an understanding of the growth of surface disturbances of certain wavelengths, which leads to the breakup of viscous Newtonian jets [2]. In jets with appreciable elasticity, however, breakup does not occur by clearly defined waves. An example is presented in Fig. 1.1.

(ii) Jet Expansion

Classical analysis of a free jet, roughly confirmed experimentally for viscous Newtonian jets at sufficiently high flow rates, indicates that the jet diameter will decrease upon exit from a tube [4]. Beyond effects due to gravity, the contraction is a consequence of momentum conservation during adjustment of the velocity distribution in the jet to a flat profile (Fig. 1.2a). Viscoelastic jets, however, typically swell upon exit from a tube as a result of relaxation of elastic forces (Fig. 1.2b).

(iii) Drag Reduction

For reasons which are far from understood, it is an experimental fact that small amounts of polymer dissolved in a liquid can drastically reduce the skin friction of a fluid in turbulent flow. A graphic practical example is shown in Fig. 1.3. One notes that it is possible for perversity to be turned to advantage.

1.4. NON-NEWTONIAN FLUID MECHANICS AND THE POLYMER INDUSTRY

The unusual flow properties of polymer melts and solutions, together with the desirable attributes of many polymeric solids, have resulted in development of the huge worldwide industry of polymer processing. We have already referred to the manufacture of synthetic fiber from polymer melts. In a typical installation, fiber is made by forcing a molten polymer, such as nylon, through a die containing perhaps a few hundred holes, each with a diameter of approximately 0.01 in. As individual filaments of molten polymer are drawn away from the die; they are cooled by the surrounding air and are simultaneously stretched to a smaller diameter. Following cooling and solidification the filaments are wound together to form a composite filament on a bobbin or take-up reel. Filament speeds in excess of 5000 ft/min are not uncommon (Fig. 1.4).

Large parts of automobiles and domestic appliances are often formed by injection molding. This is a highly unsteady process in which a molten polymer is forced into a mold and then allowed to solidify (Fig. 1.5). Often the whole process is repeated by a machine at intervals of only a few seconds.

Another important polymer processing operation is film blowing (Fig. 1.6) in which the deformation approaches biaxial straining. This is to be contrasted to injection molding operations in which the predominant motion experienced by the molten polymer is often laminar shearing, or with fiber spinning, where the flow is primarily uniaxial stretching. If one is to perform laboratory flow experiments that will be helpful in predicting behavior in polymer-processing operations, it is clear that the kinematic and dynamic distinctions between these three processes should be understood.

One cannot fail to note the importance of non-Newtonian fluid mechanics in the polymerization process itself. During the polymerization, which is generally carried out under batch conditions with transient transfer of heat and mass, the batch viscosity changes from that of water to perhaps 10^6 poise.

1.5. SOME OTHER APPLICATIONS

In many cases the marketability of a polymer is due to the rheologically complex behavior of the material. An example can be found in the compounding of materials for coating of surfaces. The non-Newtonian behavior of paints is an important factor in determining the "brushability" of a paint. Interesting tests have been devised to measure this quality in the laboratory. One wishes to have a paint that will not show brush marks after drying; on the other hand, if the paint is too thin it will not adequately cover a surface. Similarly, the art of paper coating is highly dependent on the rheology of the coating material. In conventional coating applications the coating "color", as it is called, is subjected to extreme variations of high and low shearing.

The petroleum industry uses large quantities of "drilling muds" to lubricate the drill bit and to carry rock chips out of the hole during drilling of oil wells. It is important to have muds which exhibit low viscosity under shearing but which are very thick at rest, thus preventing rapid settling of chips when the drilling unit is not in operation.

Further examples can be cited almost without limit. We note in closing this section that most foodstuffs are non-Newtonian. This is important in respect both to food processing and to the preparation of acceptable natural food substitutes.

1.6. RELEVANCE

The foregoing illustrations of non-Newtonian fluid mechanics in the polymer and related industries are not included as a prelude to the unfolding of design equations suitable for each practical engineering need. It has already been stated in the Preface that this is not a book on polymer processing. Nevertheless, it is often useful to see the possible scope for application of the fundamentals of a subject. At present, the fundamentals of non-Newtonian fluid mechanics are known to a group of academic and industrial engineers and scientists which, given the pervasiveness of industrially important operations involving non-Newtonian flow, is numerically small. It is generally recognized by educators and practitioners alike that a command of the fundamentals of classical fluid mechanics is essential for those who must deal, albeit in an approximate way, with such complex problems as ocean dynamics, aircraft design, and flow through porous media. This book is motivated by the corresponding belief that those who are engaged with non-Newtonian fluids should be conversant with the fundamentals of that subject.

REFERENCES

1. Schlichting, H., *Boundary-layer Theory*, 6th edn., p. 117 *et seq*. (New York: McGraw-Hill, 1968).
2. Meister, B. J. and Scheele, G. F., *AIChE Jl* **13**, 682 (1967).
3. Goldin, M., Yerushalmi, J., Pfeffer, R. and Shinnar, R., *J. Fluid Mech.* **38**, 689 (1969).
4. Gavis, J. and Modan, M., *Phys. Fluids* **10**, 487 (1967).

CHAPTER 2

LINEAR TRANSFORMATIONS, VECTOR SPACES, VECTORS

2.1. INTRODUCTION

One might argue that there has been sufficient proliferation of guides to vectors and tensors, either in book form [1, 2] or as adjuncts to books of interest to rheologists [3–6], to make another attempt unnecessary. Least of all, the argument might continue, should a monograph which is claimed to be an exposition of the physical behavior of fluids begin with two chapters devoted largely to an explanation of mathematical symbols.

A decision to the contrary has been prompted by several factors. It is believed that some mathematical tools unlikely to be in the firm grasp of most engineers and chemists can nevertheless be very useful in explaining problems in non-Newtonian fluid mechanics. Also, one obtains the impression from both engineering students and practitioners that an understanding of the tensor concept and its application to problems of rheological interest are difficult to obtain from any single source. It would be presumptuous to hope that appearance of one more volume will remedy the matter. Nevertheless, there does seem to be ample justification for another presentation of the subject. It is hoped that the mathematical background presented in the first two chapters will help to provide a book which is reasonably self-contained for most readers.

This preamble has been written with the hope that it will help to motivate the reader to spend time on the early chapters even though primary interests lie in the physical aspects of rheology. Those who do not find the mathematical notation or operations of this book unfamiliar, are encouraged to proceed to Chapter 4 or to some of the references cited at the end of Chapter 3, which provide more completeness and rigor than is offered here.

The purpose of this chapter is to introduce the concept of a *vector* in a manner somewhat more precise than may have been previously experienced by the reader. The reason for this is to lay a serviceable foundation for the *tensor* concept of Chapter 3. Of particular importance in subsequent paragraphs are the notions of and distinctions between vectors, base vectors, vector components, covariant components, and contravariant components. However, before launching into a host of definitions, we establish a point of departure with a familiar example.