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Nonlinear dynamics of gross variables and the renormalization of transport coefficients

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The slowly decaying hydrodynamic modes in many-body systems are obtained from a theory which avoids perturbation methods. The theory is based on a projection-operator technique which is applied to quantities characterizing the state of the system at various levels of its description. The main result is that a true transport coefficient is shown to consist of two contributions (one which decays rapidly in time and another one which decays slowly), is non-Markoffian, and arises from the nonlinear interactions among the collective modes. This contribution is obtained in a closed analytical form which is further analyzed within the context of our present-day information derived from computer and laboratory experiments. The relationship between this work and similar earlier work on this problem is also discussed.

I. INTRODUCTION

One of the most striking discoveries which has taken place during the past decade in the field of statistical mechanics of transport properties is the existence of the long tails (nonexponential decay) in the time dependence of time correlation functions for nondilute fluids. This behavior has had an important influence on our understanding of the so-called kinetic and hydrodynamic stages of such systems.[1] Also, it has brought up serious doubts on the analytical character of the transport coefficients with the density and the nonexistence of a virial expansion.[2,3]

Although there is a general attitude to accept that the time correlation functions for such quantities exhibit a time behavior which goes as $t^{-d/2}$, d being the dimensionality, the question still remains far from being settled. In two dimensions this implies that the transport coefficients diverge as $\log t$, thus questioning the existence of Navier-Stokes equations. In three dimensions this slow time decay is mainly responsible for the $n^2 \ln n$ term appearing in the transport coefficients, thus invalidating their virial expansion. These results have been confirmed by molecular-dynamics experiments on rigid disks[4] and hard parallel squares,[5] but recent studies on the Lorentz gas,[6] although confirming the two-dimensional behavior, are unable to detect a significant contribution of a logarithmic term in the density for the virial expansion of the inverse of the diffusion coefficient in the three-dimensional case. This result agrees with the conclusions drawn by Kestin *et al.*[7] from their experiments on the viscosity measurements for He, Ar, and N_2 at 25°C. Thus, from the experimental point of view, the results are not yet conclusive.

A large number of theoretical efforts have been made to explain these long-time tails by studying the slowly decaying part of the Green-Kubo formulas for transport coefficients.[8] However, none of these treatments is entirely satisfactory from the fundamental point of view. Perhaps, the most convincing arguments pointing out the existence of such slowly decaying terms were first given by Zwanzig in 1971 using field-theoretical methods[9] and later on by Zwanzig *et al.*[10] through a perturbation analysis of the exact Fokker-Planck equation describing the time evolution for the probability distribution function of a set of gross variables which was derived by the first author 14 years ago.[11]

In the first case, the same Fokker-Planck equation is conveniently transformed into a linear equation with an effective Hamiltonian for coupled harmonic oscillators, using second-quantization techniques. This equation was later reexamined by Kawasaki[12] in his attempt to give a first-principles derivation of the kinetic equation used in the mode-mode coupling approach for the time-dependent critical phenomena. It is interesting to point out that in Zwanzig's field-theoretical formulation of the problem, the example of the renormalized expression for the viscosity of a two-dimensional fluid, whose velocity is assumed to obey a nonlinear Langevin equation, was given. It illustrates how the true measurable transport coefficient is composed of two contributions, namely, one arising from a Markoffian-type behavior, called the bare coefficient, plus a renormalized contribution which is due to the nonlinear term $\vec{v} \cdot \text{grad}\vec{v}$. This contribution is shown to decay as t^{-1} for long times, thus confirming the computer results. Historically, this long-time behavior of time correlation functions was discovered by Edwards in 1964 in a study of a statistical-mechanical approach to the problem of turbulence.[13]

A somewhat similar method to provide for general equations describing how the space functions associated with gross variables of a many-body system evolve in time was set forth by Mori in 1965.[14] Using projection-operator techniques, he showed that the equation of motion of any vector defined in a Hilbert space and whose time evolution is given by

$$\frac{d\mathfrak{A}_i}{dt} = \mathfrak{O}\mathfrak{A}_i , \tag{1.1}$$

where $\mathfrak{A}_i$ is any vector and $\mathfrak{O}$ is a linear time-independent Hermitian operator, may be transformed into a linear-type equation which contains a systematic component of $\mathfrak{A}_i$ plus a random component due to the projected part of $\mathfrak{A}_i$ onto a space which is orthogonal to itself. Under these conditions this transformation is exact. Indeed, one can show that Eq. (1.1) becomes,

$$\frac{d\mathfrak{A}_i}{dt} = \sum_k i\Omega_{ik}\mathfrak{A}_i - \sum_k \int_0^t \Phi_{ik}(t')\mathfrak{A}_k(t-t')\,dt' + F_k(t), \tag{1.2}$$

where

$$i\Omega_{jk} = (\mathfrak{O}\mathfrak{A}_j , \mathfrak{A}_k), \tag{1.3a}$$

$$\Phi_{ik}(t) = -(\mathfrak{O}F_k(t), \mathfrak{A}_k(0)), \tag{1.3b}$$

and

$$F_k(t) = e^{(1-\mathcal{P})\mathfrak{O}t}(1-\mathcal{P})\mathfrak{O}\mathfrak{A}_k(0). \tag{1.3c}$$

In Eq. (1.3c), $\mathcal{P}$ is a projection operator defined as

$$\mathcal{P} \equiv \sum_j (\ \ , \mathfrak{A}_j(0))\mathfrak{A}_j(0), \tag{1.4}$$

and ( ) is the inner product. The quantity $F_k(t)$ satisfies two important properties, namely,

$$(F_k(t), \mathfrak{A}_k(0)) = 0 \tag{1.5a}$$

and

$$(F_k(t), F_l(t')) = \Phi_{kl}(t-t'). \tag{1.5b}$$

A typical case of this transformation is found in classical statistical mechanics where the $\mathfrak{A}$'s are well-defined phase-space functions, $\mathfrak{O} \equiv iL$, L being Liouville's operator, and $(\mathfrak{A}_i, \mathfrak{A}_j) = \langle \mathfrak{A}_i \mathfrak{A}_j^* \rangle$ is the equilibrium average of the product.

