RRKM and master equation approaches, or even a combination, depending on the application.

There are several subjects about which Pritchard holds unconventional views, and a strength of his book is the stimulating and clear way in which he presents these issues. An example is the importance of long-range interactions for intramolecular vibrational relaxation even in low-pressure systems. It is very useful to see a detailed exposition of what we can and cannot infer about intramolecular vibrational relaxation from completely thermal rate measurements, although many readers (and perhaps the author) will not be satisfied with the eventual invocation of a phenomenological "stirring" process. I also disagree with Pritchard's view, which is apparently still quite conventional, that tunneling contributions to chemical reactions are only rarely important. I would say they are probably important at room temperature whenever a reaction has an intrinsic barrier of more than a few kilocalories per mole and a significant hydrogenic component in the reaction coordinate. Pritchard seems too willing to accept a simple expression (his eq. 4.9) that makes the microcanonical rate constant vanish at a threshold equal to the high-pressure activation energy, especially since this is obtained by the notoriously ill-conditioned inversion of a thermal rate expression.

I hope many potential readers will not pass this book by because it doesn't include their most hallowed references reporting work that takes other approaches to unimolecular reactions. If they do, they will miss a clearly written, although idiosyncratic, account of a subject long overdue for a cohesive treatment in monograph form.

The master equation approach treats a rate process in terms of coupled kinetic equations for the time-dependent concentrations of molecules in individual quantum states. These coupled equations can always be solved by numerical integration and can sometimes be solved by eigenvalue-eigenvector methods or analytically. The associated numerical problems, once considered a serious impediment to the use of this approach, have been greatly ameliorated in the last few years by the general availability of convenient high-speed computers. For this reason, and because of very recent work extending the eigenvalue approach to non–first-order processes, I think we can expect a great increase in attention to master equation approaches in the coming years.

The two most widely cited books on the transition state approach to unimolecular reactions are by Robinson and Holbrook (*Unimolecular Reactions*, Wiley-Interscience, 1972) and Forst (*Theory of Unimolecular Reactions*, Academic Press, 1973). Despite their age both books are far from outmoded. It is a shame that Wiley let the former go out of print several years ago. The present book promises to be an instant classic, and I hope Cambridge University Press will keep it available for decades at least.

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The Liquid State

Theory of Molecular Fluids. Vol. 1, Fundamentals. C. G. GRAY and K. E. GUBBINS. Clarendon (Oxford University Press), New York, 1984. xiv, 626 pp., illus. $79. The International Series of Monographs on Chemistry, 9.

In the 1960's and '70's, methods of computer simulation joined with theory and experiment as invaluable tools in the study of the liquid state. With an attack on the subject on these three fronts, progress has been very rapid. The considerable advances up to the mid-1970's were put into context in the superb monograph *Theory of Simple Liquids* by Jean Pierre Hansen and Ian R. McDonald (Academic Press, 1976). But as that monograph went to press, developments beyond the realm of simple atomic fluids were already making incomplete the story it told. In particular, the ideas about packing effects, perturbation theory, and fluctuating forces, so useful in attaining an understanding of the structure and dynamics of simple liquids like argon, were beginning to be successfully applied to the more complex polyatomic molecular fluids. Until now, however, no monograph has appeared that describes the advances that have been made in our understanding of this aspect of the subject. Volume 1 of *Theory of Molecular Fluids* attempts to fill this gap. In an apparently tireless effort, the authors have compiled thousands of citations to the literature, with historical perspectives and pithy quotations from many of the classic papers in the field.

To judge the value of the book, it is helpful to consider the physical issues that distinguish molecular fluids from atomic noble-gas liquids. In particular, the constraints imposed by the chemical bonding of atoms in molecules introduce a variety of length scales incommensurate with the van der Waals distances characterizing intermolecular interactions. Further, the absence of spherical symmetry in molecules implies the presence of permanent electrostatic moments. These features can conspire to produce cooperative macroscopic phenomena such as dielectric effects and also phase transformations involving interesting changes in symmetries. Liquid crystallinity is one of a variety of examples. At the microscopic level, these features can produce short-ranged order or intermolecular liquid structure that is far more intricate than that encountered with simple fluids, the latter being characterized by only one length scale, the van der Waals diameter of an atom.

