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Book Review: *Molecular Diffusion and Spectra*

Molecular Diffusion and Spectra. William Coffey, Myron Evans, and Paolo Grigolini. John Wiley and Sons, New York, 1984, 378 pp.

With the development of linear response theory in the 1950s and 1960s, time correlation functions (TCFs) became standard tools for calculating thermal transport coefficients for fluids "near" equilibrium. The general relationship between dynamic responses (NMR, neutron, Rayleigh–Brillouin, ir–Raman, dielectric, fluoresence, microwave, sound...) and Fourier transforms of specific molecular TCFs was quickly appreciated and led to optimism that an improved understanding of molecular motions could result rather simply from analysis of individual line-shape widths and shifts. This hope for a synthesis of theory with the emerging molecular spectroscopies was premature. Experimental and physical complications soon became evident; phase, energy, and spin–spin relaxation processes; Fermi resonance and resonance energy transfer; vibration–rotation(Coriolis)–translation and internal mode coupling; chemical/structural heterogeneities and fluctuations; and size, shape, and local-field effects. In response to this somewhat discouraging situation, theoretical effort stepped back a bit from direct confrontation with experiment to focus on internal dynamics and relaxation of a molecule strongly interacting either with parts of itself or with the environment. Progress in this field (which has numerous applications in other areas of condensed matter physics) has been notable in recent years, often resulting from combined experimental, computational, and theoretical work. The present volume *Molecular Diffusion and Spectra* is an excellent and timely summary of part of this progress, with chief emphasis on the authors' own contributions. (An indication of the pace of research activity is that the present volume, published in 1984, is a sequel to *Molecular Dynamics*, which appeared in 1982, and will in turn be followed this year by a special edition of Advances in Chemical Physics, P. Grigolini and F. Marchesoni, *Memory Function Approach to Stochastic Problems in Condensed Matter*).

The first two chapters describe recent computer simulation results for dichloromethane, with a useful review of numerical discrepancies which exist between experimental, and experimental/computational evaluations of

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orientational correlation times. Experimental results highlighted include the zero to terahertz far infrared spectrum of normal and super-cooled dipolar liquids and nonlinear Kerr-effect experiments using megawatt laser fields. These experiments provide a specific rationale for the rest of the book which discusses model calculations and stochastic theories to describe inertial, cooperative, nonlinear and, non-Markovian dynamics for systems of one or a few degrees of freedom. Though the theoretical techniques are applicable to a wide variety of problems, dipole reorientation is the simplest liquid motion which may be significantly altered by external means, and therefore provides a convenient starting point for more general dynamical theories.

Chapters 3 and 4 review solvable dielectric relaxation models which include dipole interaction and inertial effects but which lead to linear equations of motion. Chapter 5 introduces rotational Brownian motion, with inertia and periodic or nonlinear potentials, the primary subject of rest of the book. The mathematical techniques for analyzing Kramers equation are presented with sufficient detail and references to the literature to accommodate the nonexpert.

The last chapters present and apply the "reduced model theory" (RMT) which offers a physically attractive and potentially systematic approach to evaluating the effects of many-body "heat baths" in interaction with molecular coordinates of interest. Multiplicative and non-white-noise effects are generated through deterministic coupling with virtual variables. The virtual variables are subject to Markovian white noise. The resulting system is simplified and solved using nowfamiliar projection operator methods and continued-fraction expansions of the TCF. The intuitive flavor of the Langevin-equation methods is retained, with an ability to systematically refine the model subject to analytical constraints, such as might be available for long or short time.

The writing style is a bit uneven, owing to the separate author contributions, and exposition is shorted in places in favor of lengthy mathematical development. On the whole though, this is a useful (sometimes difficult) update for the reader who wonders what new results have been found for the Kramers problem, and who wants a preview of how these results might be applied to real liquids.

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