This general property is used here to derive the slowly decaying hydrodynamic modes in many-body systems without resorting to perturbation theories. The main result is that the renormalized transport coefficients exhibit a non-Markoffian behavior which arises from the nonlinear interactions of collective or gross variables. This property is displayed through a memory kernel appearing in the time evolution equation for a correlation function of such gross variables. The memory term has an analytical closed form and thus one can study under what conditions the $t^{-d/2}$ decay may be achieved. A very similar approach to the one here outlined has been also given by Mori and Fujisaka.[15] Their results are the same as ours, and they also make explicit a set of conditions that must be satisfied in order to recover the long-time tails. However, the analysis of the various steps leading to the final result deserves a bit more of discussion and justification. Also, the comparison of this approach with previous work is also relevant. Thus, although there is a certain duplication in the mathematical formalism used, we feel that the problem is interesting and important enough to deserve further attention.

In Sec. II we derive the exact and approximate equations of motion for a set of functions $G(a; t)$ which define a hypersurface $S(a)$ in Γ space containing all the microscopic states of the system consistent with the numerical values $\{a_i\}$ of a set of phase-space functions $A_i(\Gamma)$ at a certain time t. The former equations are too complicated to be of any use for the purpose of comparison with the phenomenological equations. An approximation is made which consists of determining the position of such hypersurface $S(a)$ at any time t through the solutions to the equations of motion obeyed by the gross variables $\{a_i\}$. Furthermore, one has to state the nature of such equations of motion which are unknown. This is done in Sec. III where it is assumed that the time evolution for these gross variables is governed by a Fokker-Planck-type operator. Use of the Mori technique leads to an equation for the a's such that the random component arises solely from nonlinear interactions between them. This manifests itself in the time correlation function of the fluctuating force which is shown to satisfy a second fluctuation-dissipation theorem. In Sec. IV we show how the results obtained in the previous sections lead to two equivalent but approximate equations of motion for the phase-space functions $A_i(\Gamma)$. These equations contain a result first proven by Kubo[16] some years ago. Furthermore, when these equations are properly averaged and compared with the phenomenological ones which contain the true Onsager's matrix for the transport coefficients, it is seen that each coefficient is equal to its bare value plus a non-Markoffian contribution arising from the nonlinear interaction amongst the collective modes. This accounts for the renormalization property. Section V is devoted to some concluding remarks and a comparison with similar and earlier work on the subject.

II. TIME EVOLUTION OF THE SYSTEM

Let $\{A_i(\Gamma)\}$ be a set of functions corresponding to the set of gross or collective variables $\{a_i\}$ chosen to describe the macroscopic state of the N-particle system. The gross variables $\{a_i\}$ are just the numerical values which appear each time we "measure" the variables $A_i(\Gamma)$ which determine the state of the system. The full physical meaning of both set of quantities has been dealt with at length in the literature.[11] From the set of phase-space functions $\{A_i(\Gamma)\}$ we construct another set $\{G(a,t)\}$ where

$$G(a,t) \equiv \delta(A(\Gamma) - a) = \prod_{k=-\infty}^{+\infty} \delta(A_k(\Gamma) - a_k), \qquad (2.1)$$

and whose meaning is associated with the position at time t of the hypercell in Γ space contained between the surfaces $S(a)$ and $S(a+da)$, $S(a)$ being defined by the set of equations $A_i(\Gamma) = a_i$ for all i. This hypercell contains all microscopic states (phase space) of the system compatible with its macroscopic state characterized by the numbers $\{a_i\}$ at a given time t. Furthermore, the meaning of A_{-k} in Eq. (2.1) corresponds to the possibility of working with the Fourier components of the A's. Then the fact that such quantities are real imposes the condition that $A_{-k} = A_k^*$.

If at time $t = 0$ the system is characterized by a set $G(a,0)$, where

$$G(a,0) = \delta(A(\Gamma_0) - a_0), \qquad (2.2)$$

its time evolution will be given by the subsequent motion of all points contained in $S(a_0)$ and will be therefore determined by Liouville's operator L. Here, $A(\Gamma_0) = A(\Gamma; t=0)$.

Consider now the Hilbert space of functions $G(a,t)$ in which an inner product may be defined as

$$(G(a), G(b)) = \langle G(a) G(b) \rangle, \qquad (2.3)$$

where the angular brackets denote an equilibrium average. Then,

$$\langle G(a) G(b) \rangle = \langle G(a) \rangle \delta(a - b). \qquad (2.4)$$

Under these conditions we may now use Mori's technique to write down the equation of motion for $G(a,t)$ as we have already indicated before. Thus,

$$\frac{dG(a,t)}{dt} = \int db\, i\Omega(a,b) G(b,t) - \int db \int_0^t K(a,b,t') G(b, t-t')\, dt' + F(a,t), \qquad (2.5)$$

where according to the general results mentioned in the Introduction, we now identify the various terms in Eq. (2.5) as follows:

$$i\Omega(a,b) = \langle G(a) \rangle^{-1} (iLG(a), G(b)), \qquad (2.6a)$$

$$F(a,t) = e^{i(1-P)Lt}(1-P) iLG(a), \qquad (2.6b)$$

and

$$K(a,b,t) = -\langle G(b) \rangle^{-1} (iLF(a,t), G(b)), \qquad (2.6c)$$

where the factors $\langle G(a) \rangle^{-1}$ are introduced because of normalization. In Eq. (2.6b) P is the projection operator in Γ space defined by Zwanzig, namely, that

$$PH(\Gamma) \equiv \langle G(a) \rangle^{-1} \int d\Gamma' [A(\Gamma) - A(\Gamma')] H(\Gamma') \rho_{eq}(\Gamma'), \qquad (2.7)$$

where $H(\Gamma)$ is any phase function and ρ_{eq} is the equilibrium distribution function.