Ultimately, the precise description of these phenomena requires formulations of intermolecular potential models and methods for analyzing the spontaneous fluctuations as influenced or prescribed by the interactions. At present, there is no consensus concerning the best approach to this formulation, and the "best" way may be system-specific. One popular approach, however, is the one that provides the theme of Gray and Gubbins's book. It is based upon the semi-invariant analysis of intermolecular interactions and structure. At its simplest level, this approach expresses the deviations from spherical or radial symmetry in pair interactions and correlations in terms of expansions in spherical harmonic functions or the Wigner rotation functions. It is a particularly powerful perspective when dielectric effects driven by long-ranged dipolar interactions are under consideration. It is also very useful in the parameterization of thermodynamic perturbation theories for the equations of state of molecular liquids and liquid mixtures. Unfortunately, the semi-invariant approach has proven less satisfactory in treating the nature of short-ranged order (that is, the local relative arrangements of atoms) in fluids. The reason is rather obvious: molecules are composed of atoms bound together and forming highly nonspherical objects. Descriptions of local structures in dense materials must account for these shapes, and it is impossible to describe molecular shapes with a small number of terms in the multipole expansions of the semi-invariant analyses.

Theories in which molecules are treated as collections of atoms have been successfully formulated and applied to many systems. In addition to providing a framework for discussing local intermolecular structures, this atomistic approach to molecular fluids leads natural-

ly to descriptions of flexible species that may undergo conformational transitions and chemical rearrangements. It also seems to be the most fruitful way to think about assemblies in solution, including biopolymers, micelles, and bilayers. These interesting issues are, however, not addressed in the book. Its primary contribution is to present a detailed description of what is known about intermolecular potentials and a discussion of how to express this knowledge in terms of semi-invariants and how to perform reasonably accurate statistical-mechanical calculations, when appropriate, with semi-invariant methods. It is an exhaustive and welcome treatise that will serve as the standard source on this type of approach. Unfortunately, almost nothing is said in the book about methods of computer simulation, and only a cursory description of the atomistic formulations of molecular fluids is presented. In my opinion, it is these methods that will ultimately prove most useful in attacking problems at the new frontiers of liquid state science.

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Theoretical Physics

Theoretical Concepts in Physics. An Alternative View of Theoretical Reasoning in Physics for Final-Year Undergraduates. M. S. LONGAIR. Cambridge University Press, New York, 1984. xiv, 366 pp., illus. $49.50; paper, $14.95.

It is rare to find a course beyond the introductory level that places an entire field in perspective, so that the instructor may dwell on the subtleties and the power of the important concepts without having to worry about getting bogged down in providing the necessary technical background. M. S. Longair has had an opportunity to put together such a course, and the book under review is the happy by-product. Longair approaches the development of the theoretical concepts of physics by means of seven case studies. These are "The origins of Newton's law of gravitation," "Maxwell's equations," "Mechanics and dynamics," "Thermodynamics and statistical mechanics," "The origins of the concept of quanta," "Special relativity," and "General relativity and cosmology."

The methods of the original papers, albeit in modern notation, are used in the development of each subject. Longair departs from this procedure, however, in discussing relativity and cosmology, the subjects closest to his own specialty, astrophysics. Here he gives a concise, yet intellectually complete, introduction to each subject, using simple physical, rather than formal mathematical, arguments. At the end of most of the case studies there is an appendix in which either technical background material is provided or interesting applications of the concepts are set forth. Although occasionally containing some clever derivations, the appendixes are somewhat jarring in their interruption of the flow and style of the main narrative.

The author speaks directly to the reader in an informal manner as he traces the difficulties faced by Newton, Maxwell, Planck, Einstein, and others in their work. He occasionally uses the resolution of these difficulties as a basis for offering advice on how to approach problems in physics. He conveys a continuing sense of intellectual excitement and highlights what he considers to be remarkable and miraculous achievements.

Some amusing and little-known topics, such as Kepler's analysis of the orbits of the five innermost planets in terms of properties of the five regular solids and Maxwell's representation of a magnetic field in terms of rotating vortices, are discussed in the early chapters, but these are hard for a modern physicist or physics student to relate to. Of more current interest is the section on thermodynamics and statistical mechanics.

The centerpiece of the presentation, a story that the author obviously takes great delight in retelling, is the development of the early quantum theory by Planck and Einstein as arising from the failure of purely classical concepts to account for the properties of black-body radiation. The discussion here is very complete.

Although almost all of the material in the book can be found elsewhere, it is good to have such a diverse yet unified set of topics discussed in one place. The book will be useful not only in the type of course for which it was designed but also to bright younger students who would like to read up on the exciting parts of physics. It is unfortunate, but understandable, that, with the exception of the discussion of cosmology, Longair did not include problems that have been occupying physicists over the past 60 years. Perhaps he will write a sequel (or, more necessarily, several).

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