BOOK REVIEWS

Editor's Note: The following review by Professor Marrucci raises a number of important technical issues. I, therefore, invited the authors to respond to these comments in the interest of stimulating further discussion. Professor Marrucci was then asked to make any final comments that he might wish to add. Volume 1 was reviewed by W. R. Schowalter (34, p. 1052, 1988).

Dynamics of Polymeric Liquids
Volume 2: Kinetic Theory

By R. Ryron Bird, Charles F. Curtis, Robert C. Armstrong, and Ole Hassager, John Wiley & Sons, Inc., New York, 2nd Ed., 1987, 437 + xxi pp.

Volume 2 of Dynamics of Polymeric Liquids, which has been completely rewritten in the second edition, deals with the molecular modeling of polymer rheology. As the authors point out, this book is virtually autonomous with respect to Volume 1, which treats polymeric liquids from the viewpoint of fluid mechanics. The title given by the authors to Volume 2, *Kinetic Theory,* perhaps reflects their ambition of developing a theoretical framework which would be applicable in general. Whether or not they have succeeded in this difficult task is at least open to question. I will presently offer a few comments on this point which, I believe, is the leading theme of the book.

The book opens with an introductory chapter (Chap. 11) on the molecular models to be used in the context of polymer rheology. The authors explain that, when dealing with nonequilibrium transport properties, it becomes necessary to reduce the high structural complexity of the real polymer molecules to the relative simplicity of an artificial chain (made up of friction beads, springs, etc). The predictions which can be worked out by the use of these models are, obviously, more or less "useful" depending on the details of the molecular structure which have been incorporated in the model. The authors, however, rightly point out that the concept of usefulness varies depending on the objective and that, therefore, different details must be included in the modeling depending on whether we want to describe, for example, a steady-state flow or a high-frequency oscillatory motion. This and the following chapter (Chap. 12) describe the equilibrium properties of the polymeric model. Already in Chap. 12, the authors introduce generalized coordinates and Hamilton's equations of motion to deal with internal degrees of freedom and constrained systems.

Chapter 13 opens the sequence of several chapters dealing with dynamics and rheology. In view of its simplicity, the first molecular model which is considered is rightly the elastic dumbbell. The general section, as well as that on Hookean dumbbells, is very well done. Conversely, the section on non-Hookean dumbbells (FENE or otherwise), though obviously correct, might prove somewhat misleading. The reader may get the impression that the molecular origin of the non-Newtonian shear viscosity in dilute polymer solutions is exclusively rooted in the finite extensibility of the polymer molecule, i.e., in its non-Gaussian behavior. This interpretation is questionable. There exist other molecular effects which might be responsible for the non-Newtonian shear viscosity of dilute solutions, such as the "internal viscosity." In a shear flow, a polymer molecule continuously rotates, and its elongated shape correspondingly pulsates. The internal viscosity dampens this pulsation—the more so, the higher is the frequency (i.e., the higher the shear rate). As a consequence of an increased "rigidity" of the molecule due to such a mechanism, the shear viscosity decreases. The authors barely mention the latter mechanism in one of the problems (13 C.2) and in a list of "refinements" at the end of Chap. 15, though it seems to this reviewer that it is probably a better candidate than a nonlinear elasticity to explain the non-Newtonian behavior in shear. On the other hand, I agree with the authors that the finite extensibility may play an important role in elongational flows.

To conclude, the main criticism here (as well as elsewhere, see below) is not so much that the authors make definite, albeit questionable, choices (which is obviously legitimate and often unavoidable), but that they do so (and correspondingly oversimplify a complex matter) while conveying the impression to the inexperienced reader that their treatment is a general, virtually-comprehensive theory.

Chapter 14 deals with dilute solutions of rigid rodlike particles, particularly with the rigid dumbbell model. The chapter proceeds smoothly and comprehensively. The reader should be aware, however, that the extremely rich topic of *concentrated* solutions of rodlike particles is left out of the book entirely: i.e., it is not included in Chap. 19 that deals with concentrated solutions and melts. We recall that, by increasing the concentration of rigid rodlike molecules, the system undergoes a transition to an oriented phase, exhibiting wholly different dynamics and rheology.

