Book Reviews

Scaling Concepts in Polymer Physics

Pierre-Gilles de Gennes

Cornell University Press, Ithaca and London, 1980

This book by a theoretical physicist of many interests has been awaited with great interest, is being well-received by theoretical physicists interested in scaling theories. It presents an up-to-date summary of recipes not previously collected together. Scaling theory tries to harness for polymer science the experience accumulated in phase transition theory outside the polymer field, and De Gennes has set himself the task of bridging the communication gap which he rightly discerns. In particular, 'a new theoretical language (heavily loaded with field theoretical concepts) has appeared but has remained essentially unintelligible to most polymer scientists.' He hopes that experimentalists in polymer science may wish to incorporate the recent advances into their mode of thinking.

The basic method comes, as in other branches of physics, from the approach to Lagrangian field theory by renormalization-group methods. Although the existence of solutions of the forms postulated in this method is generally not proved, the resultant term-by-term treatment of heuristic perturbation series has had considerable success in quantum electrodynamics. These successes led Kallen at the end of his book (Quantum Electrodynamics, Springer, 1972) to the hope that 'the present formalism might be the limit of some future more complete theory and that study of the present theory will be rewarding. One can hardly say the same thing about meson theories in their present form!' They wary experimentalist in a third areas, polymer science, faced with a similar decision, whether study of the present scaling formalisms is rewarding, is likely to assess first their claims to fit experimental data. Here, the book under review is, in several instances, open to the criticism of straining literature data almost to tensile failure. Examples require detailed discussion, so that one must suffice.

In a table (p 185) the exponent z, relating relaxation time to coil size, has been calculated using results from five different measurement techniques in four published papers. The high consistency of these five z-values (2.84, with standard deviation of 0.05) will surprise experimentalists. Reference to one of the original papers, that by Massa, Schrag and Ferry, who are credited with data ('other mechanical data') from which the value $z = 2.78$ is calculated, seems to reveal actually only three data points suitable for testing an exponent plot. (These relate to samples of molecular weights 19.8, 82, and 267×10^3, for which the authors list viscosity increments in the same solvent under comparable conditions). *Assuming* that these molecular weights, are high enough to allow comparison with the asymptotic scaling model for infinite chain length, one may reluctantly proceed with a linear regression to the exponent plot for a mere three points. I calculate the resulting exponent to be $z = 3.00$, with regression coefficient $r^2 = 0.993$. While this is wide of the value in de Gennes' table, it is ironically the 'correct' value for the crude asymptotic scaling theory.

Several results in de Gennes' book depend, as does the example just given, on a sound theory relating coil size to molecular weight in good solvents. Scaling theory expresses this relation asymptotically through an exponent ν, which varies in that theory only over a range of about 0.1 when passing from precipitants to good solvents. He seems to imply that this value could be measured to about ± 0.01. This is hardly a view supported by experimentalists, or all theoreticians for that matter. The reader is referred, on this score, to a report (*Macromolecules*, 1978, **11**, 506) by an eminent team at Kyoto. These authors also cite computer results which – in agreement with their own highly accurate light scattering and viscosity measurements – might suggest that there is no difference in the true asymptotic exponent in very good and very bad solvents. Probably scaling theory can be refined to digest this result if indeed it is so. Physical theory has its own dynamics, and evolves best in constant contact with the labours of the experimentalist. De Gennes' enthusiasm for improving such contacts is, of course, highly commendable, but to overplay the finality with which the data support what is still very much an evolving theory, will harm his purpose. This reservation being noted, *Scaling Concepts in Polymer Physics*, is the first survey of its kind, and its value to theoretical physicists familiar with the field is probably substantial.

M. Gordon

Structure of Crystalline Polymers

Hiroyuki Tadokoro

John Wiley & Sons, New York 1979: Price £21.35

The ubiquity of polymeric substances is unquestionable: they encompass and dominate vast territories in both natural and synthetic material. The enormous diversity of properties exhibited by polymers emanates from the variety of chemically distinct monomeric units, the ways in which these units are linked together and the particular sequence in which they are juxtapositioned; all of which control the three-dimensional shape of the macromolecule. Polymers with very complex chemical constitutions, such as the long non-repeating sequences of amino acids, typical of the enzymes trace out highly convoluted pathways resulting in a condensed globule. The chemically simpler homopolymers consisting of a single repeating monomeric species, such as polyethylene, cellulose, nylon etc., form, in general, extended helical conformations. Professor Tadokoro's book is in the main concerned with this latter class of polymers: the fibrous polymers, and the bulk of the examples chosen for discussion are the synthetically produced polymers so important in modern materials science. In this respect the title of the book is not as all embracing as it would suggest.

Fibres are composed of very many long, slender crystallites or micelles. Usually, but not always, there is not correlation between the azimuthal orientation of individual micelles about their long axis and so the diffraction signals recorded are similar to those expected from a single crystal rotation photograph. A unique feature of Professor Tadokoro's book is the welding together of X-ray diffraction investigations and their results and interpretation with the corresponding results from infra-red and Raman spectroscopy of fibrous polymers.

The first part of the book provides an introduction to polymer structure, configuration and conformation. When discussing symmetry there are two types of notation: the Schoenflies and Hermann Mauguin which are used in spectroscopy and crystallography respectively, and in view of what is to follow both types of notation are introduced and explained. These introductory topics are refreshingly concise. The application of X-ray diffraction to fibrous polymers is discussed in detail. The author quickly gets to grips with the features associated with fibre diffraction and utilises examples from his own experience to illustrate and help explain the procedures and problems. Interestingly the use of the Weissenburg camera is covered in some detail and its ability to conveniently scan areas of reciprocal space not usually accessible in fibre diffraction is highlighted. There is a section on preparation and modification of samples, amply illustrated with X-ray diffraction patterns from the author's extensive collection. The process of structure elucidation is unravelled in a gentle manner which should be especially helpful to the beginner. The author first describes the procedure for tackling a straightforward case, utilising the background techniques introduced earlier, and then inserts additional topics as and when required to aid in the solution of a sequence of progressively more complex systems and situations. Real examples are used throughout and provide a stable scaffolding for the development of concepts and procedures in the structure determination of fibrous polymers.

S similar technique is used in the subsequent section on infra-red and Raman spectroscopy. The various methods of specimen preparation are discussed together with deuteration exchange and polarisation experiments. Factor group analysis and calculation of normal modes of vibration are covered in depth including many useful examples. A chapter outlining energy calculations is inserted before proceeding to an exceedingly useful section describing the structures of a variety of crystalline synthetic polymers. A long table (Table 7.1) provides a valuable summary of crystallographic data of some 140 or so polymers. It was pleasing to find that both the name and chemical formulae are provided for most of these substances. Polyethylene, the poly-α-olefins, vinyl and vinylidene polymers, polyethers, polyesters and polyamides are discussed in detail together with some related polymers.

This book is a valuable addition to the area of structure analysis of synthetic polymers. The dual nature of the methodology employed and their results are expounded by an expert in both techniques. This, together with the author's vast experience spanning a broad spectrum of synthetic polymers yields a unique book which will be warmly welcomed by students, fibre diffractionists and fibre spectroscopists alike.

Edward Atkins