BOOK REVIEWS

Constitutive Equations for Polymer Melts and Solutions

By R. G. Larson, Butterworths, Boston, 1988, 364 pp., $39.95

Polymer melts and solutions, due to their complex molecular structure, have very specific and highly nonlinear rheological properties which reflect their intermediate position between liquids and solids. That is why the constitutive (or, in this case, rheological) equations that relate such macroscopic quantities as stress and strain tensors are very complicated and involve in their deriving, deep physical and mathematical ideas. Besides the academic interests, these equations find many applications in solution of practical problems arising in modern technology.

Unfortunately, there are several tens of such equations which are in competition nowadays. This situation shows that the science in this particular field of study is far from being completed. The field began, almost forty years ago, when the first invariant viscoelastic constitutive equations were proposed, and there was recently a trend to the rational mechanics followed by molecular dynamics and statistical derivation of rheological equations, which are so popular nowadays.

The approach developed by the author of this book could be related to a semiphenomenological statistical microapproach. The main idea is to consider first, as a primitive relation, the kinetic equation for the "strand end-to-end vector," R, undergoing some external gradient velocity field, ∇v. The next step is substituting this equation into a stochastic continuity equation for distribution function in the "strand's space." Also, one needs some additional hypothesis about the dependence of microscopic stress or free energy on R. The final step is the procedure of averaging over the nonequilibrium distribution function in order to obtain both the macroscopic stress and its evolution equation. Thus, the center of the approach is micromodelling of the kinetic equation for the strands. Also, there are generally some mathematical difficulties in obtaining the closed set of macroscopic viscoelastic rheological relations expressed in terms of stress and strain rate tensors and their time derivatives. If the strand kinetic equation is linear in both R and ∇v, one can obtain in this way, even without knowledge of distribution function, all simple (one-relaxational) constitutive equations known in literature, which are quasilinear with respect to stress. When the strand kinetic equation is nonlinear in R, the problem is more complicated and generally requires solving the coupled strand and Liouville equations before overcoming the averaging procedure. Usually, it results in a closed constitutive equation only after arbitrary simplifications. Nevertheless, this approach seems to be very fruitful for applying new physical ideas, and the author demonstrates his skill in doing so. Also, this approach allows the author to compare various constitutive equations and to classify them. All constitutive equations which the author could not derive from the strand analysis are declared in the book as semiempirical.

This book consists of ten chapters. The first three introduce the reader to the basic viscoelastic effects, rheological concepts, and well known phenomenological and molecular models. The fourth chapter deals with detailed discussion of the reptation theory and its improvements and generalizations. The next two chapters of the book consider the rheological equations with nonaffine motions of the strands, which are nonderivable from the simple strand analysis, being mainly nonlinear in stress. Though the most important predictions of the models are compared immediately after their introduction, a special chapter (Ch. 7) is devoted to the mutual comparison of constitutive equations and their basic predictions. Chapter 9 discusses the special applications and general form of constitutive equations for polymer melt and solutions in the shear and extentional rheometric flows. Chapter 8 and 10 review the physics of dilute polymer solutions and nondilute solutions of rigid macromolecules in light of physical concepts proposed comparatively recently.

Thus, the underlying idea of this book is to show how the rheological equations can be derived from simplified molecular considerations. Though this has been very useful, the approach demonstrated by the author cannot eliminate the principal arbitrariness in the various constitutive equations. Therefore, the final criterium to the validity of rheological equations is the coincidence of their predictions with a few standard tests in rheometric shear and extensional flows. But this criterium looks somewhat disappointing because almost all known rheological models, independently of how different they are, could be, in principle, derived in this way, and almost all the equations could be improved or generalized to better satisfy the data.

But there is another fundamental criterium of validity of rheological equations which is not even mentioned in this book. It is the demand of the second law of thermodynamics that for any constitutive equation the dissipation has to be positive in an irreversible state. Unfortunately, for the vast majority of the rheological equations, the dissipation term is not so easy to define. The analysis of this term is, however, necessary to guarantee the thermodynamic stability of rheological equations, i.e., the stability of the rest state with respect to arbitrary disturbances and, to some extent, the evolution conditions. The practical use of analyzing this term is determination of the dissipative heat generation for nonisothermal flow.

Even without this, the book provides deep insight into the physics underlying the constitutive equations for polymeric melts and solutions. It can serve as a guidebook for the broad range of specialists in polymer science and technology and could be useful as a textbook for a lecture course in advanced polymer rheology.

A. I. Leonov
Department of Polymer Engineering
The University of Akron
Akron, OH 44325

Thermo- and Laser Anemometry

Edited by A. F. Polyakov, Hemisphere Publishing Corp., New York, 1988, 173 pp.

For the reader who is an expert in the use of hot-wire or laser Doppler anemometers, this compilation of papers in English from a workshop held by the Division of Heat Transfer of the Institute for High Temperatures, USSR Academy of Sciences, and the Danish company, Dantec Elektronik, has a few papers of interest. This is not a book for the beginner in these experimental tools for turbulent-flow measurement. These techniques, however, are becoming more common as we need to know more details about turbulent mixing.

The first three articles deal with thermo anemometers for the measurement of velocity and temperature. Petukhov et al. discuss the relationship between velocity fluctuations in the flow-to-voltage fluctuations in a single hot-wire probe. This relation between the instrument and the property to be measured is important in any method. In the case of hot-wire anemometers, we must look at the frequency response of the wire, the filtering effect of the holder which has a large mass compared to the wire, and the length of the wire compared to the smallest fluctuations in the flow. These are all treated mathematically, and an experimental method to correct for the last effect is verified. The second article in this section treats the calibration of a triple-split probe that can be used in two-dimensional reversing flows. The last article presents measurements in a boundary layer over a porous plate with injection.

There are seven laser Doppler articles, all concerned with equipment design. The first Dantec article discusses optical fibers suitable for use with a laser Doppler anemometer (LDA) system. Transmitting and receiving light through fiber optics can make positioning easier than for a conventional lens system. The next Dantec paper reviews the optical calculations for typical one- and three-dimensional arrangements. A major objective here is to obtain a sufficiently large number of fringes in the direction of the velocity component to be measured. A third paper from Dantec contains a derivation of the equations for the fluctuations due to refractive index variations in the optical path. The Dantec papers are available in Dantec publications in more detail.

The last two papers by Soviet authors are merely lists of equipment, but the other two are the highlights of the volume. They give keys to the Russian literature and, perhaps, some new ideas for the improvements to LDA systems. The disadvantage is that significant details may only be available in Russian. One paper on the "Spectral Method of Measuring the Structure of Turbulence," gives results of a comparison of a counter and a "spectral method" signal processor. The "spectral method" is a homemade unit to directly measure the energy spectrum of the photocurrent from the photodetector of the LDA. The Russian authors claim that their spectral method is inexpensive, but commercial photon correlators using fast Fourier transforms are now promoted at much higher costs. Another article, "Techniques of LDA Measurements in Cylindrical or Conical Models," presents several optical arrangements of three or four beams to measure two components of velocity. Problems associated with the refraction at solid fluid interfaces are discussed. This article should be of particular interest to students using LDA in cylindrical tubes.

Most of the articles were translated from Russian and although the text is generally understandable, the translation is only fair. Many of the figures and handwritten equations are not readable. The Russian articles are good introductions to experimental design for the researcher who knows the fundamentals of the hot-wire and laser Doppler anemometry. The book is appropriate for a research library but not for an individual.

Neil S. Berman
Dept. of Chemical, Bio, and
Materials Engineering
Arizona State University
Tempe, AZ 85287