Chapters 15 and 16 present a generalization to multiple bead-spring (i.e., Rouse-Zimm) and multiple bead-rod-spring models, respectively. Chapter 16, by considering various possible "complications" such as branched structures, mixtures, beads with different masses, etc., opens the way to Chaps. 17 and 18, where the maximum generality is attained. Chapter 17, which also opens Part VII of the work, lays down the "Phase-Space Theory of Polymeric Liquids."

At a formal level, the scope of this theory is unquestionably extremely wide. The generality is obtained by: i) allowing the chains to be modeled by a collection of beads of arbitrary shapes, linked by either springs or rigid links or freely rotating joints or any combination of those; and ii) by allowing the Hamiltonian of the entire system (the collection of chains plus solvent, if any) to incorporate any kind of intra- and intermolecular potential. As far as I can tell, the only effect which is left out at this level of formalism is the already-mentioned internal viscosity. Being a kinetic effect, linked to the overcoming of internal potential barriers, it is not included in the Hamiltonian, which depends only on coordinates, not on their rate of change. The high level of generality reached in Chap. 17 is only formal, however. The problem is at best formulated and certainly not solved. Nor could it possibly be solved either by the authors or by anyone else. In order to obtain solutions, one must again step down from the general to the particular and make *ad hoc* assumptions and/or approximations, questionable ones, as all assumptions inevitably are, sometimes highly questionable.

We skip discussing Chap. 18, where dilute solutions are revisited, as well as Chap. 20, which offers a good review of the network models, and go directly to Chap. 19, which contains the specialization of the general theory to the important case of concentrated solutions and melts, i.e., the celebrated Curtiss-Bird theory, often compared to that of Doi and Edwards. The approximations used by the authors to reduce the general theory to a manageable level are as follows: i) the interaction of one chain with the neighboring ones is described by an anisotropic Stokes' law, which favors the motion along the chain over the transverse motion; ii) a similar anisotropy in the Brownian motion; and iii) a mild-curvature approximation, whereby consecutive links of the chain (which, incidentally, is made up exclusively of rigid links) can differ only mildly in orientation. This is not a list of approximations in a mathematical sense, however, which would then clearly define a range of application where the approximate form of a general theory is valid. Rather, it is a list of drastic, *ad hoc* assumptions. Once these assumptions are used, the general theory is completely lost, and one is left with nothing more than a "model" in the semi-empirical sense. This conclusion is further reinforced, if one considers that additional, *ad hoc* quantities are inserted in the model as the need arises, like the chain constraint exponent β, which, if possible, is even more arbitrary and gratuitous.

I must express disagreement with respect to the sentence (p. 315) concerning the anisotropy of Brownian motion, which reads: "It should be pointed out, however, that, since Eq. 19.2-5 evaluated at equilibrium is inconsistent with Eq. 19.2-4, the reptation approximation cannot be exact at equilibrium. Nevertheless, it appears to be a good approximation away from equilibrium." There is no doubt that the inexperienced reader would get from this sentence the message that the reptation mechanism, as proposed by deGennes and further developed by Doi and Edwards, "cannot be exact at equilibrium," and is at best "a good approximation away from it." This is certainly incorrect. In the theory of the above-mentioned physicists, the Brownian motion of the chain beads is correctly isotropic at equilibrium. Indeed, in the model of Doi and Edwards, the primitive chain and the actual chain are random walks at equilibrium. Now, if a bead performs a three-dimensional random walk (even a predetermined walk, as is the case for the hypothetical bead belonging to the primitive chain), it is (trivially) isotropic in space since Brownian motion generates the walk itself. In fact, I believe that the sentence of the book applies only to the Curtiss-Bird version of the reptation idea, where the chain obeys the mild curvature assumption. Needless to say, random walks do not obey any such assumption.

To conclude the comments on this controversial chapter, I note a sentence on p. xi of "Comments on Volume 2," which reads: "Generation of the theory in this way (i.e., by the phase-space approach) makes it clear how the original reptation theories for melts can be extended and improved upon in the future." Frankly, I hold the opposite opinion in view of the impossibility of actually specifying (or, if specified, of using) the Hamiltonian for the case at hand. Any real progress can be made only by a direct understanding (and appropriate modeling) of the physical reality of these complex systems, along the lines set forth by Edwards, deGennes, Doi, etc.

