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A Unified Approach for Deriving Kinetic Equations in Nonequilibrium Statistical Mechanics. I. Exact Results

Leopoldo S. García-Colín[1,2] and Jose Luis del Rio[3,4]

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A unified method for deriving exact kinetic equations for dynamical quantities of a many-body system is presented. The well-known results of Mori and Zwanzig are recovered as special cases. Furthermore, it is shown that they differ only by the way in which the system is prepared at the initial time. Connections between this method and others recently developed are also discussed.

KEY WORDS: Linear and nonlinear transport equations; generalized Langevin equation; kinetic equation; coarse-grained (mesoscopic) variables; projection operators; generalized projection operator; correlation function; memory function; Fokker–Planck operator.

1. INTRODUCTION

In recent years several attempts have been made to obtain the macroscopic transport equations that govern the time evolution of a many-body system starting from first principles.[1] Among these it is worth emphasizing those of Zwanzig[2] and Mori,[3] which made wide use of the projection operator technique introduced by Zwanzig.[4] In Ref. 2 a rigorous derivation of a kinetic equation was accomplished starting from Liouville's equation, from which nonlinear transport equations were obtained.[5,6] In Ref. 3 the time evolution of the phase space functions describing the states of the system were studied and it was found that the time evolution equation has the form

[1] Department of Physics and Chemistry, Universidad Autónoma Metropolitana, Iztapalapa, México.
[2] Faculty of Sciences, Universidad Nacional Autónoma de México, México.
[3] School of Higher Studies in Physics and Mathematics IPN, Zacatenco, México.
[4] Fellowship of COFAA-IPN.

of a generalized Langevin equation from which linear transport equations may be derived.

Recently, Nordholm and Zwanzig[7] obtained a unified derivation of both the kinetic equation and the Langevin-type equation found by Mori, using Liouville's equation and using nonlinear projection operators. From this method they extracted nonlinear Langevin-type equations for the coarse-grained (or mesoscopic) variables and showed how to obtain an exact kinetic equation for the coarse-grained distribution function.

Independently, Mori *et al.*[8] followed an alternative procedure to derive a similar kinetic equation starting from the time evolution equation of a cell defined in phase space by the numerical values of the relevant phase space functions.[9] They also managed to cast this kinetic equation in terms of a power series expansion in a "slowness" parameter and applied it to the study of nonlinear processes. Yet, the relationship between the two methods is not clear at all, nor is it explicit in their own structure.

The purpose of this work is twofold. First, we present a unified method for deriving this type of result starting only from the scanty knowledge that one has about the initial distribution function and the dynamics in phase space. Second, we show that both the Zwanzig and Mori *et al.* results are special cases of this scheme, which depend *only* on how the system was prepared at the initial time $t = 0$. Lastly, we point out that all the results derived here are exact and will be used for extracting some interesting applications in future papers.

Section 2 is devoted to a review of a set of general definitions and concepts which will be of continuous use. Here it is stressed that in Zwanzig's scheme the time dependence is in the phase space distribution function, whereas the observables characterized by the set of phase space functions $\{A(\Gamma)\}$ do not depend explicitly on time. On the other hand, in Mori's scheme these functions are time dependent and are averaged over time-independent initial distribution functions. We also construct the generalized projector operator, which will yield a general exact kinetic equation for various quantities, namely the hypercell defined in phase space by the numerical values of the functions $\{A(\Gamma)\}$, a correlation function defined with appropriate vectors, and finally the coarse-grained or mesoscopic distribution function $g(a, t)$.[2] The exact kinetic equations for these quantities are derived in Section 3. Finally, in Section 4 the generalized projector operator derived in Section 3 is shown to be equivalent to various forms leading to the results obtained by the aforementioned authors.