Equation (2.5) can be simplified a bit more. Indeed Eq. (2.6a) may be evaluated using the following property of the δ function, namely, that

$$iL\delta(A(\Gamma) - a) = \frac{d}{dt} \delta(A(\Gamma) - a), = -\sum_k \frac{dA_k}{dt} \frac{\partial}{\partial a_k} \delta(A(\Gamma) - a). \qquad (2.8)$$

Then,

$$-i\Omega(a,b) = \langle G(a) \rangle^{-1} \sum_k \frac{\partial}{\partial a_k} \langle \dot{A}_k G(a) \rangle \delta(a-b). \qquad (2.9)$$

Substitution of Eq. (2.9) back into Eq. (2.5) yields

$$\frac{dG(a,t)}{dt} + \sum_k \frac{\partial}{\partial a_k} [v_k(a) G(a,t)] = -\int_0^t dt' \int db\, K(a,b,t') G(b, t-t') + F(a,t) \qquad (2.10)$$

where $v_k(a)$ is an average streaming velocity in Γ space defined by

$$v_k(a) = \langle G(a) \rangle^{-1} \langle \dot{A}_k G(a) \rangle. \qquad (2.11)$$

It is also important to remark that the force $F(a,t)$ which, according to Eq. (2.4b), contains only the projected part of $G(a)$ satisfies three important properties,

$$\langle F(a,t) \rangle = 0, \qquad (2.12a)$$

$$\langle F(a,t) G(b) \rangle = 0, \quad t > 0, \qquad (2.12b)$$

and

$$\langle F(a,t) F(b,0) \rangle = \langle G(b) \rangle K(a,b,t). \qquad (2.12c)$$

The first two properties are inherent to Mori's technique, and the third one follows from Eq. (2.6c) by writing $G(b) = (1 - P + P) G(b)$ and noticing that the product $(F(a,t), P\, iLG(b)) = 0$ because of the orthogonality of the two terms. Equation

(2.12b) states that $F(a,t)$ is statistically uncorrelated with any function of the dynamical variables $A(\Gamma)$ and not only with a linear one.

Equation (2.10) is an exact equation of motion for the G functions in Γ space, which for all practical purposes it is too complicated. In order to extract from it equations which may be used to study the macroscopic properties of the system, we shall introduce a simplification getting rid of the term which contains the time convolution in G. First, let us write it in a more convenient form. Define a quantity $R_j(t)$ as

$$R_j(t) = e^{(1-P)iLt}(1-P)iLA_j(0), \tag{2.13}$$

so that

$$F(a,t) = -e^{i(1-P)Lt}\sum_j R_j(0)\frac{\partial}{\partial a_j}\delta(A(\Gamma)-a), \tag{2.14}$$

where use has been made of Eqs. (2.6b) and (2.8). With the aid of this result, Eq. (2.12c) may be cast into the following form:

$$K(a,b,t) = \langle G(b)\rangle^{-1}\sum_{j,k}\left\langle R_k(t)\frac{\partial}{\partial a_k}\delta(A(\Gamma)-a)R_j(0) \times\frac{\partial}{\partial b_j}\delta(A(\Gamma)-b)\right\rangle. \tag{2.15}$$

Putting Eq. (2.15) back into the first term in the right-hand side of Eq. (2.10), performing an integration by parts with the b-dependent integrals, using the fact that $\delta(A(\Gamma)-a)\delta(A(\Gamma)-b) = \delta(A(\Gamma)-a)\delta(a-b)$, and carrying over the b integral, we finally obtain that

$$\frac{dG(a,t)}{dt}+\sum_k\frac{\partial}{\partial a_k}[v_k(a)G(a,t)] = \sum_{k,j}\frac{\partial}{\partial a_k}\int_0^t dt'\,\langle R_k(t')R_j(0)\rangle G(a)\rangle \times\frac{\partial}{\partial a_j}\left(\frac{G(a,t-t')}{\langle G(a)\rangle}\right)+F(a,t). \tag{2.16}$$

Equation (2.16) describes the motion in time of the hypersurface $S(a)$ in Γ space. For this reason it is too complicated if one wants to extract from it information about average values of microscopic variables which may be compared with phenomenological results. To get an approximate equation which is suitable for this purpose we shall introduce an assumption in order to dispose of the time convolution appearing in the G function in the second term of Eq. (2.16). The assumption consists in setting $G(a;t-t')$ equal to $G(a,t)$ for all times. This is, however, subtle and nontrivial because this function is not a probability distribution and so arguments invoking sharpness or slow variation in time with respect to microscopic time scales are not valid. The physical meaning of this assumption may be understood as follows: If we knew the exact equation of motion for the gross variables $\{a_i\}$ then the value of the function $G(a;t-t')$ could be obtained by computing the function $\delta(A(\Gamma)-a(t-t'))$ since this would be numerically equal to $\delta(A(\Gamma_{t-t'})-a)$. However, this is not the case. The gross variables satisfy equations of motion which are not governed by Liouville's operator. However, knowledge of these equations would allow us to compute from them the values of a_i $(i=1,2,\dots)$ at any time t. Furthermore we can think that such gross variables *do* change slowly in time for microscopic time scales and hence $a(t-t')$ can be approximately set equal to $a(t)$ for all $t'<t$. Then we can use these values of the gross variables to determine the approximate position of $S(a)$ at any time t. It is in this sense that we can understand the approximation and thus write that

$$\delta(A(\Gamma_{t-t'})-a) = \delta(A(\Gamma)-a(t-t')) \simeq \delta(A(\Gamma)-a(t)),$$

where $a(t)$ has still to be determined.

