

Nonlinear Transport Equations from Statistical Mechanics^{*)}

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A systematic procedure is described for deriving nonlinear transport equations from statistical mechanics. The procedure is based on the Chapman-Enskog point of view. It makes use of operator methods that are standard in linear response theory. As an illustration, the resulting transport equations are expanded to second order in deviations from equilibrium, and also to second order in gradients.

Introduction

The purpose of this article is to describe a systematic method for deriving nonlinear transport equations from statistical mechanics. The method is used to determine explicitly the form of transport equations to second order in deviations from equilibrium. The results involve only operators that are familiar in linear response theory, and have a structure that may be amenable to calculation.

A number of methods intended to accomplish this purpose have been described already. Several different approaches have been proposed. One of these, based on ideas of Brownian motion theory, has been discussed in some detail by Nordholm and Zwanzig,¹⁾ by Mori and Fujisaka,²⁾ and by Garcia-Colin and del Rio,³⁾ and by others. Another approach, modeled on the Chapman-Enskog point of view was originated by Robertson,⁴⁾ and has been discussed by Piccirelli,⁵⁾ by Kawasaki and Gunton,⁶⁾ and by Ernst, Hauge, and van Leeuwen.⁷⁾ A third approach, based on higher order Kubo theory, was developed by Weare and Oppenheim.⁸⁾

The present article is a further development of the Chapman-Enskog point of view. The basic idea here is that the phase space distribution function, as it evolves in time, always stays close to a local equilibrium form. Initial deviations from local equilibrium are expected to decay rapidly, and later deviations are expected to develop and to remain proportional to gradi-

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ents of thermodynamic forces. In our treatment, we *assume* (as others have) that the initial distribution has the local equilibrium form, and we *calculate* the later deviations explicitly. Calculations of this sort were presented in Refs. 4)~7); they make use of time-dependent projection operators. While such operators are convenient for formal manipulations, they are extremely difficult to cope with in practical calculations. The present treatment also uses projection operators, but ours are exactly the same ones that appear in Mori's well-known linear response theory; they are time-independent, and they do not present serious difficulties in practical calculations.

We proceed immediately to the derivation, and return afterwards to a discussion of the relation of our approach to earlier ones.

Liouville equation

A point in phase space is denoted by Γ . The phase space distribution function at time t is $f(\Gamma; t)$. Its time dependence is determined by the Liouville equation

$$\frac{\partial}{\partial t} f = -L f, \tag{1}$$

where L is the Liouville operator. (Note that the frequently used factor $\sqrt{-1} (=i)$ has been omitted.) The phase space distribution function at equilibrium is $f_e(\Gamma)$. Deviations from thermal equilibrium are represented by the quantity $W(\Gamma; t)$, defined by

$$f(\Gamma; t) = f_e(\Gamma) \exp W(\Gamma; t). \tag{2}$$

Then (in classical mechanics only!) W obeys the same Liouville equation,

$$\frac{\partial}{\partial t} W = -L W. \tag{3}$$

Projections

We are concerned with a particular set of dynamical variables, denoted collectively by the vector $A(\Gamma)$. These are chosen so that their equilibrium averages vanish,

$$\langle A \rangle = 0. \tag{4}$$

[Throughout this article, $\langle \ \rangle$ means the equilibrium average.] The matrix of second moments at equilibrium is M ,

$$\langle AA \rangle = M. \tag{5}$$

The inner product of two dynamical variables is (A, B) , and is defined by

$$(A, B) = \langle AB \rangle. \quad (6)$$

Using this inner product, we may define a projection operator P by its action on some dynamical variable G ,

$$PG = (G, 1) + (G, A) \cdot M^{-1} \cdot A(I). \quad (7)$$

This is the projection operator that appears in Mori's form of linear response theory. [The extra term $(G, 1)$ is just the equilibrium average of G , and is included for completeness.] We shall need also the adjoint of P ,

$$\bar{P}F = (1, F) + A(I) \cdot M^{-1} \cdot (A, F). \quad (8)$$

This is an adjoint in the sense

$$(F, \bar{P}G) = (PF, G). \quad (9)$$

Evaluation of W

Let us use \bar{P} to separate W into two parts,

$$W = \bar{P}W + (1 - \bar{P})W. \quad (10)$$

In the same way, we separate the Liouville equation for W into two equations. These equations can be solved by a standard procedure, leading to

$$(1 - \bar{P})W(t) = \bar{U}(t)(1 - \bar{P})W(0) - \int_0^t ds \bar{U}(t-s)L\bar{P}W(s) \quad (11)$$

and

$$\begin{aligned} \frac{d}{dt}\bar{P}W(t) = & -\bar{P}L\bar{P}W(t) + \int_0^t ds \bar{P}L\bar{U}(t-s)L\bar{P}W(s) \\ & -\bar{P}L\bar{U}(t)(1 - \bar{P})W(0), \end{aligned} \quad (12)$$