2. DEFINITIONS

Consider a many-particle system which at time zero is prepared in a constrained equilibrium state. By removing some of these constraints the

system is allowed to relax to a new equilibrium state. This process is described macroscopically through the transport equations, which are known from phenomenological theories. To derive these equations from the equations of motion obeyed by each particle in the system is a more difficult question. To undertake this task, let us assume that to each macroscopic observable $\alpha_j(t)$ ($j = 1,...$) there corresponds a phase function $A_j(\Gamma)$ such that

$$\alpha_j(t) = \int \rho(\Gamma, t) A_j(\Gamma)\, d\Gamma \tag{1}$$

where $\rho(\Gamma, t)$ is the probability density defined in Γ space at time t and Γ is a short-hand notation for a point in this space, $\Gamma \equiv (\mathbf{q}, \mathbf{p})$. Thus, if one knows what the time evolution equation for ρ is, he can in principle find the time rate equations for the macroscopic variables. One way of accomplishing this is by recasting Liouville's equation, which is satisfied by ρ, into an appropriate form. This is the approach followed by Zwanzig and Nordholm.[2,7] Alternatively, one can study the equation of motion satisfied by $A_j(\Gamma)$. Indeed, since formally

$$\rho(\Gamma, t) = e^{-iLt}\rho(\Gamma, 0) \tag{2}$$

where $\rho(\Gamma, 0)$ is the initially constrained probability distribution and L is Liouville's operator, one can easily see that

$$\alpha_j(t) = \int \rho(\Gamma, 0) A_j(\Gamma, t)\, d\Gamma \tag{3}$$

where

$$A_j(\Gamma, t) = e^{iLt} A_j(\Gamma, 0) \tag{4}$$

Equation (3) shows that if we know the time behavior of A_j, then we can obtain the time-dependent macroscopic variables. This method has been followed by Mori.[3]

Whichever scheme we follow, it is important to have a knowledge of the distribution function $\rho(\Gamma, 0)$. However, our experimental information about the system is clearly very restricted to comply with this fact. At most, what we know are the first two moments of the distribution, namely, that

$$\int \rho(\Gamma, 0)\, d\Gamma = 1 \tag{5}$$

$$\int \rho(\Gamma, 0) A_j(\Gamma)\, d\Gamma = \alpha_{0j} \tag{6}$$

α_{0j} being the macroscopic variables at the initial time. Thus, more information will be required, usually such that $\rho(\Gamma, 0)$ maximizes the Gibbs H function.[3,7]

In order to establish a link between the macro and microscopic descriptions of the system, needed, for instance, to account for fluctuations around

the macroscopic variables, we will introduce the so-called mesoscopic variables (or coarse-grained variables) $\{a_j\}$. These are the numerical values of the phase functions $A_j(\Gamma)$ and will be regarded in their own status as stochastic variables. This implies that the time evolution in the mesoscopic level may be described either by (a) stochastic differential equations with a structure similar to that of Langevin's equation used in Brownian motion; or (b) kinetic equations describing the time evolution of a distribution function $g(\mathbf{a}, t)$ for the a variables. This function is so defined that $g(\mathbf{a}, t)\, d\mathbf{a}$ is equal to the probability that at time t, $A_j(\Gamma)$ has a value a_j within a range da_j for all j.

Following the latter description introduced by Zwanzig,[2] we immediately notice that $g(\mathbf{a}, t)$ can be found from a knowledge of $\rho(\Gamma, t)$. In fact,

$$g(a, t)\, d\mathbf{a} = \int_{\mathbf{a} \le A(\Gamma) \le \mathbf{a} + d\mathbf{a}} \rho(\Gamma, t)\, d\Gamma = \left[\int \rho(\Gamma, t) G(\mathbf{a}, 0)\, d\Gamma \right] d\mathbf{a} \tag{7}$$

where

$$G(\mathbf{a}, 0) = \delta[A(\Gamma) - \mathbf{a}] = \prod_j \delta[A_j(\Gamma) - a_j] \tag{8}$$

If one wants to think of the A_j as the Fourier components of observables for ordinary systems, e.g., fluids, magnets, etc., such as the particle momentum or energy density, then j can take positive and negative values and $A_{-j}(\Gamma, 0) = A_j^*(\Gamma, 0)$. Equation (8) determines a hypercell at time $t = 0$ in Γ space, whose physical significance has been discussed earlier.[9]

An alternative equation for $g(\mathbf{a}, t)$ can be found in terms of $A(\Gamma, t)$. Indeed, from Eqs. (2) and (7) we see that

$$g(\mathbf{a}, t) = \int \rho(\Gamma, 0) G(\mathbf{a}, t)\, d\Gamma \tag{9}$$

where $G(\mathbf{a}, t) = e^{iLt} G(\mathbf{a}, 0)$.