Under these conditions we now obtain an approximate equation of motion for the G functions, namely

$$\frac{dG(a,t)}{dt} = DG(a,t)+F(a,t), \tag{2.17a}$$

where D resembles a Fokker-Planck operator defined by

$$DG(a,t) = -\sum_{k=-\infty}^{+\infty}\frac{\partial}{\partial a_k}[v_k(a)G(a,t)] +\sum_{k=-\infty}^{+\infty}\sum_{j=-\infty}^{+\infty}\frac{\partial}{\partial a_k}[\langle G(a)\rangle\gamma_{kj}(a)]\frac{\partial}{\partial a_j}\left(\frac{G(a,t)}{\langle G(a)\rangle}\right) \tag{2.17b}$$

and

$$\gamma_{kj}(a) = \langle G(a)\rangle^{-1}\int_0^t dt'\,\langle R_k(t')R_j(0)G(a)\rangle. \tag{2.18}$$

From these equations it follows that $\gamma(a)$ plays the role of an a-dependent transport matrix. But Eq. (2.17a), although it resembles a Fokker-Planck equation of $G(a,t)$, is only an approximate equation of motion for the function $G(a,t)$ in Γ space under the assumption discussed above.

One can further simplify Eqs. (2.17a) and (2.17b) if we let $t\to\infty$ in the definition of $\gamma(a)$ and replace the matrix by its equilibrium average value. Thus, if we assume that

$$\gamma_{kj}(a) \simeq \gamma_{kj}^0 \equiv \langle\gamma_{kj}(a)\rangle = \int_0^\infty \langle R_k(t)R_j(0)\rangle\,dt \tag{2.19}$$

and we take for the equilibrium distribution of the G function, a Gaussian function,

$$\langle G(a)\rangle = C\exp\left(-\sum_{i=-\infty}^{+\infty} a_i^2\right), \tag{2.20}$$

where C is a constant, Eq. (2.17) trivially reduces to

$$\frac{dG(a,t)}{dt} = \hat{D}G(a,t) + F(a,t), \tag{2.21a}$$

where

$$\hat{D} \equiv -\sum_k \frac{\partial}{\partial a_k}\left(v_k(a) - \sum_j \gamma_{kj}^0 a_j\right) + \sum_{k,j} \gamma_{kj}^0 \frac{\partial}{\partial a_k}\frac{\partial}{\partial a_j}. \tag{2.21b}$$

Once more Eq. (2.21) is an approximate equation of motion for $G(a,t)$ in Γ space with a systematic part governed by the operator $\hat{D}$ given in Eq. (2.21b) and a random part which arises from a random-type force given by $F(a,t)$. Equation (2.21a) when averaged over a microcanonical ensemble and written in terms of a conditional probability in a space reduces to the Fokker-Planck equation used by Green in 1954.[17]

Summarizing, the exact equation of motion for the G functions in Γ space can be written in the two approximate versions given by Eqs. (2.17) and (2.21) which resemble but are not proper Fokker-Planck equations. However, their complete analysis still requires an additional piece of information, namely, the prescription to calculate the values of the gross variables as functions of time. This will be the subject of the following section.

III. DYNAMICS IN a SPACE

The approximation invoked in the previous section to derive the approximate equation of motion for the function $G(a,t)$ in Γ space requires that we establish the equations of motion for the gross variables $\{a_i\}$. Indeed, the solution to these equations with the prescribed initial condition [cf. Eq. (2.2)] yield the values of a_i $(i=1,2,\ldots)$ at time t through which we determine the position of $S(a)$ at time t. Such equations of motion are not known and no unique well-defined method is available to obtain them from Liouville's equation. Here we shall postulate them in an intuitive fashion.

Assume that each variable a_i is a vector in a Hilbert space with an inner product defined as follows,

$$(a_i, a_l) \equiv \langle\langle a_i\, a_l\rangle\rangle = \int da\, a_i\, a_l \langle G(a)\rangle, \tag{3.1}$$

where $\langle G(a)\rangle$ is just the equilibrium average of $G(a)$. Notice that if this average is a Gaussian, then the set $\{a_i\}$ is also orthonormal with a proper normalization constant. Now recall that from Eq. (2.17a) the operator D governs the approximate time evolution of the function $G(a,t)$ in Γ space. But such an operator arises after the time convolution in Eq. (2.10) has been neglected. Consistently we now assume that the a's obey a linear equation of motion governed by the adjoint operator of D. Thus, if $h(a)$ and $f(a)$ are two arbitrary functions which vanish in the boundaries of the a space, we define Λ, the adjoint of D, as

$$\int [\Lambda h(a)] f(a)\, da = \int h(a)[Df(a)]\, da, \tag{3.2}$$

and that

$$a_i(t) = e^{\Lambda t} a_i, \tag{3.3}$$

where $a_i = a_i(0)$.

Under these assumptions one can apply Mori's technique once more to show the equivalence between Eq. (3.3) and a linear equation in which the projected and unprojected dynamics of a_i are separated. Thus,

$$\frac{da_i}{dt} = \sum_k i a_k \tilde{\Omega}_{ik} - \sum_k \int_0^t dt'\, \psi_{ik}(t') a_k(t-t') + f_i(t), \tag{3.4}$$

where

$$i\tilde{\Omega}_{kl} = (\Lambda a_k, a_l), \tag{3.4a}$$

$$f_k(t) = e^{(1-P_a)\Lambda t}(1-P_a)\Lambda a_k, \tag{3.4b}$$

and

$$\psi_{kl}(t) = -(\Lambda f_k(t), a_l), \tag{3.4c}$$

where

$$P_a \equiv \sum_j (\ , a_j) a_j \tag{3.5}$$

is the projection operator in a space. Also, it follows from Eqs. (2.17b) and Eq. (3.2) after an integration by parts, that

$$\Lambda = \sum_k \left(v_k(a) + \sum_l \langle G(a)\rangle^{-1} \frac{\partial}{\partial a_l}[\langle G(a)\rangle \gamma_{kl}(a)]\right)\frac{\partial}{\partial a_k} + \sum_k \sum_l \gamma_{kl}(a) \frac{\partial}{\partial a_k}\frac{\partial}{\partial a_l}. \tag{3.6}$$

It is important to stress the point that Eq. (3.3) is equivalent to the linear equation $\dot{a}_k = \Lambda a_k$ and the quantities (3.4a)–(3.4c) are a direct consequence of Mori's technique. Their physical meaning will become clear in the course of their study.

