PHYSICAL REVIEW A VOLUME 5, NUMBER 6 JUNE 1972

COMMENTS AND ADDENDA

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Memory Effects in Irreversible Thermodynamics: Corrected Derivation of Transport Equations

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(Received 14 February 1972)

An error in an earlier paper [Phys. Rev. 124, 983 (1961)] is corrected. This error occurred in the derivation of nonlinear transport equations from a generalized Fokker-Planck equation, and took the form of neglecting certain fluctuations. When these are accounted for, the resulting transport equations contain fluctuation-renormalized transport coefficients.

Some years ago one of us presented a statistical mechanical theory of nonlinear and non-Markoffian transport processes.[1] The main result of that paper was an exact generalized Fokker-Planck equation for the probability distribution of a set of dynamical variables, together with formally exact expressions for various quantities in the equation.

In that paper it was claimed that nonlinear transport equations for the *average values* of macroscopic variables could be obtained easily from the Fokker-Planck equation, and some results were given. Our purpose here is to point out an error in this part of the earlier paper and to show how correct results can be obtained.

The error was as follows. In deriving transport equations for average values, it was asserted that when the dynamical variables were macroscopic one could safely neglect fluctuations from the average values. Specifically, the average of a function was approximated by the same function of the average. We have found that this is not correct; even though the fluctuations are of a microscopic order of magnitude and are not seen in ordinary macroscopic experiments, they have a striking effect on the transport equations. In particular, they cause a "renormalization" of the transport coefficients that appear in the Fokker-Planck equation. The phenomenon can be described loosely as a nonlinear mixing of thermal noise with a macroscopic relaxation process.

The nature of the error and the structure of the corrected transport equations are illustrated here by considering a simple example. Instead of using the exact generalized Fokker-Planck equation of Ref. 1, we use a simple special case in which irrelevant details are eliminated; this allows us to focus attention on the main point. A future article will present a more detailed analysis. (The relation of the equation used here to the exact Fokker-Planck equation has been discussed, in a different context, by Kawasaki.[2])

Let a denote the numerical values of a set $(a_1, a_2, \ldots)$ of dynamical variables. The probability density of these variables at time t is $g(a;t)$. The average values of the variables at time t are given by

$$c_k(t) = \langle a_k; t\rangle = \int da\, a_k\, g(a; t) \ . \qquad (1)$$

We suppose that these variables have been chosen so that their averages vanish at equilibrium and their equilibrium second moments are

$$\langle a_k a_l;\ \mathrm{eq}\rangle = \delta_{kl} \ . \qquad (2)$$

We are concerned here with the transport equations for these average values. In particular, we seek transport equations of the form

$$\frac{\partial}{\partial t}\, c_k(t) = F_k(\{c_l(t')\}) , \qquad (3)$$

where the right-hand side is a functional of the average values.

According to the results of Ref. 1, the time evolution of $g(a;t)$ is governed by a generalized Fokker-Planck equation, which contains nonlocal and non-Markoffian transport coefficients, and various nonlinearities. To illustrate the effect these nonlinearities produce in the derived transport equations, we consider here the much simpler Markoffian-Fokker-Planck equation

$$\frac{\partial}{\partial t}\, g(a;t) + \sum_k \frac{\partial}{\partial a_k}\, [v_k(a)\, g(a;t)] = \sum_k \eta_k \frac{\partial}{\partial a_k}\left[\frac{\partial}{\partial a_k}\, g(a;t) - F_k(a)\, g(a;t)\right] . \qquad (4)$$

This equation corresponds to Eq. (33) of Ref. 1, in the limit that the memory kernel is sharp in time. The quantities η_k are transport coefficients. The velocities $v_k(a)$ describe a streaming motion in a space, and the $F_k(a)$ are thermodynamic forces. We assume, for simplicity, that the forces are linear, $F_k(a) = -a_k$, and that the streaming velocities are quadratic in deviations from equilibrium,

$$v_k(a) = \sum_l \sum_m V_{klm}\, a_l a_m \ . \qquad (5)$$

The coupling constants V_{klm} obey certain symmetry conditions,

$$V_{klm} = V_{kml} , \quad \textstyle\sum_k V_{kkm} = \sum_m V_{kmm} = 0, \qquad V_{klm} + V_{lmk} + V_{mkl} = 0. \qquad (6)$$

These can be justified by requiring that this Fokker-Planck equation has the equilibrium solution

$$g(a:\mathrm{eq}) \sim \exp(-\tfrac{1}{2}\textstyle\sum_k a_k^2). \qquad (7)$$

We consider only a special initial density $g(a;0)$, Gaussian with the equilibrium second moments but with nonzero initial average values $c_k(0)$,

$$g(a;0) \sim \exp\{-\tfrac{1}{2}\textstyle\sum_k [a_k - c_k(0)]^2\} . \qquad (8)$$

Thus the initial probability density is simply a displaced equilibrium density.