where

$$\bar{U}(t) = \exp[-t(1 - \bar{P})L](1 - \bar{P}). \quad (13)$$

This is the adjoint of $U(t)$,

$$U(t) = \exp[t(1 - P)L](1 - P) \quad (14)$$

because

$$(F, \bar{U}(t)G) = (U(t)F, G). \quad (15)$$

The projected part of W is

$$\bar{P}W = (1, W) + A(I) \cdot M^{-1} \cdot (A, W). \quad (16)$$

In the following, we use the notation

$$(A, W) = c, \tag{17}$$

$$M^{-1} \cdot (A, W) = b.$$

Then the equation for PW is equivalent to an equation for $c(t)$,

$$\frac{d}{dt}c(t) = i\Omega \cdot c(t) - \int_0^t ds K(t-s) \cdot c(s) + (F^+(t), W(0)). \tag{18}$$

Not only does this have the same structure as in Mori's linear response theory, but the quantities Ω , $K(t-s)$, and $F^+(t)$ are identical with Mori's expressions for them. [To see this, one uses Eq. (15) to replace \bar{U} by U .] Because we are not going to need the explicit form of $c(t)$ in the following discussion, we do not pursue this here.

The remaining part of W can be evaluated from Eq. (11). It contains a contribution from the initial value $(1-\bar{P})W(0)$ and a contribution proportional to $c(t)$,

$$(1-\bar{P})W(t) = \bar{U}(t)(1-\bar{P})W(0) + \int_0^t ds \mathcal{F}(t-s) \cdot M^{-1} \cdot c(s), \tag{19}$$

where \mathcal{F} is given by

$$\mathcal{F}(t) = -\bar{U}(t)LA. \tag{20}$$

Finally, we note that $(1, W)$ is a numerical constant w_0 that is independent of time. This plays a role of a normalization factor.

When these results are combined, we find that W has four distinct contributions,

$$W(\Gamma; t) = w_0 + A(\Gamma) \cdot b(t) + \int_0^t ds \mathcal{F}(\Gamma, t-s) \cdot b(s) + \bar{U}(t)(1-\bar{P})W(0). \tag{21}$$

If the initial ensemble has the local equilibrium form

$$f(\Gamma; 0) = f_e(\Gamma) \exp[w_0 + A \cdot b(0)], \tag{22}$$

then the contribution from $(1-\bar{P})W(0)$ vanishes for all t . On the other hand, if the initial ensemble deviates from the local equilibrium form, then this extra contribution is a kind of "noise", just as in linear response theory. In the following, we assume initial local equilibrium and we omit this term.

Time dependent averages

Now that an expression for $f(\Gamma; t)$ has been obtained, we can use it to

find average values. But first, some further notation is needed. The time dependent average of $G(I)$, taken with $f(I; t)$, will be denoted by $\langle G \rangle_t$,

$$\langle G \rangle_t = \int dI G(I) f(I; t). \quad (23)$$

We use the abbreviation

$$\psi_{rt} = \int_0^t ds \mathcal{F}(I, t-s) \cdot \gamma(s), \quad (24)$$

where $\gamma(s)$ is any arbitrary function of s , and we omit the term in $W(t)$ arising from $(1 - \bar{P})W(0)$. Then the average is

$$\langle G \rangle_t = \int dI G(I) f_e(I) \exp[\tau \omega_0 + A(I) \cdot b(t) + \psi_{bt}]. \quad (25)$$

Next, we introduce the local equilibrium average $\langle G \rangle_b$,

$$\langle G \rangle_b = \langle G \exp A \cdot b \rangle / \langle \exp A \cdot b \rangle. \quad (26)$$

Note that the factor $f_e(I)$ has been absorbed in the symbol $\langle \rangle$. Whenever it is important to remember that b is a function of time t , we indicate this by $\langle \rangle_{bt}$. Now the average of G can be written in the form

$$\langle G \rangle_t = \langle G \exp \psi_{bt} \rangle_{bt} / \langle \exp \psi_{bt} \rangle_{bt}, \quad (27)$$

where the denominator accounts for normalization.

In particular, the average of A , denoted by $a(t)$, is

$$a(t) = \langle A \rangle_t = \langle A \exp \psi_{bt} \rangle_{bt} / \langle \exp \psi_{bt} \rangle_{bt}, \quad (28)$$

and its time derivative is the average of LA ,

$$da(t)/dt = \langle LA \rangle_t = \langle (LA) \exp \psi_{bt} \rangle_{bt} / \langle \exp \psi_{bt} \rangle_{bt}. \quad (29)$$

Both of these are functionals of $b(t)$. By eliminating $b(t)$, we can find an expression for da/dt as a functional of $a(t)$. This is analogous to the theory of the equation of state of a gas in the grand canonical ensemble. There, both the pressure and the density are functions of the chemical potential. The equation of state is found by eliminating the chemical potential. In the present case, the elimination of $b(t)$ can be accomplished easily, at least to low order, by expanding $a(t)$ and da/dt in powers of $b(t)$.