Thus, both the transport equations for the macroscopic variables and the kinetic equation for $g(\mathbf{a}, t)$ may be investigated following either Zwanzig's or Mori's approach starting in either case with knowledge of the phase space distribution function $\rho(\Gamma, 0)$.

To finish the general review of definitions, it is relevant to point out that $G(\mathbf{a}, t)$ is also related to $A_j(\Gamma)$, since, trivially,

$$A_j(\Gamma, t) = \int a_j G(\mathbf{a}, t)\, d\mathbf{a} \tag{10}$$

and, furthermore, from Eqs. (3), (9), and (10) we find that

$$\alpha_j(t) = \int g(\mathbf{a}, t) a_j\, d\mathbf{a} \tag{11}$$

The macroscopic variables are the first moments of the distribution function $g(\mathbf{a}, t)$.

Thus, two different situations arise. In one, which we shall call the Zwanzig scheme (ZS), all the time dependence of the varying quantities is contained in $\rho(\Gamma, t)$. To the observables $\alpha_j(t)$ and $g(\mathbf{a}, t)$ in the macro and mesoscopic levels one associates phase functions $A_j(\Gamma)$ and $G(\mathbf{a}, 0)$, respectively, which are time independent. In the other one, referred to as the Mori scheme (MS), one studies the explicit time dependence of the phase functions $A_j(\Gamma)$ if one is interested in transport properties, or of the phase functions $G(\mathbf{a}, t)$ if one is interested in kinetic equations. In both cases the phase space distribution function $\rho(\Gamma, 0)$ does not depend on time.

Following the ideas set forth by Zwanzig and Nordholm,[7] we shall derive exact kinetic equations for the quantities $g(\mathbf{a}, t)$ and $G(\mathbf{a}, t)$ described above. For this purpose we begin by constructing a Hilbert space of functions of Γ following the steps which are clearly indicated in Ref. 7.

Thus,

$$(A, B) = \int d\Gamma\, w(\Gamma) A(\Gamma) B^*(\Gamma) \tag{12}$$

where the asterisk stands for complex conjugation and $w(\Gamma)$ is the metric of the space. This space will be denoted $H_g(w|\Gamma)$. Also, we shall require that this metric is time independent, so that

$$iLw(\Gamma) = 0 \tag{13}$$

Using these definitions, we see that in the ZS we can write for the mesoscopic observables $g(\mathbf{a}, t)$ that

$$g(\mathbf{a}, t) = (G(\mathbf{a}, 0), \nu(\Gamma, t)) \tag{14}$$

where we have written $\rho(\Gamma, t) = \nu(\Gamma, t) w(\Gamma)$, which for a given metric defines the phase space function $\nu(\Gamma, t)$. Notice that

$$\dot{\nu}(\Gamma, t) = -iL\nu(\Gamma, t) \tag{15}$$

as follows from Eq. (13) and Liouville's equation.

As it is well known,[7] the stationary condition imposed on $w(\Gamma)$ implies that L is Hermitian in $H_g(w|\Gamma)$, or that

$$(A, LB) = (LA, B) \tag{16}$$

This property will allow us to switch from Zwanzig's scheme to Mori's scheme because from the formal solution to Eq. (15) we can easily see that Eq. (14) may be rewritten as

$$g(\mathbf{a}, t) = (G(\mathbf{a}, t), \nu(\Gamma, 0)) \tag{17}$$

which is precisely Eq. (9), the equation for $g(\mathbf{a}, t)$ in Mori's scheme.