To get a transport equation for the time-dependent average $c_k(t)$, we multiply Eq. (4) by a_k and perform several partial integrations,

$$\frac{\partial}{\partial t}\, c_k(t) = -\eta_k c_k(t) + \langle v_k(a); t\rangle \ . \qquad (9)$$

This equation contains the average of the streaming velocity.

Next, we apply here the same approximation that was used in Ref. (1) to get transport equations. We replace the average of the streaming velocity $\langle v_k(a); t\rangle$ by the streaming velocity $v_k(c(t))$ at the average position in a space, and we obtain the nonlinear transport equation

$$\frac{\partial}{\partial t}\, c_k(t) \simeq -\eta_k c_k(t) + \sum_l \sum_m V_{klm}\, c_l(t)\, c_m(t). \qquad (10)$$

This result, which is a prototype of the transport equations "derived" in Ref. 1, *is not correct.* The quantity that was neglected in this approximation is

$$\Delta v_k(t) = \sum_l \sum_m V_{klm} c_{lm}(t), \qquad (11)$$

where $c_{lm}(t)$ denotes the second cumulant

$$c_{lm}(t) = \langle a_l a_m : t\rangle - \langle a_l; t\rangle \langle a_m; t\rangle \ . \qquad (12)$$

At $t = 0$ and at equilibrium (or infinite time), the second cumulant is just

$$c_{lm}(0) = c_{lm}(\infty) = \delta_{lm}, \qquad (13)$$

and $\Delta v_k(t)$ vanishes because of the condition $\sum_m V_{kmm} = 0$. If the second cumulant actually maintained its equilibrium value for all times, then Eq. (10) would be exact. But this is not so; it turns out that extra fluctuations build up and then decay as the system relaxes toward equilibrium. The approximate Eq. (10) must be replaced by the exact form

$$\frac{\partial}{\partial t}\, c_k(t) = -\eta_k c_k(t) + \sum_l \sum_m V_{klm}[c_l(t) c_m(t) + c_{lm}(t)] , \qquad (14)$$

and we must relate the second cumulant $c_{lm}(t)$ to the average $c_k(t)$.

This will be done by a perturbative method. Let us assume that the nonlinear coupling constants are small,

$$V_{klm} = O(\lambda), \quad \lambda \to 0 . \qquad (15)$$

Our goal is an expansion in powers of λ of the functional on the right-hand side of Eq. (3).

An equation for $c_{lm}(t)$ can be obtained by the same procedure used to get the equation for $c_k(t)$. The Fokker-Planck equation is multiplied by $a_l a_m$, partial integrations are performed, and terms arising from the time derivatives of $c_l(t)$ and $c_m(t)$ are subtracted. The result is

$$\frac{\partial}{\partial t}\, c_{lm}(t) + (\eta_l + \eta_m) c_{lm}(t) - 2\eta_l \delta_{lm} = \sum_n \sum_p V_{lnp}[c_{mmp}(t) + c_n(t)\, c_{mp}(t) + c_p(t)\, c_{mn}(t)]$$

$$+ V_{mnp}\left[c_{lnp}(t) + c_n(t)\, c_{lp}(t) + c_p(t)\, c_{ln}(t)\right], \quad (16)$$

where $c_{mnp}(t)$ denotes the third cumulant

$$c_{mnp}(t) = \langle a_m a_n a_p; t\rangle - \langle a_m a_n; t\rangle\langle a_p; t\rangle - \langle a_m a_p; t\rangle\langle a_n; t\rangle - \langle a_n a_p; t\rangle\langle a_m; t\rangle + 2\langle a_m; t\rangle\langle a_n; t\rangle\langle a_p; t\rangle\ . \quad (17)$$

Again by following the same procedure, we can get an equation for the third cumulant,

$$\frac{\partial}{\partial t}\, c_{mnp}(t) + (\eta_m + \eta_n + \eta_p)\, c_{mnp}(t) = V\{\cdots\}\ . \quad (18)$$

The curly brackets on the right-hand side contain the average, and also the second, third, and fourth cumulants—but the whole quantity is of order λ.