However, as earlier workers have found, it is more useful to adhere to the local equilibrium description as closely as possible. If the average $a(t)$ is given, then there is a local equilibrium distribution function with time dependent parameters $B(t)$ which gives precisely the average $a(t)$,

$$a(t) = \langle A \exp A \cdot B(t) \rangle / \langle \exp A \cdot B(t) \rangle = \langle A \rangle_{Bt}. \quad (30)$$

As in the Chapman-Enskog procedure for deriving transport equations, the parameters $B(t)$, or the “thermodynamic fields”, play a more natural role than the averages themselves. This suggests that we should use Eqs. (28) and (30) to relate $B(t)$ to $b(t)$, and then use this relation to find da/dt as a functional of $B(t)$. This also can be done by constructing power series expansions.

Expansion in B

By using the various definitions, it is easy to carry out the expansion to terms of order B^2 . We will do this now.

First, both da/dt and $a(t)$ are expanded in powers of $b(t)$. Factors of b can come from the local equilibrium averages or from ψ_{bt} . The expansion is facilitated by the observation that ψ_{bt} contains the projection $(1-\bar{P})$, so that $\langle\psi_{bt}\rangle$ and $\langle A\psi_{bt}\rangle$ both vanish.

To second order in b , the time derivative is

$$\begin{aligned} da(t)/dt = & \langle(LA)A\rangle \cdot b(t) + \frac{1}{2}\langle(LA)AA\rangle : b(t)b(t) + \langle(LA)\psi_{bt}\rangle \\ & + \langle(LA)\psi_{bt}A\rangle \cdot b(t) + \frac{1}{2}\langle(LA)\psi_{bt}^2\rangle + O(b^3). \end{aligned} \tag{31}$$

Similarly, the average itself is

$$\begin{aligned} a(t) = & \langle AA\rangle \cdot b(t) + \frac{1}{2}\langle AAA\rangle : b(t)b(t) + \langle A\psi_{bt}A\rangle \cdot b(t) \\ & + \frac{1}{2}\langle A\psi_{bt}^2\rangle + O(b^3). \end{aligned} \tag{32}$$

But the average can be obtained also from $\langle A\rangle_{Bt}$,

$$a(t) = \langle AA\rangle \cdot B(t) + \frac{1}{2}\langle AAA\rangle : B(t)B(t) + O(B^3). \tag{33}$$

On comparing Eqs. (32) and (33), we find that $b = B + O(B^2)$. More specifically, the relation is

$$\begin{aligned} b(t) = & B(t) + \Delta B(t), \\ \Delta B(t) = & -M^{-1} \cdot \{ \langle A\psi_{Bt}A\rangle \cdot B(t) + \frac{1}{2}\langle A\psi_{Bt}^2\rangle \} + O(B^3). \end{aligned} \tag{34}$$

Note the subscript B on ψ_{Bt} .

Now we put this into Eq. (31), collecting terms to order B^2 and using the definition of the projection \bar{P} , we obtain

$$\begin{aligned} \frac{da(t)}{dt} = & \langle(LA)A\rangle \cdot B(t) + \frac{1}{2}\langle(LA)AA\rangle : B(t)B(t) + \langle(LA)\psi_{Bt}\rangle \\ & + \langle(LA)(1-\bar{P})\psi_{Bt}A\rangle \cdot B(t) + \frac{1}{2}\langle(LA)(1-\bar{P})\psi_{Bt}^2\rangle + \langle LA\psi_{\Delta Bt}\rangle \\ & + O(B^3). \end{aligned} \tag{35}$$

Recall that ψ_{ABt} is defined by Eq. (24), and is linear in ΔB . In deriving this expression for da/dt , we have assumed that the initial phase space distribution has the local equilibrium form, and we have neglected all terms of order B^3 and higher. Subject to these restrictions, the result is exact.

