

tion to model flow numerically in megascopic systems, including the multiple porosity situation that occurs in fractured systems. The author does not refer to this literature. He revisits percolation theory and fractal concepts continually.

The strength of this book is the inclusion of fractures—it is done very well. Its shortcoming, however, is a lack of discussion of experimental and field data, which are used only to compare with various models but not as information.

The first five chapters introduce concepts used throughout the remainder of the book, such as heterogeneity and length scales, Darcy's law, the use of fractals and percolation models, the diagenetic process, porosity, surface area, tortuosity and porosimetry.

Chapter 6 is a cursory discussion of models of porous media including the spatially periodic model, lattice models, and network models. The most interesting part is the review of pore surface roughness. Chapter 7 on the multiporosity models for fractures and fractured rock describes nicely network models for fractures in one, two and three dimensions. Chapter 8 presents a volume-averaged "derivation" of Darcy's law. This, however, is not a derivation; it simply shows that Darcy's law is consistent with the Stokes equation. Volume averaging depends on the porous media being spatially periodic. Natural porous media are aperiodic.

The discussion in Chapter 9 on dispersion in porous media is classic and includes percolation methods. The author points out that in megascopic systems the normal or classical techniques do not work. Evidence is clear that most natural systems are not spatially periodic or at least the length scales are so large that the period is not stationary. Chapter 10 on flow and dispersion in fractures is excellent. Chapter 11 on a cursory view of miscible displacement discusses Hele-Shaw models in length. Although this model is a two-dimensional analog of flow in porous media and provides some visual results that might occur in porous media, it does not offer a three-dimensional picture and may be misleading.

Chapter 12 discusses stability and contact angles and their measurement in immiscible systems. There is a discussion of how fractals describe this particular problem. The displacement of blobs and trapping is described well. Chapter 13 is interesting because it discusses flow and transport in unconsolidated porous media. Most authors have not made the distinction between con-

solidated and unconsolidated media as succinctly. Chapter 14 shows various ways of numerically modeling flow in porous media. Discussion of automata approaches in this chapter is merely a short literature review rather than an explanation.

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### **Conformational Theory of Large Molecules: The Rotational Isomeric State Model in Macromolecular Systems**

By Wayne L. Mattice and Ulrich W. Suter, Wiley, New York, 1994, 449 pp. \$54.95.

This book endeavors to bring up-to-date the large body of work which has grown up around the well-established rotational isomeric state (RIS) model of macromolecules. At first glance, it might seem passé in today's world of molecular simulation for handling complex and descriptive models to revitalize a model at the root of which is the fundamental approximation of discretizing the continuum of molecular conformational space into a finite (and for all practical purposes small) fraction of isolated states. As the authors correctly point out, however, the RIS model distinguishes itself as one that strikes a delicate balance between retention of chemical-level detail and a computationally tractable theoretical analysis for which the more complex molecular models have no parallel. The idea of the isomeric state model for molecular conformations is not new, dating back to Volkenstein's work in the 1950s, but the techniques that may be applied to it to extract important properties of polymers are powerful, and both the underlying statistical mechanical fundamentals of RIS theory and the application of these techniques have continued to improve since the publication 25 years ago of Paul Flory's classic text, *Statistical Mechanics of Chain Molecules*.

This book of 400+ pages attempts to serve the several goals of providing a self-instruction text for the novice as well as a reference text for the expert of generalizing the matrix formalism for rendering the model useful in macromolecular systems of almost arbitrary complexity and for a wide range of properties, and of providing a near-comprehensive compendium of works where the RIS model has found appli-

cation to date. Clearly, it will have special appeal to those working with the physical chemistry of polymers, but the speed and ease of use of the methods described in this book should prove useful as well to other chemical engineers in product or process design and engineering who are willing to make the initial investment in model construction.

The book with 15 chapters is divided into four parts. The first two chapters present introductory material to put the RIS model in perspective relative to the panoply of models common in polymer science and experimental observables frequently addressed by RIS methods. The next four chapters follow a pedagogical development of the RIS model and the matrix techniques for computing the partition function and some basic geometric properties of simple chains. The third section, the largest portion of the book, details the important, and somewhat advanced, features of the matrix methods which allow for treatment of complex molecular architectures, ranging from treatment of tacticity and comonomers in polymers chains to dealing with stars, grafts, and other articulated structures. Interspersed within this section are a description of a hybrid technique which samples the conformation space of the RIS model to access quantities that do not lend themselves to the more direct matrix multiplication approach, and a treatment of helix-coil and sheet-coil transitions which is similar in form to the RIS model and avails itself of the same methods of analysis. The final three chapters demonstrate the utility of the RIS matrix formalism to treat other conformation-dependent properties, including tensorial quantities, approximate incorporation of excluded volume interactions, stereochemical equilibria, and time-dependent behavior. Each chapter concludes with something on the order of ten self-test problems to check comprehension; solutions to 72% of these are provided at the end of the book. A sample program is also provided.

