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Book Review: *Rotational Brownian Motion and Dielectric Theory*

Rotational Brownian Motion and Dielectric Theory. James McConnell, Academic Press, N.Y., 1980 (300 pp., $56.50).

This book presents a detailed account of the theory of rotational relaxation of a polar molecule in a nonpolar solvent. The Debye theory, appropriate to noninertial reorientation of a vector located in a spherical molecule, leads to exponential decay of the orientation correlation function with time constant inversely proportional to the rotational diffusion constant. If inertial effects are included, the short-time behavior (high frequency) is modified and this feature shows up in deviations from semicircular shape of Cole–Cole plots.

Before actually calculating correlation functions a long excursion is embarked on into probability theory of Gaussian Markov processes, the Wiener process, the Ornstein–Uhlenbeck process, and stochastic differential equations of these processes. Averaging methods of solutions of stochastic differential equations are discussed as well as the equivalent partial differential equations such as the Fokker–Planck equation. Rigid-body rotations are also covered. The topics are treated at an elementary level and should be accessible to chemists and physicists.

With these tools the Euler–Langevin equations corresponding to rigid-body rotation driven by white noise with frictional dissipation are then approximately solved for angular and orientational time correlation functions for various rigid-body symmetries.

The framework is of stochastic process theory, where a model of the molecule motion is assumed, as opposed to a statistical mechanical theory where one starts with a Liouville equation. Because it focuses on such a special problem, much of the unification of linear response theory as applied to the variety of probes of rotational motion is not evident. This is unfortunate since it limits the scope of the work. For such a detailed

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exposition as is given here, one would also have liked a more extensive comparison with the wealth of dielectric relaxation data available.

I would recommend this book for those with a critical involvement in dielectric relaxation theory and for those who wish to apply this approach to other rotational relaxation problems. It is too specialized, though, for a text in relaxation phenomena but should be in library collections.

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