Book Review: Nonequilibrium Thermodynamics and its Statistical Foundation

Nonequilibrium Thermodynamics and its Statistical Foundations. H. J. Kreuzer. Clarendon Press, Oxford, 1981, 438 pages.

This book contains a discussion of a number of interesting topics, as can be gleaned from its table of contents: balance equations of irreversible thermodynamics; linear phenomenological laws; stability and fluctuations; chemical reactions; Bénard convection; classical statistical mechanics and kinetic theory; microscopic derivation of balance equations: quantum-mechanical theory; linear response theory; master equations; irreversibility and the approach to equilibrium; and transient effects in the time evolution of an ideal gas in an external potential. Since these subjects have been discussed in a variety of texts and monographs, the criteria for the utility of this book are one or more of the following: a unifying point of view which illuminates the physics of nonequilibrium thermodynamics and statistical mechanics; a clear, novel, and precise presentation of some of the material; a valuable juxtaposition of topics which do not appear together in a recent book.

The book does have a unifying point of view which is perceptive and useful. The text focuses on the properties of fluctuations in large systems whether in equilibrium or in nonequilibrium. The relatively simple description of nonequilibrium systems by master equations, macroscopic equations of thermohydrodynamics, and linear response techniques is ascribed to the properties of these fluctuations.

The major fault of the book is its presentation of some of the material. The discussion on pp. 50-51 implies that the time dependences of fluctuations in nonequilibrium systems are related to the decay of macroscopic quantities in the same way as in equilibrium systems. This is not true, as is indicated, for example, by the recent spate of work on fluctuations in steady-state systems. The discussion of stability of equilibrium states is based on Eq. (4.18), which is incorrect. For a simple system, the equation TdS - dU - pdV = 0 is always true where S is the entropy; U, the internal energy; V, the volume; T, the uniform temperature; and p, the uniform pressure.

The derivation of the Boltzmann equation on pp. 177 et seq. is based on the out-moded approach of Bogulyubov, Born, Green, and Kirkwood, although reference to more recent work is given on p. 190. There is no mention of the elegant work of Irving and Zwanzig on the derivation of the quantum mechanical balance equations in Chapter 8. In his treatment of linear response theory, the author implies that the linear response expression is valid for the *N*-particle distribution function (which is not true) as well as for macroscopic variables (which is true). His dismissal of van Kampen's objections (p. 294) is cavalier and unjustified. Finally, his discussion of the van Hove approach to the derivation of the master equation in Chapter 10 is puzzling.

There is a nice discussion of the Loschmidt and Zérmelo paradoxes in Chapter 11.

My overall impression is that this book is useful for specialists in the field because of its occasional insights, but I would not recommend it to neophytes.

Irwin Oppenheim Chemistry Dep't. Mass. Inst. of Technology Cambridge, Ma. 02139