Anyone familiar with the Flory's classic text will appreciate both the similarities and differences between the 1969 original and this update. In good Flory tradition, the authors have embedded in footnotes much useful and sometimes essential information regarding notations, conventions, and derivations in each chapter. Along the way, they take the time to point out and clarify some of the conflicting or confusing nomenclature which has arisen over the years in polymer statistical mechanics due to

influences from different fields of science. Their efforts toward explanation and generalization of the matrix formalism reflect important insights and contributions which appeared subsequent to the 1969 publication of Flory's text. The practicing engineer and researcher alike will appreciate the large number of references to RIS studies of organic and inorganic polymers to date. For the casual user, the ready access to references that provide definitions of the necessary RIS matrices for a particular polymer of interest circumvents one of the most often-encountered hurdles to application of the method. Nevertheless, the treatment of topics in the later chapters becomes noticeably terse, with markedly little explanatory material. For example, one of the more stimulating areas of recent development in RIS theory, so-called dynamic RIS, the application to time-dependent behavior, is summarized, in a section of only six pages. For a fuller explanation, the interested student must resort back to the literature, or else await the next update, perhaps in 25 years. In the meantime, this book represents the definitive text on RIS theory and application in polymer science and engineering.

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## Polymers and Neutron Scattering

By Julia S. Higgins and Henri C. Benoit, Oxford University Press, Oxford, England, 1994, 436 pp., \$98.00.

In his classical book titled *Principles of Polymer Chemistry* (Cornell Press, 1953), Paul Flory made his case, largely based on intuitive logic, for the existence of the unperturbed random coil as the configurational state of a macromolecule in undiluted amorphous polymeric materials. Periodically, experimental observations would arise to challenge Flory's views, but the often heated debates were largely inconclusive. Flory, never doubting the correctness of his views, despaired only of the apparently impossible task of constructing the appropriate experiment to prove himself right. In his second book, *Statistical Mechanics of Chain Molecules* (Interscience, 1969), Flory wrote: "Thus, in the bulk amorphous state perturbations

of the configuration may be predicted to vanish. These assertions follow from considerations of a theoretical nature which are at once simple and virtually incontrovertible. They are not readily susceptible to experimental verification, however, owing to difficulties attending determination of molecular dimensions at high concentrations."

Within a few years of Flory's writing of this passage, European-based teams of polymer scientists began to exploit a then-unique experimental resource, the high flux cold neutron beam at the Institut Laue-Langevin in Grenoble, France. In the early 1970s, these groups began publishing the results of their small angle neutron scattering (SANS) studies, which proved beyond doubt that Flory's vision of macromolecules in the bulk amorphous state was entirely correct. Deuterium-labeled polymer chains embedded in a sea of otherwise identical proteopolymer chains provided the essential ingredients for the previously unattainable experimental requirements: sufficient contrast for scattering and essentially no thermodynamic mismatch between the labeled and unlabeled chains.

This "golden ring" of polymer research was thus snared by the Europeans. The U.S. polymer community scrambled to catch up, finding interesting problems to solve in the area of complex ordered polymer and copolymer systems and by examining in more detail the "zero interaction" hypothesis of the early deuterium labeling studies.

Twenty years later, we find an adequate supply of state-of-the-art neutron scattering facilities in the U.S. and abroad. Teams of polymer scientists and engineers from academia and industry now use neutron scattering almost routinely as one of their characterization tools, in both basic scientific inquiry and in problem-driven R&D activities. This apparently tranquil, productive state of affairs, however, has produced another problem. Molecular-based engineers and scientists who desire to add SANS experiments to their repertoire have been largely required to learn the basics of the technique by word of mouth (from a handful of practitioners attached to neutron scattering facilities) or via a laborious, nomenclature-nightmarish plowing through the literature. A basic and thorough textbook on the subject has been greatly needed.

Once again, it is the Europeans to the rescue. Julia Higgins of the Department of Chemical Engineering at Imperial College, London, and Henri Benoit,

Université Louis Pasteur, Strasbourg (leader of one of the early SANS teams of the 1970s) have collaborated to produce the very text we have been waiting for. In *Polymers and Neutron Scattering*, these authors succeed completely in their stated goal to "provide an introductory work which will help the newcomer both to find his or her feet among the experimental techniques and to penetrate the complexities of the theoretical formulae needed to interpret the results." After a brief, but skillfully-crafted Introduction, there are two chapters on hardware, neutron sources and spectrometers, and one on scattering theory. These three chapters provide just the right amount of background for the nonspecialist to approach SANS experiments intelligently. The chapter on deuterium labeling (and the Appendix that beautifully clarifies the interrelations between contrast factors for various types of scattering experiments) will be heavily used by researchers in the preparation of the actual polymer samples for SANS experiments; it becomes immediately clear why the capability to synthesize specially designed and labeled macromolecules is so central to success in the field of polymer SANS. Methods of SANS data interpretation and a carefully distilled compilation of experimental results from the vast SANS literature comprise another three chapters. The text ends with one chapter on neutron scattering experiments designed to probe polymer chain dynamics and the other on neutron reflection experiments used for studying polymer surfaces and interfaces.

These ten chapters result in a concise 400-page text in which there are few if any wasted words, figures or equations. The nomenclature is clear and consistent throughout. There is ample guidance to the reader toward the primary literature for more depth and detail. In sum, the authors have written the perfectly-timed book, aiming at just the right audience—the large community of problem- or product-driven, molecular-based engineers and scientists who are neither specialists in nor practitioners of scattering physics. As neutron scattering experiments continue to become an integral component of the pursuit of new and otherwise unattainable information, members of this community will find this book to be essential reading.

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