I realize that, so far, I have emphasized the limitations of this book rather than its merits. It is time to do the authors justice for their effort, which is unquestionably a major one. The book provides a well-organized reference which, I am sure, is going to last a very long time. It contains an enormous amount of material which will prove very useful to many people working in the field.

Although the nomenclature shows some asperities, it is rational and well-conceived. Misprints are very few, and there is a continuing effort by the authors to eliminate them from future editions.

G. Marrucci
University of Naples
Dipartmento Di Ingegneria Chimica
Napoli 80125, Italy

Response by the Authors of the Book:

We wish to thank Professor Denn for giving us the opportunity to comment on Professor Marrucci's review of our book on polymer kinetic theory. It is inevitable that there will be many schools of thought in a scientific subject that is still in a state of development. In preparing a textbook it is not possible to present all points of view, and we have included only those topics that we felt were sufficiently well-developed and understood. We will now address several of Professor Marrucci's specific comments, with the intent of discussing some of the scientific details.

According to Professor Marrucci, "The reader may get the impression that the molecular origin of non-Newtonian shear viscosity in dilute polymer solutions is rooted exclusively in the finite extensibility of the polymer molecule." On p. 81 of Chap. 13, we specifically warn the reader that "... there are many other effects—such as hydrodynamic interaction, excluded volume, internal viscosity, perturbation of the velocity gradient, wall effects, friction coefficient varying with dumbbell extension, and nonisotropic frictional drag. . ." On pp. 172-3 of Chap. 15, we also mention these additional effects and give extensive references.

The idea of including internal viscosity in a molecular model has been highly controversial. Yamakawa, in his book entitled *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1971), gives only two references in passing to this subject, and the more recent book by Doi and Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, 1986), makes no mention of internal viscosity. In Problem 13C.2 on p. 105, we give the standard definition of internal viscosity and point out that "since it involves nonconservative forces, we cannot use the methods of Chap. 12 (i.e., equilibrium statistical mechanics) to obtain the equilibrium configurational distribution function, and hence we do not have a proper starting point for developing the nonequilibrium kinetic theory." We feel that this is a serious shortcoming of the model. In Eq. 13C.2-2, we suggest that this shortcoming can be overcome by replacing the time derivative of the interbead distance by its momentum-space average. This allows one to proceed with problem-solving, but nothing is known about the seriousness of this assumption. In addition, many authors have introduced the internal viscosity "dashpots" into chain models *after* transformation to normal coordinates, thereby generating a model of questionable physical interpretation. Because of these and other unresolved questions about internal viscosity, we felt it appropriate to relegate it to a problem at the end of the chapter.

We purposely omitted a discussion of concentrated solutions of rigid rodlike macromolecules feeling that there were too many unresolved issues and conflicting viewpoints in the research literature. In addition, we had not done research in this area and hence were not prepared to present the topic in a manner consistent with the rest of the book at the time we were writing. We feel strongly that this problem will ultimately be solved by means of the phase-space theory of Chaps. 17–19. A first step in this direction has been taken by Raghu K. Menon, Robert A. Brown, and Robert C. Armstrong in a paper entitled "Kinetic Theory and Rheology of Liquid Crystalline Polymers," to be published soon.

Professor Marrucci does not seem to appreciate the importance of the phase-space theory given in Chap. 17. This theory was purposely placed toward the end of the book, because it is a difficult subject in nonequilibrium statistical mechanics that requires depth of understanding and considerable skill. Our presentation is, in a sense, an extension of the phase-space theory of polymeric solutions presented in 1944 in *Physica* by H. A. Kramers (the Dutch theoretical physicist), and in the series of papers (1948–1958) by J. G. Kirkwood on the foundations of nonequilibrium statistical mechanics. We begin with the equations of motion for the polymer molecules and solvent molecules (if any)—a fundamental physical starting point. The statistical ideas enter via ensemble theory and the Liouville equation in the complete phase space, from which a "general equation of change" for an arbitrary dynamical variable B is obtained. By making various choices for B, one gets the hydrodynamic equations of change, with explicit molecular expressions for the stress tensor and the mass flux (for diffusion). In addition, still other choices for B lead to equations for the various distribution functions and the equations of motion for the polymer and solvent molecules. In this way, we can use one well-defined molecular model: 1) in the expressions for the physical quantities, such as the stress tensor and diffusion flux; and 2) in developing the dynamical equation leading to the expression for the nonequilibrium distribution function. We feel that it is extremely important that the two main parts of the kinetic theory be based on the same physical ideas and on the same molecular model.