Let us expand the second and higher cumulants in powers of λ. When the equations governing their time dependence are solved, and the initial distribution (8) is used to fix their initial values, we find

$$c_{lm}(t) = \delta_{lm} + O(\lambda), \quad c_{mnp}(t) = O(\lambda). \quad (19)$$

This means that, to terms of first order in λ, Eq. (16) may be replaced by

$$\frac{\partial}{\partial t}\, c_{lm}(t) + (\eta_l + \eta_m)\, c_{lm}(t) - 2\eta_l\, \delta_{lm} = \sum_n \sum_p V_{lnp}\left[\delta_{mp}\, c_n(t) + \delta_{mn}\, c_p(t)\right] + V_{mnp}\left[\delta_{lp}\, c_n(t) + \delta_{ln}\, c_p(t)\right] + O(\lambda^2). \quad (20)$$

When this equation is solved as an inhomogeneous first-order differential equation, the result is

$$c_{lm}(t) = \delta_{lm} + 2\sum_n (V_{lnm} + V_{mnl}) \times \int_0^t ds\, e^{-(\eta_l+\eta_m)(t-s)}\, c_n(s) + O(\lambda^2). \quad (21)$$

The second cumulant has a contribution of order λ which arises from nonlinear mixing of equilibrium thermal noise with a macroscopic quantity. The relaxation of $c_n(t)$ *induces* extra correlations in $c_{lm}(t)$.

When this result is substituted into Eq. (14), and the symmetry conditions (6) are used to combine terms, we find

$$\frac{\partial}{\partial t}\, c_k(t) = -\eta_k\, c_k(t) + \sum_l \sum_m V_{klm}\, c_l(t) c_m(t) - \sum_n \int_0^t ds\, \phi_{kn}(s)\, c_n(t-s) + O(\lambda^3), \quad (22)$$

where

$$\phi_{kn}(s) = 2\sum_l \sum_m V_{klm} V_{nlm}\, e^{-(\eta_l+\eta_m)s} + \cdots\ . \quad (23)$$

The kernels $\phi_{kn}(s)$ are additional non-Markoffian transport coefficients, associated with the linear part of the relaxation.

Evidently this calculation can be carried out to higher orders in λ, although the results get progressively more complicated. In particular, the kernels $\phi_{kn}(s)$ have additional contributions of order λ^4, λ^6, and further terms, nonlinear in the averages, appear in higher orders of λ. At least in principle, however, we have available a method for generating an expansion in powers of λ of the functional describing the time evolution of $c(t)$.

If we had assumed a more general initial probability density than that given by Eq. (8), then we would have found extra terms in the transport equation for $c_k(t)$ describing the relaxation of initial nonequilibrium correlations.

The main result of this derivation (to second order in λ) is the "fluctuation renormalization" of a linear transport coefficient. Results analogous to this have already been found, although by quite different methods. For example, mode-mode coupling theory leads to similar conclusions. Linear-response theory has been applied[3] to essentially the same Fokker-Planck equation studied here, and the same renormalized transport coefficient was obtained. Finally, the Brownian motion of a nonlinear oscillator has been investigated.[4] (In this calculation, the nonlinearity appeared in a nonlinear driving force in the transport part of a Fokker-Planck equation, rather than in a streaming velocity.) Again, the bare transport coefficient was renormalized by the nonlinear mixing of thermal noise.

In summary, we have presented a corrected derivation of a nonlinear transport equation, starting from a simple-model Fokker-Planck equation containing a quadratic streaming velocity. Nonlinearities provide a coupling between thermal fluctuations and the decay of a nonequilibrium average value, and this coupling gives rise to a renormalization of a transport coefficient.

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*Research supported by NSF Grant No. NSF GP 29534.
†Research performed in part as NAS-NRC Postdoctoral Research Associate, National Bureau of Standards, Wash., D. C.

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