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Perspective

Perspective on "Statistical mechanical theory of irreversible processes. I. General theory and simple applications to magnetic and conduction problems."

Kubo R (1957) J Phys Soc Jpn 12: 570

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Abstract. Kubo's paper on linear-response theory provided a unified language to describe a wide variety of transport phenomena, both quantum and classical, in a suitable "microscopic" language. The paper has been crucial for subsequent developments in numerical simulation.

Key words: Linear-response theory – Correlation function – Fluctuation-dissipation theorem – Reaction rates

It is sometimes difficult to indicate precisely which paper heralds an important change in a particular field. In retrospect, one can often observe precursors and parallel developments in other publications; however, Kubo's paper on linear-response theory, although it certainly did not appear in a scientific vacuum, clearly marks a watershed.

Kubo's linear-response theory provides the full, quantum-mechanical relation between the response of a system to external perturbations and the spontaneous decay of fluctuations in the unperturbed system. Of course, the paper had important predecessors: Nyquist's [1] paper on thermal noise in resistors and Onsager's [2] seminal paper on the relation between decay of macroscopic and microscopic fluctuations, to name but the earliest.

The linear-response approach has played an important role in the construction of most modern theories of transport processes (see, e.g. Ref. [3]). Moreover, it has had a profound impact on the development of classical molecular dynamics simulations – a field that was emerging at the same time. Linear-response theory showed how linear transport coefficients can be computed in a simulation, by studying the decay of fluctuations in equilibrium. More specifically, most transport coefficients can be expressed as time integrals of (auto)correlation functions of microscopic "fluxes" (e.g. the current density, in the case of electrical conductivity) – the famous "Green–Kubo" relations. The microscopic fluxes that appear in these relations are explicit functions of the particle coordinates and momenta and can, therefore, be computed in a standard molecular dynamics simulation.

In fact, Kubo's paper also provided much of the language for the subsequent development of nonequilibrium molecular dynamics simulations; however, nonequilibrium molecular dynamics adresses problems that could not be handled in the context of the original linear-response theory (see, e.g. Ref. [4]).

However, when I focus on the implications of Kubo's paper for theoretical chemistry, two topics spring to mind that were subsequently affected by this work: "spectroscopy" and "chemical kinetics".

Let us first consider spectroscopy. Linear-response theory, in particular the fluctuation dissipation theorem – which relates the absorption of an incident monochromatic field to the correlation function of (e.g. dipole) fluctuations in equilibrium – has changed our perspective on "spectroscopy" of dense media. It has moved away from a static "Schrödinger" picture – phrased in terms of transitions between immutable (but usually incomputable) quantum levels – to a dynamic "Heisenberg" picture, in which the spectral line shape is related by Fourier transform to a correlation function that describes the decay of fluctuations. Of course, any property that cannot be computed in the Schrödinger picture, cannot be computed in the Heisenberg picture either; however, correlation functions, unlike wavefunctions, have a clear meaning in the classical limit. This makes it much easier to come up with simple (semi) classical interpretations and approximations.

The Kubo approach has also proven to be extremely fruitful for the theory of chemical rate processes. In fact, chemical rate constants can also be expressed as an integral of a flux autocorrelation function. As was shown by Chandler [5], however, the "brute-force" approach does not work in this case. In fact, in the context

of diffusion in solids, this had been noted by Bennett [6]. Chandler showed how the expression for the rate constant of a unimolecular reaction can be cast in a form that can be used efficiently in computer simulations.

As is clear from the above, linear-response theory has stimulated many important developments; yet Kubo's approach has not been uncontroversial. In particular, in a paper that cannot be found in most libraries, van Kampen [7] has criticized the assumption made in linear-response theory that, for sufficiently weak fields, the change in the phase-space density is linear in the applied perturbation. In fact, due to the exponential divergence of phase-space trajectories, even the weakest perturbation will, on a macroscopic time-scale, result in large changes in the phase-space density; however, as was shown in the subsequent numerical work by Ciccotti et al. [8], on the microscopic time-scales that are usually relevant for the dynamical response of a system to a sudden perturbation, the linear-response assumption holds quite well.

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