In commenting on the general phase-space kinetic theory of Chap. 17, Professor Marrucci says that "in order to obtain solutions, one must . . . make . . . assumptions . . . sometimes highly questionable." We certainly agree that assumptions do have to be introduced. It is very important, however, to have some key "starting equations" (such as Eq. 17.6-11 for the stress tensor, Eq. 17.6-12 for the mass flux, Eq. 17.5-14 for the distribution function, and Eq. 17.5-15 for the equations of motion) that are solidly based and ready to use. Furthermore, it is conceptually satisfying to have a single, unified starting point for dilute and concentrated systems, rigid and flexible polymers, monodisperse and polydisperse fluids, and systems with and without constraints. No other book offers this.

In Chap. 18, we show how the formal results of Chap. 17 are applied to dilute solutions. The assumptions introduced are carefully set forth (they are not concealed) so that they can be challenged; we hope that these assumptions can be removed or replaced by better ones, but this may take considerable time. The "short-range force assumption" is introduced to avoid the necessity for developing expressions for the distribution functions in the space of pairs of molecules—solvent-solvent, solvent-polymer, and polymer-polymer (*terra incognita* in polymer kinetic theory). The "Stokes law empiricisms" for hydrodynamic forces have been used for years by polymer physicists; and we are almost forced to introduce some kind of empiricism at this point, again in the absence of information about pair distribution functions. The use of such an expression was first justified by Kirkwood (1948) in a publication in which he developed an expression for the friction coefficient in terms of a time-correlation function; and these ideas have been recently generalized to the polymer solution problem (C. F. Curtiss, *J. Rheol.*, **32**, pp. 403–427, 1988). The general Brownian force expression in Eq. 18.3-1 cannot be found elsewhere in the literature; it contains momentum-space averages, and in the absence of information about the momentum distribution function (more *terra incognita*), we offer two assumptions—the standard equilibration-in-momentum-space assumption leading to the usual Brownian motion expression in Eq. 18.3-5, and a novel alternative assumption leading to Eq. 18.3-16, which we have found useful in a theory for melts using elastic dumbbells (Section 13.7). The assumptions made in this chapter lead directly to the earlier results of Kirkwood, Zimm, and others for the fluid dynamics and diffusion in dilute solutions, but many new results are obtained as well. Chapter 18 is fertile ground for further developments and applications.

In Chaps. 19 and 20, which deal with polymer melts, we are in a rapidly developing and far-from-complete subject. We feel that our presentation of "network theories" in Chap. 20 has elements of novelty, particularly in pointing out similarities to and differences from the elastic dumbbell theory; we have summarized the famous models of Lodge, Phan Thien and Tanner, Acierno et al., Wagner, and others, and have carefully listed the many assumptions that are inherent in these theories. Chapter 19 deals with the "single-chain-in-a-mean-field theories." We have emphasized the Curtiss-Bird (CB) theory, because it is a direct descendant of the general theory of Chap. 17, following in the theoretical physics tradition established by Kramers and Kirkwood. As in Chaps. 18 and 20, we have highlighted the three main assumptions in the development, so that later researchers can remove or improve on them: 1) an anisotropic Stokes law, containing three empirical constants, for the hydrodynamic force; 2) an assumption describing anisotropic Brownian motion; and 3) a mild-curvature approximation.

We have not discussed in any detail the Doi-Edwards (DE) development inasmuch as there are still many questions which we do not feel competent to answer:

1) Are the "tubes" and "sliplinks" essential to the theory? Do they move affinely?

2) Does the polymer chain exchange momentum and energy with the tubes and sliplinks, and if so, how?

3) How does the friction coefficient enter the theory, and what kind of modified Stokes law is implied in their model (none is explicitly stated and no physical mechanism is offered)?

4) Are the "Maxwell demons" really needed in obtaining the stress tensor expression, and is it physically defensible to use these Maxwell demons to require that the tension in the polymer chains be identical to the chain tension at equilibrium regardless of the flow field?