Take first Eq. (3.4a). Using the definition of the inner product stated in Eq. (3.1), the form of Λ given in (3.6) and performing the integrals as-

suming that $\langle G(a)\rangle$ vanishes at the boundaries, we find that

$$i\tilde{\Omega}_{kl} = i\omega_{kl} - \gamma^0_{kl}, \tag{3.7}$$

where

$$i\omega_{kl} = \int v_k(a) a_l \langle G(a)\rangle \, da = \langle \dot{A}_k A_l \rangle \tag{3.8}$$

and

$$\gamma^0_{kl} = \langle\!\langle \gamma_{kl}(a)\rangle\!\rangle = \int \langle G(a)\rangle \gamma_{kl}(a)\, da. \tag{3.9}$$

Notice that $i\omega_{kl}$ is related to the "angular momentum" moments of the phase-space functions $\{A_i(\Gamma)\}$. The importance of these "frequencies" ω_{kl} will become clearer later. On the other hand, the γ^0_{kl} are just the averaged values in a space of the a-dependent quantities $\gamma_{kl}(a)$, which are identical to those introduced in Eq. (2.19).

With Eq. (3.7), Eq. (3.4) reduces to the following form:

$$\frac{da_i}{dt} = \sum_k (i\omega_{ik} - \gamma^0_{ik}) a_k - \sum_k \int_0^t dt' \, \psi_{ik}(t') a_k(t-t') + f_i(t). \tag{3.10}$$

Let us now consider the properties of $f_k(t)$ and the possible connection between the correlation function of f_k in a space and the memory kernel ψ_{kl} which is not explicit in Eq. (3.4c).

Notice first that by arguments analogous to those used in the previous case, and because of the structure of $f_k(t)$, we can immediately conclude that

$$\langle\!\langle f_k(t)\rangle\!\rangle = 0 \tag{3.11a}$$

and

$$\langle\!\langle f_k(t) a_l(0)\rangle\!\rangle = 0, \tag{3.11b}$$

meaning that $f_k(t)$ is statistically uncorrelated with any *linear* function of the a's.

The third property should come out of Eq. (3.4c). Using Eqs. (3.1) and (3.2), we see that

$$\psi_{kl}(t) = -\langle\!\langle \Lambda f_k(t) a_l \rangle\!\rangle = -\langle\!\langle f_k(t) \langle G(a)\rangle^{-1} D[a_l \langle G(a)\rangle]\rangle\!\rangle. \tag{3.12}$$

Noticing that

$$P_a \langle G(a)\rangle^{-1} D[\langle G(a)\rangle a_l] = -\sum_r (i\omega_{lr} + \gamma^0_{lr}) a_r,$$

one can add and subtract this quantity from the term inside the angular brackets in Eq. (3.12) because of property (3.11b) for $f_k(t)$. This allows one to rewrite Eq. (3.12) in the following way,

$$\psi_{kl}(t) = -\langle\!\langle f_k(t)(1-P_a)\langle G(a)\rangle^{-1} D[a_l \langle G(a)\rangle]\rangle\!\rangle. \tag{3.13}$$

But it is a matter of a straightforward computation to show that

$$(1-P_a)\langle G(a)\rangle^{-1} D[a_l \langle G(a)\rangle] = (1-P_a) v_l(a). \tag{3.14}$$

Furthermore, $(1-P_a)v_l(a)$ is the projected part of the average velocity $v_l(a)$ and it is trivial to show by direct use of Eq. (3.5) that

$$(1-P_a) v_l(a) = v_l(a) - \sum_r i\omega_{lr} a_r \equiv v'_l(a) \tag{3.15}$$

or that the projected part of $v_l(a)$ contains all the terms representing nonlinear interactions amongst the gross variables. Thus, the memory kernel $\psi_{kl}(t)$ depends on these nonlinear interactions since by Eqs. (3.13), (3.14) and (3.15) we see that

$$\psi_{kl}(t) = \langle\!\langle f_k(t) v'_l(a)\rangle\!\rangle. \tag{3.16}$$

It remains to show that $v'_l(a)$ is somehow related to $f_l(0)$ to complete the interpretation. This is also a simple matter. Indeed,

$$f_l(0) = (1-P_a)\Lambda a_l = \Lambda a_l - \sum_r \langle\!\langle \Lambda a_l, a_r\rangle\!\rangle a_r, = v'_l(a) + \sum_r \left(\langle G(a)\rangle^{-1} \frac{\partial}{\partial a_r} [\langle G(a)\rangle \gamma_{lr}(a)] + \gamma^0_{lr} a_r \right). \tag{3.17}$$

