ChE **book review**

STATISTICAL MECHANICS OF CHAIN MOLECULES

Paul J. Flory
Oxford University Press, 200 Madison Ave., New York, NY 10016; $49.95 (1989)

Reviewed by
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The late Paul J. Flory's book, *Statistical Mechanics of Chain Molecules,* was first published in 1969 by John Wiley and Sons. This edition, published by Carl Hanser Verlag and distributed in the U.S. by Oxford University Press, is a reprint of the 1969 volume with corrections and additional remarks by Flory.

Flory was a remarkable scientist whose career included industrial research and development (DuPont, 1934-37; Exxon, 1940-43; and Goodyear, 1943-48) and distinguished academic teaching and research (University of Cincinnati, 1937-40; Cornell University , 1948-57; Mellon Institute, 1957-61; and Stanford University from 1961). By the time of his death in 1985, he had received a number of prestigious awards, including the 1974 Nobel Prize in Chemistry, and many honorary degrees.

Flory devoted his scientific career to the elucidation of the physical principles underlying the conformational and thermodynamic properties of polymers in solution. The theoretical framework was provided by statistical mechanics. The systems were characterized experimentally through techniques such as light scattering, neutron scattering, and thermophysical property measurements. *Statistical Mechanics of Chain Molecules* brings together into one coherent work the many contributions made by Flory, his co-workers, and other researchers into developing a statistical mechanical description of the conformational properties of chain molecules. The approach is to focus on the statistical mechanics of single chains so that the solvent is regarded as a continuum.

In the preface, Flory states that one of his goals in writing the book was to provide full details of mathematical derivations in order to make the book as self-contained as possible. In consequence, the layout of the book is quite methodical.

Chapter I introduces the concepts of spatial distributions of chain molecules, mean square end-to-end distance $\langle r^2 \rangle$ and mean square radius of gyration $\langle s^2 \rangle$. Some simple models for polymer chains—the freely jointed chain (a random flight with fixed bond lengths, random bond angles, and free rotation around bonds) and the freely rotating chain (with fixed bond lengths, fixed bond angles, and free rotation around bonds)—are introduced.

In Chapter II, the term random coil is introduced to define an isolated chain molecule which, due to the absence of constraints, is free to take up any of the vast number of configurations allowed by rotations about bonds between neighboring units in the moelcule. Some of the experimental techniques used to determine $\langle r^2 \rangle$, $\langle s^2 \rangle$, and $d \ln \langle r^2 \rangle / dT$ where T is temperature, such as intrinsic viscosity, hydrodynamical measurements (sedimentation velocity and diffusion coefficient), and light scattering, are described and representative measurements reported for a large class of polymer repeat units.

Chapters III and IV describe the principal mathematical techniques used to compute the partition functions of chain molecules with realistic bond potentials and steric, disperion, and multipolar interactions between atoms in the polymer. The key simplification is the adoption of the rotational isomeric state approximation which assumes that, once the conformational energy has been computed to determine the rotational potential, the minima in the potential are taken as the only possible conformations of the bond. Thus, each bond is treated as occurring in one or another of several discrete rotational states. The rotational isomeric state approximation allows the partition function for the molecule to be treated as a summation over a finite number of states. The summation can be represented succinctly as matrix products once the statistical weight matrix U is known. The element U_{ij} essentially gives the probability that a bond in rotational state i will be followed in the chain by a bond in rotational state j. The elements of U can therefore be obtained from torsional and intramolecular potentials. All the properties of interest—such as moments of the spatial distribution including the dielectric constant—can then be obtained from the partition function by matrix manipulation of products (including direct products) of the statistical weight matrices.

Chapters V, VI, and VII then implement the rotational isomeric state model to compute the conformational properties of, respectively, symmetric chains (n-alkanes, polyethylene, and other polymers whose repeat unit does not contain a symmetry-breaking

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sidechain), asymmetric vinyl chains (chains whose repeat unit does contain a sidechain), and polypeptides and proteins. For each repeat unit studied, the statistical weight matrix is derived from physical considerations and direct computation of the conformational energies. Relevant moment properties are then computed and compared with experiment.