5) The formula "from rubber elasticity" is used for the stress tensor expression. But, is this really appropriate for reptating chains with loose ends?

6) Have the same physical assumptions been made and has the same molecular model been used in the two main parts of the kinetic theory—that is, in the stress tensor expression and in the equation for the configurational distribution function?

7) What is the physical justification for the DE treatment of polydisperse systems?

Doi and Edwards have published no comparisons between their theory and experimental rheological properties; we have made extensive comparisons for both CB and DE and found that the DE theory gives unrealistic results for viscosity, normal stresses, elongational viscosity, molecular weight dependence of the study shear compliance, and rod climbing. Attempted refinements of the DE theory have led to some improvements in the comparisons with experiment, but the seven questions above still remain unanswered in the modified theories.

Professor Marrucci's criticism of our Eq. 19.2-5 is not pertinent inasmuch as there is no stated equivalent of Eq. 19.2-5 in the DE theory. In this equation, we are forced to introduce an assumption because of lack of knowledge about the momentum distribution function. This assumption is our way of introducing anisotropic Brownian motion. It is perhaps unfortunate that we associated the word "reptation" with this equation; it seems to us, however, that our assumption is related to the DE restriction of the fluctuating motion of the chain to within a tube (actually they restrict the motion to be one-dimensional, as on a wire).

We want to emphasize that the DE and CB theories are totally different as to viewpoint and structure. The CB theory is a part of a larger formal development, in which systematic reductions are performed from the full-phase space to lower-order spaces. It is made clear where, how, and why various assumptions are introduced. The DE theory, on the other hand, is a development specifically designed for polymer melts, not clearly related to the theories for polymer solutions. It is a semiintuitive development, with lots of pictures of polymer molecules wiggling in "tubes" and through "sliplinks," which seems to have a great deal of appeal to some polymer chemists. Their theory is a collage of ideas taken from the theory of stochastic processes, rubber elasticity, and scaling theory; it apparently contains inconsistencies that we have not been able to resolve. Because of the differences between the DE and CB developments as to philosophy and structure, they should not be considered as "competing" theories. We want to make it clear, however, that we have great respect for the trail-blazing publications of Doi and Edwards and that we admire very much some of the excellent physical intuition and mathematical work in their papers, particularly their solution of the differential equation for the single-link distribution function.

R. B. Bird
C. F. Curtiss
R. C. Armstrong
O. Hassager

Further Comments by G. Marrucci:

As the authors say, the Doi-Edwards and Curtiss-Bird theories are totally different as to viewpoint and structure. That the CB theory is a part of a larger formal development, i.e., of the full phase-space theory, is more apparent than real, however. In fact, the CB theory is but a single-chain theory where a very strange mean-field is used: one which takes the Brownian motion of the chain beads to be anisotropic at equilibrium! No such inconsistency is found in the DE theory.

On the other hand, are there different inconsistencies, perhaps more serious ones, in the DE theory? By using the rhetorical form of questions, the authors imply that there are many. I hold an opposite view (irrelevant as this may be), but of course this is not the place to go into a long and perhaps fruitless discussion. One point requires further comment, however.

When the authors mention having compared both CB and DE predictions against experiments and having found that the DE theory gives unrealistic results for several rheological quantities, they appear to overlook an aspect which is certainly relevant to the comparison, i.e., the number of adjustable parameters that the theory incorporates. It is true that the DE theory, especially in its original formulation, does not always compare favorably with experiments, but various refinements and/or extensions have improved on this (as the authors acknowledge) without adding to the number of unknown parameters, but rather by accounting for physical effects which had been initially left out. Unfortunately, the book does not adequately portray the continuing, and fruitful, effort towards understanding the complex behavior of dense polymeric systems, originating from the fundamental work of Doi and Edwards on both flexible and rigid rod-like polymers: a process which is still very lively today. Conversely, the book emphasizes a general phase-space theory, the fruits of which are yet to be seen.

Effective Writing for Engineers, Managers, Scientists

By H. J. Tichy with Sylvia Fourdrinier, 2nd Ed., John Wiley & Sons, 1988.

A second edition of Tichy on *Effective Writing*, thoroughly revised, augmented, and updated is welcome indeed. It is probably the most complete and readable