If we now assume that $\gamma_{lm}(a)$ may be replaced by γ^0_{lm} everywhere and use Eq. (2.20) for $\langle G(a)\rangle$, the second term in Eq. (3.17) vanishes identically and $f_l(0)$ is given by the term $v'_l(a)$ containing *all* the nonlinear terms in the a variables. Hence,

$$\psi_{kl}(t) = \langle\!\langle f_k(t) f_l(0)\rangle\!\rangle. \tag{3.18}$$

Summarizing, Eq. (3.10) is the linear equation of motion satisfied by the vectors $\{a_i\}$ in a space, the term $f_k(t)$ containing all of its projected dynamics. The solution to this equation is used to determine the approximate equation of motion for the function $G(a,t)$ in Γ space. Under the approximation that $\gamma_{kl}(a)$ may be everywhere replaced by its average value γ^0_{kl} and $\langle G(a)\rangle$ is a Gaussian function, which means that the operator D reduces to $\hat{D}$, the time equation for $a_i(t)$ becomes one in which the fluctuating force $f_k(t)$ arises only from the nonlinear interactions amongst the a's. These nonlinear interactions manifest themselves in the memory kernel $\psi_{kl}(t)$ through the second fluctuation-dissipation theorem given by Eq. (3.18). This property may be also obtained by direct substitution of Eq. (3.15) into Eq. (3.8a) yielding

$$\int v'_k(a) a_k \langle G(a)\rangle \, da = 0, \tag{3.19}$$

which implies that $v'_k(a)$ cannot contain terms linear in the a's.

These results will be used in the following section to obtain two equivalent equations for the phase-space functions $A_i(\Gamma)$ which in turn will lead us to the renormalization of the transport coefficients.

IV. MACROSCOPIC VARIABLES

In the previous sections we have obtained two relevant results. Firstly, an equation of motion for the hypercells $S(a)$ in Γ space which is approximate in the sense that its time evolution is determined through the values of the gross variables $\{a_i\}$ at time t. If one imposes the additional restriction that the matrix $\underline{\gamma}(a)$ can be substituted by its equilibrium value, then the resulting expression is given in Eq. (2.21). Secondly, the prescription for calculating $a(t)$ through a linear equation governed by the Fokker-Planck operator $\hat{D}$ led us to Eq. (3.10) which contains a random force $f_k(t)$ which under the same restriction for $\underline{\gamma}(a)$ as above, obeys the second fluctuation-dissipation theorem and arises solely from the nonlinear interaction amongst the a's. In this sense, Eqs. (3.10) and (2.21) are equivalent, they describe the time evolution of the state of the system in Γ space and in a space. Now we can use these facts to relate these descriptions with the time behavior of the phase-space functions $A_i(\Gamma)$ themselves. Indeed we can obtain two equations for these quantities which contain the same information, that is, in the above sense, are equivalent.

Indeed, we first notice that because of Eq. (2.1) one has trivially that

$$A_i(\Gamma) = \int da\, \delta(A(\Gamma) - a) a_i . \tag{4.1}$$

Next, we may derive an approximate equation of motion for $A_i(\Gamma)$ if we multiply Eq. (3.10) by $G(a,t)$ and integrate over the whole a space. This leads to

$$\frac{dA_k}{dt} = \sum_l (i\omega_{kl} - \gamma^0_{kl}) A_l - \sum_l \int_0^t dt'\, \psi_{kl}(t') A_l(t - t') + L_k(t), \tag{4.2}$$

where

$$L_k(t) = \int da\, G(a,t) f_k(t). \tag{4.3}$$

Equation (4.2) is a generalized Langevin-type equation for the bare or unaveraged macroscopic phase function $A_k(\Gamma)$ with a fluctuating force $L_k(t)$. As it is shown in the Appendix, this force satisfies the usual conditions, namely, that

$$\langle L_k(t) \rangle = 0, \tag{4.4a}$$

$$\langle L_k(t) A_m \rangle = 0, \quad t > 0, \tag{4.4b}$$

and

$$\langle L_k(t) L_m(t') \rangle = \psi_{km}(t - t'). \tag{4.4c}$$

The third condition states that the memory the system keeps due to the action of the fluctuating force, is not an instantaneous one. The fluctuating force satisfies the second fluctuation-dissipation theorem, and the memory stems solely from the nonlinear interactions among the A's.

On the other hand, from Eq. (2.21a) one can also obtain an equation of motion for $A_i(\Gamma)$. In fact, after multiplication by a_k and integration over the a space, we get that

$$\frac{dA_k}{dt} = v_k(A) - \sum_l \gamma^0_{kl} A_l + R_k(t) \tag{4.5}$$

where

$$R_k(t) = \int da\, a_k F(a,t) \tag{4.6}$$

and

$$v_k(A) = \left(\frac{dA_k}{dt}\right)_{A=a}. \tag{4.7}$$

Equation (4.6) follows directly from Eqs. (2.13) and (2.14), and represents the random force in a space arising from the projected dynamics of the G functions in Γ space. Thus, it could be understood as a random force which affects the motion of the phase-space function $A_i(\Gamma)$ arising from microscopic fluctuations. Equation (4.7) is just the time derivative of A_k lying on the hypersurface $S(a)$.

Equation (4.5) is a nonlinear Langevin-type equation for the A's with an instantaneous memory kernel and thus a fluctuating force that satisfies the first fluctuation-dissipation theorem. In fact, Eq. (2.19) is consistent with Eq. (4.5) if

$$\langle R_k(t) R_j(0) \rangle = 2\gamma^0_{kj}\, \delta(t). \tag{4.8}$$

Furthermore $v_k(A)$ is the average value over the hypersurface $S(a)$ of $v_k(a)$ and this latter function contains all linear and nonlinear terms in the a's [cf. Eq. (3.15)]. Hence all nonlinear terms in the A's which appear in Eq. (4.5) must be contained in the expression for $v_k(A)$.