Chapter VIII contains a more detailed statistical mechanical analysis of the freely jointed and other model chains, and Chapter IX describes the theoretical background required to relate optical properties and radiation scattering measurements to moments of the spatial distribution.

In summary, this text contains a very complete description of the application of the rotational isomeric state model. The mathematical manipulations in Chapter I-III were found to be quite straightforward and followed easily from material contained within the text. Derivations in later chapters are not as transparent; however, references to the original papers are very complete. The physical and chemical arguments used to derive statistical weight matrices are very informative in understanding conformational properties of polymers. Thus, in general Flory does achieve his goal of a self-contained treatise. He has written a clear, complete overview of the statistical mechanics and physical basis of conformations in isolated chain molecules in solution. For researchers interested in this subject area, this book is excellent.

However, the book may prove to be too specialized to attract much attention from the general chemical engineering audience. For example, the interest of chemical engineers is often in the bulk thermodynamic properties of polymer solutions and/or their rheological properties; this book does not touch on either of the subjects (except obliquely by, for example, describing methods for calculating the mean square radius of gyration which can be related to hydrodynamic radius).

It is therefore unlikely that the book could be used as the text for an undergraduate or graduate course in chemical engineering. Since the book was written as a research monograph, it does not lend itself to use as a textbook—for example, there are no exercises or assignable problem sets. Faculty who are teaching courses in applied statistical mechanics courses may find it useful in preparing several lectures on the rotational isomeric state model and its application to real polymer chains. This would certainly serve as an extension of the material on the statistical thermodynamics of polymers found in typical statistical mechanical textbooks, such as D.A. McQuarries' *Statistical Thermodynamics*.

In summary, the text is recommended to researchers interested in the physical basis and mathematical description of polymer conformations, and some of the material in Chapters I, II, III, and V might be suitable as part of an upper-level graduate course in statistical mechanics. ❐

ChE books received

Cooling Technology for Electronic Equipment, by Win Aung; Hemisphere Publishing Co., 79 Madison Ave., New York, NY 10016-7892; 838 pages, $125 (1988)

Transport Properties of Fluids: Thermal Conductivity, Viscosity, and Diffusion Coefficient, by Kestin and Wakeham; Hemisphere Publishing Corp., 79 Madison Ave., New York, NY 10016-7892; 344 pages, $98 (1988)

Properties of Inorganic and Organic Fluids, by Liley, Makita, and Tanaka; Hemisphere Publishing Corp., 79 Madison Ave., New York, NY 10016-7892; 309 pages, $80, (1988)

Specific Heat of Solids, by Cezairliyan; Hemisphere Publishing Corp., 79 Madison Ave., New York, NY 10016-7892; 484 pages, $98 (1988)

Flexible Manufacturing Systems in Practice, by Roger Bonetto; Hemisphere Publishing Corp., 79 Madison Ave., New York, NY 10016-7892; 208 pages, $37 (1988)

Standard Methods of Hydraulic Design for Power Boilers, by Lokshin, Peterson, and Schwarz: Hemisphere Publishing Corp., 79 Madison Ave., New York, NY 10016; 345 pages, $52.50 (1988)

Encyclopedia of Engineering Materials: Part A, Polymer Science and Technology, edited by N. P. Cheremisinoff (Vol. 1 of 3); Marcel Dekker, Inc., 270 Madison Ave., New York, NY 10016; 783 pages, $185 (or $157.25 each for all 3), (1988)

Natural Rubbers Science and Technology, edited by A. D. Roberts; Oxford Science Publications, 200 Madison Ave., New York, NY 10016; 1136 pages, $150 (1988)

Adsorption and Ion Exchange: Fundamental and Applications, edited by LeVan, Knaebel, Sircar, and Wankat; AIChE, 345 East 47th St., New York, NY 10017; $18 members, $35 non-members (1988)

Resource Recovery of Municipal Solid Wastes, Peter J. Knox, Editor; AIChE, 345 East 47th St., New York, NY 10017; $23 members, $45 others (1988)