The first two terms in da/dt are in fact the expansion of $\langle LA \rangle_{Bt}$, the flux calculated at local equilibrium. Terms involving ψ have a dissipative character. The first of these is exactly what one finds in linear response theory; to see this, one uses Eq. (24) to relate ψ to \mathcal{F} , then Eq. (20) for \mathcal{F} , and finally Eq. (15) to take the adjoint of $\bar{U}(t)$. When this is done, we obtain

$$\langle (LA) \psi_{Bt} \rangle = - \int_0^t ds K(t-s) \cdot M \cdot B(s), \quad (36)$$

where the kernel $K(t)$ has Mori's form,

$$K(t) = (U(t) LA, LA) \cdot M^{-1}. \quad (37)$$

The next term in Eq. (35) can be reduced in the same way,

$$\langle (LA) (1-\bar{P}) \psi_{Bt} A \rangle \cdot B(t) = - \int_0^t ds B(t) \cdot K^{(2)}(t-s) \cdot B(s), \quad (38)$$

where the kernel $K^{(2)}(t)$ is

$$K^{(2)}(t) = (U(t) A(1-P) LA, LA). \quad (39)$$

The other terms in da/dt are messier to write out explicitly; however, they are proportional to $(LA)^3$ and $(LA)^4$, and may not be so interesting if LA introduces a parameter of smallness. This is what happens in the gradient expansion.

Gradient expansion

Another kind of expansion which can be carried out easily to low order is the gradient expansion. We have in mind here the standard "hydrodynamic" situation, where the variables A are characterized by a wave vector k (or a gradient), and their rates of change LA are proportional to k .

If LA is of order k , then \mathcal{F} and ψ are also of order k . This suggests the expansion of $\exp \psi$ in powers of ψ , keeping $b(t)$ to all orders. In this way, we can get da/dt to order k^2 for all $b(t)$, and $a(t)$ to order k for all $b(t)$. On converting from $b(t)$ to $B(t)$, we find that $\Delta B(t)$ is of order k . When this is worked out in detail, we obtain the result

$$\frac{d}{dt} a(t) = \langle LA \rangle_{Bt} - \int_0^t ds K_B(t, s) \cdot B(s) + O(k^3), \quad (40)$$

where the B -dependent kernel $K_B(t, s)$ is given by

$$K_B(t, s) = \langle [LA - \langle LA \rangle_{Bt}] P_{\perp}(t) \bar{U}(t-s) LA \rangle_{Bt}. \quad (41)$$

In this expression, $P_{\perp}(t)$ is the projection operator used by Ernst, Hauge and van Leeuwen,⁷ or the projection operator $1 - \mathcal{P}(t)$ used by Kawasaki and Gunton.⁶ (While these operators are not quite the same, they have the same effect in this expression.)

It is not hard to find the expansion of $K_B(t, s)$ to first order in B ; the result is

$$K_B(t, s) = K(t-s) \cdot M + B(t) \cdot K^{(2)}(t-s), \quad (42)$$

where $K(t-s)$ is given by Eq. (37), and $K^{(2)}(t-s)$ is given by Eq. (39). It is comforting that, at least to order $k^2 B^2$, it does not make any difference whether one expands first in B and then in k , or vice versa.

Comparison with earlier work

Here we make some remarks about the relation of this procedure to earlier ones. The preceding results, to order B^2 , can be obtained also by a brute force expansion of the general results of Kawasaki and Gunton, or to order k^2 , by an expansion of the results of Ernst et al. They are equivalent to results obtained by Weare and Oppenheim, on allowing for their Markoffian approximations. (I thank J. Brey for showing this to me.) If only an expansion is desired, the present procedure appears simpler and more direct than the others; but if a general formalism is required, the procedure due to Piccirelli or to Kawasaki and Gunton may be preferable.

Does the expansion converge?

Kawasaki and Gunton, and Ernst and coworkers,⁹ have investigated the nonlinear dependence of the stress tensor σ on the rate of shear D ; they find, for a simple fluid, that the Newtonian stress tensor must be corrected by a term $\Delta\sigma \sim D^{3/2}$. This suggests that a straightforward expansion in powers of B may not converge. However, it should be noted that they calculate a steady state stress, without including external forces required to maintain the steady state, and without a sink to remove the heat that is generated in a steady shear. It is not clear whether or not these omissions have seriously affected their conclusions. If similar calculations are performed explicitly on the time dependent B^2 correction to the Newtonian stress tensor, it may turn out that these corrections diverge at long times or zero frequencies. There is precedent for such behavior in the theory of linear transport coefficients of dense gases. In that case, it may be necessary to include higher orders in B , and to re-sum divergent terms to get the $D^{3/2}$ effect.

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Discussion

M. S. Green: I would like to point out that when the terms indicated by dots' in Prof. Zwanzig's equations are taken into account it is possible to have divergencies or non-analyticities. It seems that the appearance of such divergences is a universal phenomena in transport equations derived by projection onto the slowly varying macroscopic variables. They occur in the two most carefully investigated cases, i.e., the long time tails in hydrodynamics and the divergences associated with recollisions in the kinetic theory of dense gases. These divergences usually do not interfere with the physical usefulness of the first approximation but they indicate that physical concepts such as Markoffian character, reduction of the description, expansion in powers of the gradient, break down in higher order.