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Book Review: *Dynamics of Molecular Liquids*

Dynamics of Molecular Liquids. Walter G. Rothschild. Wiley-Interscience, New York, 1984, 415 pp.

This book is a timely presentation of the current status of the theories of rotational and vibrational dynamics in molecular liquids. The author has covered an enormously vast literature and has suceeded in presenting most of the diverse viewpoints in a coherent and clear fashion. The book is self-contained, so that one can go through it without constant referral to other texts. The theoretical presentations are rigorous and yet clear even for those who are not experts. A great virtue of this book is that the theoretical presentations are usually followed by discussions of specific experiments to which the theory is relevant, with an analysis of the data that brings out the important points to be stressed. The author has clearly gone out of his way in this respect, collecting published and unpublished data and calculations. This constant comparison of theories and experiments makes the content and utility of the former more persuasive, and makes clear the necessity of further work in this field. To paraphrase the author, the book should not leave the impression that this field is now well understood and that little further work need be done. On the contrary, the directions in which further work should proceed are clearly defined.

The book is unique in the material that it covers and in the point of view that it takes. The author's purpose is to place the current theories in proper perspective with respect to one another and with respect to certain types of experiments; it is also to help scientists become experts in this field. The author succeeds in both.

The book is divided into three chapters. The first deals with the general formulation of spectroscopic data in terms of appropriate correlation functions in the liquid. A discussion of correlation functions and fluctuation-dissipation relations is followed by a presentation of the kinds of correlation functions that are related to the different experimental techniques addressed in the book. The statistical mechanical/quantum mechanical background for these relations is considered. The second chapter deals with rotational relaxation and orientational motion. Here are covered in detail most of the models that have been constructed to deal

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with rotational motion, starting from the diffusion (Debye) and M- and J-extended diffusion models (Gordon) all the way through the most recent generalizations of these models. The author deals in great detail with all the variations of the models (e.g., effects of molecular shape, effects of environmental anisotropy, effects of rotational–vibrational coupling, etc.). At each stage appropriate experimental data are introduced to illustrate these effects, thereby persuading this reader of the relevance of each such modification. At the close of this long chapter the author makes clear that all of the extensive theory that has been developed concerns the rotational motion of *individual* molecules in a sea of others, and that a great deal of work remains to be done in the area of collective motions that surely occur in strongly interactive systems.

Chapter 3 deals with vibrational relaxation, both in two-level systems and in multilevel systems. Vibrational dephasing is considered in the slow, fast, and intermediate modulation regimes and even in a glassy environment, and once again ample experimental data are brought to bear to illustrate each regime. The effects of resonance vibrational transfer, of broadening by concentration fluctuations, and of couplings with other motions are considered. The theoretical background is amply discussed, and again the chapter ends with the author's reflections on future work in these areas.

Finally, we note the large number of extremely useful appendices that follow at the end of the book. In these appendices are collected a variety of useful reference topics, such as a discussion of cumulant averages, the interaction representation, spectral moments, etc. I find the separation of this basic material into clearly identified appendices extremely helpful.

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Book Review: *Statistical Physics II: Nonequilibrium Statistical Mechanics*

Statistical Physics II: Nonequilibrium Statistical Mechanics. R. Kubo, M. Toda, and N. Hashitsume. Springer-Verlag, New York, 1985, 279 pp.

This volume is a welcome addition to the textbooks in this field. It covers material that is either not covered or only cursorily covered in most statistical mechanics texts. The book is small (in number of pages) and can be either read or covered in a course in a reasonable amount of time. It contains an excellent selection of topics both modern and more traditional. The authors clearly distinguish phenomenological from rigorous treatments, but take the pragmatic viewpoint of seeing the utility in both. The material covered therefore includes an ample component of phenomenological material and an even more extensive portion on the rigorous connection of macroscopic descriptions to their microscopic bases. It is noteworthy and unusual that both classical and quantum systems are covered. The book is written in a clear and pedagogical fashion and is equally useful to students in physics and physical chemistry. A student who works through this volume, although not an expert in nonequilibrium statistical mechanics, should thereby gain a firm basis for more detailed studies in nonequilibrium statistical mechanics, and should be quite able to understand the current literature that uses the concepts covered in the text. I find myself using it as a useful reference to material that is standard and yet not always easy to find in a single place.

The book is divided into five chapters. The first two cover phenomenology, the last two cover the microscopic basis of nonequilibrium statistical mechanics, and Chapter 3 provides a link between the two approaches. Chapter 1 discusses Brownian motion and introduces the notions of stochastic processes, Gaussian processes, the Langevin equation, and the important ideas of fluctuation-dissipation theorems. These ideas are generalized in Chapter 2 to other physical processes, most notably to the problem of random frequency modulation. Here the concepts of Markovian processes, master equations, and Fokker–Planck equations are introduced, as is the derivation of these equations using projection

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operator techniques. The discussion of the Langevin equation, the master equation, and the Boltzmann equation within the same conceptual framework establishes the relation among them that is frequently elusive to the casual observer. Chapter 3 establishes the link between the phenomenological and microscopic approaches by defining the physical observables that are usually calculated. This chapter introduces the notion of the linear response of a system to external and internal forces and covers the main ideas of irreversibility, relaxation and absorption phenomena, response functions, mechanical and thermal forces, and dispersion relations. Chapter 4 turns to the microscopic (statistical mechanical) formulation of linear response theory and relates the response function of a system to its Hamiltonian. The chapter deals with correlation functions, fluctuation-dissipation relations, Kramers–Kronig relations, and Onsager's postulate on the regression of thermal fluctuations. Finally, Chapter 5 addresses the application of the methods of quantum field theory in statistical mechanics. Here the authors introduce retarded, advanced, causal, and temperature Green's functions, diagram techniques and other perturbation methods, the Dyson equation, one- and two-particle Green's functions, etc., and carefully link this material to that of Chapter 4.

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