Notice should be made of the fact that one of the advantages of expressing an observable like $g(\mathbf{a}, t)$ as an inner product is that it is unnecessary to have knowledge of the complete $\nu(\Gamma, t)$ function in ZS or of $G(\mathbf{a}, t)$ in MS to calculate the observable $g(\mathbf{a}, t)$. For this purpose let $H_G(w|\Gamma)$ be the subspace spanned by the set of vectors $G(\mathbf{a}, 0)$ for all possible values of the vector $\mathbf{a}$. Let P_G be a projection operator defined in such a way that if applied to a vector in H_g, it generates a vector in the subspace H_G. Schematically,

$$P_G H_g(w|\Gamma) = H_G(w|\Gamma)$$

We propose for P_G the explicit form

$$P_G = \int d\mathbf{b} \frac{(\ldots, G(\mathbf{b}, 0))}{[G(\mathbf{b}, 0)]} G(\mathbf{b}, 0) \tag{18}$$

where

$$[G(\mathbf{b}, 0)] = \int d\Gamma\, w(\Gamma) G(\mathbf{b}, 0) \tag{19}$$

Following from the definition of inner product, one has that

$$(G(\mathbf{a}, 0), G(\mathbf{b}, 0)) = [G(\mathbf{b}, 0)]\, \delta(\mathbf{a} - \mathbf{b}) \tag{20}$$

It follows at once from the definition of P_G that it is indeed a projection operator, namely that

$$P_G{}^2 H_g(w|\Gamma) = P_G H_g(w|\Gamma) \tag{21}$$

and that it is Hermitian,

$$(A, P_G B) = (P_G A, B) \tag{22}$$

Furthermore, it is trivial to see that

$$P_G G(\mathbf{a}, 0) = G(\mathbf{a}, 0) \tag{23}$$

With the aid of Eqs. (22) and (23), Eq. (14) may be written as

$$g(\mathbf{a}, t) = (G(\mathbf{a}, 0), P_G \nu(\Gamma, t)) \tag{24}$$

and this proves that to calculate $g(\mathbf{a}, t)$ one only needs to know the part of $\nu(\Gamma, t)$ that is in $H_G(w|\Gamma)$.

Using the definition of P_G, we can also write that

$$\nu(\Gamma, 0) = \int d\mathbf{b} \frac{g(\mathbf{b}, 0) G(\mathbf{b}, 0)}{[G(\mathbf{b}, 0)]} + (1 - P_G)\nu(\Gamma, 0) \tag{25}$$

which clearly displays how from the information contained in the mesoscopic observable $g(\mathbf{b}, 0)$ at $t = 0$ we can only learn about the part of $\nu(\Gamma, 0)$ that is

in $H_G(w|\Gamma)$. The projected part $(1 - P_G)\nu(\Gamma, 0)$ will be arbitrarily dropped out by assuming that

$$\nu(\Gamma, 0) = P_G\nu(\Gamma, 0) \tag{26}$$

This assumption is of a fundamental nature. It is analogous to the random phase approximation introduced to obtain the quantum master equation[11] and is used by Mori and Zwanzig in a manner which will be discussed later.

To finish with the properties of our projector P_G, it is important to emphasize that although it is linear in the vectors $G(\mathbf{a}, t)$ as shown by Eq. (23), it is a nonlinear one for arbitrary phase functions. Indeed, if $f(\Gamma)$ is an arbitrary phase function,

$$P_G f(\Gamma) = \int d\mathbf{b} \frac{(f(\Gamma), G(\mathbf{b}, 0))}{[G(\mathbf{b}, 0)]} G(\mathbf{b}, 0) = f(A(\Gamma)) \tag{27}$$

which is the value of f depending only on the phase space variables through $A(\Gamma)$. In order to show this, it is sufficient to examine the structure of the integral

$$P_G f(\Gamma) = \frac{\int d\Gamma'\, w(\Gamma')\, \delta[A(\Gamma') - A(\Gamma)] f(\Gamma')}{\int d\Gamma'\, w(\Gamma')\, \delta[A(\Gamma') - A(\Gamma)]} \tag{28}$$

and so to notice that the above statement follows directly. In the form given by Eq. (28), it is a generalization of Zwanzig's projector, which is defined with $w(\Gamma) = 1$. As a side note, if $w(\Gamma) = \rho_{eq}(\Gamma)$, then P_G reduces to the projector used by Mori *et al.*[8] to derive kinetic equations and by others to study the nonlinear dynamics of stochastic variables.[9,10] This latter choice implies that

$$\rho(\Gamma, 0) = p_{eq}(\Gamma)\nu(\Gamma, 0) \tag{29}$$

so that at time $t = 0$ the system is in a state which is close to the final equilibrium state.

