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Book Review

Chemical Dynamics in Condensed Phases. Abraham Nitzan, Oxford University Press, New York, 2006.

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This is an excellent book which is intended to be a text for a graduate course in condensed matter chemistry and physics. It is extremely well written from the pedagogic and literary points of view. I particularly enjoyed the extremely pertinent quotations from Lucretius at the beginning of each chapter.

The book contains three parts. The first is a more or less standard presentation of the fundamentals of classical and quantum mechanics, statistical mechanics, electrodynamics, and properties of solids and liquids. This part is well done, but there are a few points which need some comment.

There is no distinction between quasistatic and reversible processes. It is not emphasized that all ensembles—whether microcanonical, canonical, or grand canonical—consist of collections of isolated systems. On pp. 29, 177, and 178 recourse is taken to the ergodic theorem in order to make connections between time averages and ensemble averages. The simple relationship of equality between these two averages is true for isolated systems and the microcanonical ensemble. It has to be modified for closed and open systems.

The section on reduced distribution functions in the chapter on liquids is well done but states that the pair distribution function factorizes into single distribution functions when the separation between the particles is large. This is true only in the grand canonical ensemble and not in the canonical and microcanonical ensembles.

The second part of the book covers methodologies useful in discussing time dependent phenomena in equilibrium and nonequilibrium systems. It contains chapters on time correlation functions, stochastic processes and equations of motion, quantum relaxation processes, the quantum mechanical density operator, linear response theory and the spin-boson model. This part is very well done. It could be (and has been) used as a text of a graduate course in nonequilibrium statistical mechanics. This part is my favorite portion of the book.

There are a few negative comments to be made despite the excellence of the presentation. There is a clumsy notation for correlation functions on p. 185. There is a mention of instantaneous normal moles on p. 197, and it would have been nice to have a more extended discussion. Some of this occurs on p. 216. Again, on pp. 201 and 222, there is a misuse of the ergodic theorem for nonisolated systems. There is a statement on p. 204 that correlation functions are analytical functions of time. This neglects the phenomena of long-time tails, which lead to nonanalytic functions.

In the discussion of the Langevin equation in Chapter 8, it is stated that the stochastic process is Markovian. This is certainly true for the linear equation, but is it true for nonlinear equations? A discussion of this point would have been helpful. Similarly, the physics behind the Fokker-Planck equation needs more explication. In particular, why do things break down when expansions are carried out beyond quadratic terms?

In Chapters 9 and 10, there is a reasonable discussion of the origin of irreversibility but no discussion of the difficulties that may arise in the derivation of quantum mechanical master equations and the initial properties of the overall density matrix.

The chapter on linear response theory is well done, but it should be emphasized that whereas averages of dynamical quantities and reduced distribution functions can be obtained, N particle functions never approach an equilibrium form once they have been perturbed.

The introductions to the chapters in this part contain good pedagogic discussions of the physical bases for the validity of the techniques described.

The third part of the book focuses on a selection of important dynamical processes in condensed phase systems. These include vibrational relaxation, chemical reactions, solvation dynamics, electron transfer in bulk and interfacial systems, and spectroscopy. The presentations cover experimental and theoretical developments up to the last decade. Since the author is a specialist in these fields, I will not make many substantial comments except to say that the chapters are readable, informative, and incisive.

The only misprint I found in the book is on p. 453. As an example of the completeness of the discussions in this part, the list of topics covered in Chapter 14 on chemical reactions is: introduction; unimolecular reactions; transition state theory; dynamical effects in barrier-crossing—the Kramers model; observations and extensions including a discussion of the shortcomings of the Kramers theory; non-Markovian effects and the normal mode representation; experimental observations; numerical simulation of barrier crossing; and diffusion controlled reactions.

In summary, this is an excellent book and should be read by researchers and students of dynamics in condensed phases. It can certainly be used as a text for graduate courses on condensed phases and statistical mechanics.

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