Thus, we have shown that a linear equation for the time evolution of the phase functions A with a fluctuating force satisfying the second fluctuation-dissipation theorem is equivalent to a nonlinear equation with a fluctuating force which obeys the first fluctuation-dissipation theorem. This equivalence was first pointed out by Kubo.[16] Clearly, the quantities γ^0_{kl} appearing in both equations are the bare transport coefficients.[9,12]

In order to compare these results with the macroscopic equations obeyed by the time correlation functions corresponding to the gross variables, we first prove an important property for the phase functions A. If we formally solve Eq. (2.21a) for $G(a,t)$, multiply the result by a_k, and integrate over a, we find that

$$A_k(t) = \int a_k(t) G(a_0)\, da + \int_0^t dt' \int da\, a_k(t-t') F(a,t'), \tag{4.9}$$

where $A_k(t) = A_k(\Gamma;t)$, $G(a_0) = \delta(A(\Gamma) - a_0)$, the initial value of the G functions, and use has been made of Eq. (3.2).

This result shows that the time dependence of the phase function $A_k(\Gamma)$ corresponding to the gross variable a_k, has a systematic component in phase space which is governed in time by the Fokker-Planck-like operator $\hat{D}$, and a random component which arises from the projected part of its motion and is characterized by the microscopic fluctuations.

The sought comparison can be now achieved in a straightforward manner. Indeed,[15] one can define the time correlation function of the phase-space quantities $A_k(\Gamma)$, say

$$C_{km} = \langle A_k(t) A_m(0) \rangle, \tag{4.10}$$

and use Eq. (4.9) together with Eq. (2.12b) to show that this expression is identical to the time correlation function for the corresponding gross variables. Thus,

$$\langle A_k(t) A_m(0) \rangle = \langle a_k(t) a_m(0) \rangle. \tag{4.11}$$

Next, two equations for the time change of $C_{km}(t)$ can be readily obtained. One arises from Eq. (4.2) after multiplication by $A_m(0)$ and averaging over an equilibrium ensemble. Thus, we obtain that

$$\frac{dC_{km}}{dt} = \sum_l i\omega_{kl} C_{lm} - \sum_l \int_0^t dt'\, \varphi_{kl}(t') C_{lm}(t-t'), \tag{4.12}$$

where $\varphi_{kl} = \psi_{kl} + 2\gamma^0_{kl}\,\delta(t)$.

The other equation follows from a straightforward application of Mori's theorem to the equation of motion obeyed by the space function $\{A_i(\Gamma)\}$. Indeed, since

$$\frac{dA_i}{dt} = iLA_i, \quad i = 1, 2, \ldots, \tag{4.13}$$

one can immediately show that

$$\frac{dA_i}{dt} = \sum_j i\omega_{ij} A_j - \sum_j \int_0^t dt'\, L_{ij}(t') A_j(t-t') + F_{\text{fluct}}, \tag{4.14}$$

where $\underline{L}$ is the correct Onsager's matrix for the phenomenological coefficients, and F_{fluct} is the fluctuation force. Following the same procedure as above, noting that $\langle A_k F_{\text{fluct}} \rangle = 0$, one gets that

$$\frac{dC_{km}}{dt} = \sum_l i\omega_{kl} C_{lm} - \sum_l \int_0^t dt'\, L_{kl}(t') C_{lm}(t-t'). \tag{4.15}$$

Since Eqs. (4.12) and (4.15) must be identical, we see that after a Laplace transformation

$$L_{kl}(i\omega) = 2\gamma^0_{kl} + \psi_{kl}(i\omega), \tag{4.16}$$

which means that the true transport coefficient $L_{kl}(i\omega)$ consists of two terms, a rapidly decaying one which is twice the value of the "bare" transport coefficient γ^0_{kl} plus another term which is non-Markoffian and arises from the nonlinear interactions amongst the gross variables $\{a_i\}$. Here,

$$L_{kl}(i\omega) = \int_0^\infty e^{i\omega t} L_{kl}(t)\, dt. \tag{4.17}$$

Equation (4.16) is the sought result. The main advantages of its derivation is that the slowly decaying non-Markoffian term $\psi_{kl}(t)$ has a closed analytical form in the space of the gross variables as indicated by Eq. (3.18). One can then find its time dependence if the term $v'_l(a)$ containing the nonlinear interactions is known. At this stage, however, this question plays the essential role for this theory to be compared with experiment. From our present knowledge of real systems it remains unanswered. Yet, as we shall see shortly some information can be obtained under certain assumptions. But these results should be taken more as speculative than as indicative of how nature behaves.

V. CONCLUDING REMARKS

Mori's powerful technique which allows one to obtain linear equations of motion for sets of functions obeying prescribed properties, in terms of the projected and unprojected dynamics in a Hilbert space, has been used to derive several results whose meaning we will now emphasize.

Firstly, Eq. (2.10), which is exact, and Eq. (2.16) are equations of motion for the G functions in phase space. They are not equivalent in content, although similar in structure, to those derived by Zwanzig in 1961[11] or by Kawasaki about ten years later.[18] These authors obtain exact equations of motion for the probability distributions of the gross variables, namely, for

$$g(a,t) = \int G(a,t)\, \rho(\Gamma,t)\, d\Gamma, \tag{5.1}$$

where $\rho(\Gamma; t)$ is the time-dependent phase-space distribution function. Thus, the time equations for the g functions are given in the space of gross variables $\{a\}$ and not in Γ space.

If we multiply Eq. (2.16) by $\rho(\Gamma; t)$ and integrate over Γ, we get that

$$\frac{dg(a,t)}{dt}+\sum_k \frac{\partial}{\partial a_k}[v_k(a)\,g(a;t)] = \sum_{j,k}\frac{\partial}{\partial a_k}\int_0^t dt'\,\langle R_j(0)\,R_k(t')G(a)\rangle \frac{\partial}{\partial a_j}\left(\frac{g(a,t-t')}{\langle G(a)\rangle}\right)+\langle F(a,t)\rangle, \tag{5.2}$$

where

$$\langle F(a,t)\rangle = \int d\Gamma\,\rho(\Gamma,t)\,F(a,t), \tag{5.3}$$

which is identical to the equation derived by Zwanzig and Kawasaki after their diagonalization assumption has been used [cf. Eq. (30) in Ref. 11, and Eq. (2.17) in Ref. 18] and one neglects the ensemble average of the fluctuating force given by Eq. (5.3). It is worth stressing that Eq. (5.2) results without the necessity of arguing the diagonality in a space of the memory term found by the previous authors.

Of course, after this identification has been made, the remaining approximate equations for the g functions obtained from this formalism coincide with those obtained by Zwanzig and Kawasaki.

Secondly, it is convenient to remark that the averaged gross variables, defined by Zwanzig and Kawasaki as the first moments of the gross variable distribution function $g(a,t)$, would correspond to the phase-space or ensemble average of the phase functions as given by Eq. (4.1). Thus,

$$\alpha_j(t) = \int a_j\,g(a,t)\,da = \int da\,a_j\int\delta(A(\Gamma)-a)\,\rho(\Gamma,t)\,d\Gamma. \tag{5.4}$$

Although these are the quantities appearing in the phenomenological laws of irreversible thermodynamics which contain the transport matrix $\underline{L}$, we have made no use of them in the renormalization analysis because we worked directly with the time correlation functions for the phase-space functions. Yet it is important to stress here that such equations may be obtained directly from Eq. (4.9) if we average over an initial phase-space distribution consistent with the constraints imposed on the system. This would lead to transport equations of the same structure as those obtained by Zwanzig [cf. Eq. (36) of Ref. 11] whose relation with the ordinary Onsager equation is well known.

Finally, it is worth emphasizing the significance of the structure of the memory kernel $\psi_{kl}(t)$ responsible for the non-Markoffian behavior of the transport coefficients. From Eqs. (3.18), (3.17), and (3.4b) one can see that

$$\psi_{kl}(t) = \int da\,\langle G(a)\rangle\,v_k'(a)e^{(1-P_a)\Lambda t}v_l'(a). \tag{5.5}$$

If one knows the expression for $v_k'(a)$, then this quantity can be computed, in principle, in a closed form. As it was pointed out before, the main problem lies in how to select the nonlinear interactions amongst the gross variables. If one assumes that $\psi_{kl}(t)$ is diagonal, that

$$v_k'(a) = \sum_p{}' V_{kp}\,a_p\,a_{k-p} \tag{5.6}$$

where $|V_{kp}|^2 \sim k^x p^y$, the prime in the summation excluding short-wavelength components (the k's denoting wave vectors) and taking for the bare transport properties appearing in Λ a quadratic dependence on p, one finds that[15]

$$\psi_k(t) \simeq k^x\,t^{-(d+y)/2}, \tag{5.7}$$

which is the well-known result obtained in computer experiments for systems in two dimensions and from the many theoretical analysis referred to in the Introduction.[8]

The question we want to raise here is concerned with a deeper point. Do real systems satisfy the assumptions made to arrive at Eq. (5.7)? It is clear that for other forms of $v_k'(a)$ or different k and p dependence of the coupling constants V_{kp}, as well as the inclusion of other terms, the results would be different. Thus, for various sets of assumptions we would very likely get various results. Which one of them is correct depends on the experiment and so far, in three dimensions the importance of the logarithmic term in the density appearing in the virial expansion of transport coefficients which ultimately arises from this non-Markoffian term, has been found to be unimportant, if not altogether negligible. Therefore, it would be rather useful to devise a method such that it would allow us to obtain a guide for establishing the appropriate rules for evaluating expressions like Eq. (5.5) to avoid extensive meaningless mathematical manipulations. At this present stage we are unable to do so but we hope the problem will become more accessible in the future.

Note added in proof. It has been brought to our attention by J. L. del Río that in a recent paper, Mori *et al.* [Prog. Theor. Phys. 51, 109 (1974)] have shown Eq. (2.16) to be a first approximation of a more general result. The nature of this approximation as well as its implications within the context of this paper will be discussed elsewhere.

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APPENDIX

In this appendix we shall sketch the proof of Eqs. (4.4a)–(4.4c) given in the text, containing some relevant properties of the fluctuating force $L_k(t)$.

Using Eq. (4.3), which defines this quantity, we see immediately that

$$\langle L_k(t)\rangle = \int da \int d\Gamma\, \rho_{eq}(\Gamma)\delta(A(\Gamma)-a) f_k(t)$$

$$= \int da\, f_k(t)\langle G(a)\rangle = 0$$

because of Eq. (3.11a).

Also,

$$\langle L_k(t) A_m\rangle = \int da \int d\Gamma\, \rho_{eq}(\Gamma)\delta(A(\Gamma)-a) f_k(t) \times \int da'\, \delta(A(\Gamma)-a')\, a'_m,$$

which by reordering the integrals and use of Eq. (4.1) reduces to

$$\langle L_k(t) A_m\rangle = \int da \int da'\, f_k(t)\delta(a-a')a'_m \times \int \delta(A(\Gamma)-a)\rho_{eq}(\Gamma)\, d\Gamma$$

$$= \int da\, f_k(t) a_m \langle G(a)\rangle = 0$$

because of Eq. (3.11b).

Finally, by a similar procedure we find that

$$\langle L_k(t) L_m(0)\rangle = \int d\Gamma\, \rho_{eq}(\Gamma) \int da\, \delta(A(\Gamma)-a) f_k(t) \times \int da'\, \delta(A(\Gamma)-a') f_m(0)$$

$$= \int da\, f_k(t) f_m(0)\langle G(a)\rangle,$$

and

$$\langle L_k(t) L_m(0)\rangle = \psi_{km}(t),$$

which is the second fluctuation-dissipation theorem. This last equality follows from Eq. (3.18) and is only valid under the corresponding approximations for which such result holds.

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*On leave of absence.

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