The foregoing discussion clarifies the fact that although $P(w(\Gamma) = 1)$ and $P_Z(w(\Gamma) = \rho_{eq})$ are similar in structure, they correspond to different physical preparations of the system at $t = 0$.

The property of P_G shown by Eq. (27) implies that our basic assumption contained in Eq. (26) consists in asserting that the distribution function $\rho(\Gamma, 0)$ at the initial time is only a function of the phase functions $\{A_j(\Gamma)\}$, if we include the integrals of motion in the set $\{A_j(\Gamma)\}$.

3. KINETIC EQUATIONS

This section will be devoted to the derivation of exact kinetic equations first using Mori's scheme and then using Zwanzig's scheme.

To accomplish our goal, we start from Eq. (17), which, after its time derivative is taken, reads

$$\frac{dg(\mathbf{a}, t)}{dt} = \left(\frac{dG(\mathbf{a}, t)}{dt}, \nu(\Gamma, 0)\right) \tag{30}$$

We now sketch Mori's ideas to provide for an equation for $G(\mathbf{a}, t)$ which is of the generalized Langevin type.[3,9] Let $\mathscr{C}(a, t|b)$ be the time correlation function of the vectors $G(\mathbf{a}, t)$ and $G(\mathbf{b}, 0)$, namely[5]

$$\mathscr{C}(\mathbf{a}, t|\mathbf{b}) = [G(\mathbf{b}, 0)]^{-1}(G(\mathbf{a}, t), G(\mathbf{b}, 0)) \tag{31}$$

Then it is shown in Appendix A that

$$d\mathscr{C}(\mathbf{a}, t|\mathbf{b})/dt = \int d\mathbf{c}\, i\Omega(\mathbf{a}, \mathbf{c})\mathscr{C}(\mathbf{c}, t|\mathbf{b}) - \int_0^t ds \int d\mathbf{c}\, K(\mathbf{a}, \mathbf{c}, s)\mathscr{C}(\mathbf{c}, t - s|\mathbf{b}) \tag{32}$$

where

$$i\Omega(\mathbf{a}, \mathbf{b}) = (iLG(\mathbf{a}, 0), G(\mathbf{b}, 0))/[G(\mathbf{b}, 0)] \tag{33}$$

$$K(\mathbf{a}, \mathbf{b}, t) = (F(\mathbf{a}, t), F(\mathbf{b}, 0))/[G(\mathbf{b}, 0)] \tag{34}$$

and

$$F(\mathbf{a}, t) = \{\exp[(1 - P_G)iLt]\}(1 - P_G)iLG(\mathbf{a}, 0) \tag{35}$$

Equation (32) is a linear closed equation for the quantity $\mathscr{C}(\mathbf{a}, t|\mathbf{b})$ with a memory function that involves the correlation function of the projected dynamics of the phase space function $\dot{G}(\mathbf{a}, 0)$. If we define an operator $Z(\mathbf{a}, t)$, the Zwanzig operator (ZO), as

$$Z(\mathbf{a}, t)f(\mathbf{a}, \mathbf{b}, t) = \int d\mathbf{c}\, i\Omega(\mathbf{a}, \mathbf{c})f(\mathbf{c}, \mathbf{b}, t) - \int_0^t ds \int d\mathbf{c}\, K(\mathbf{a}, \mathbf{c}, s)f(\mathbf{c}, \mathbf{b}, t - s) \tag{36}$$

then Eq. (33) may be rewritten in a shorter way, namely,

$$d\mathscr{C}(\mathbf{a}, t|\mathbf{b})/dt = Z(\mathbf{a}, t)\mathscr{C}(\mathbf{a}, t|\mathbf{b}) \tag{37}$$

The next step in Mori's procedure is to separate the vector $G(\mathbf{a}, t)$ into

[5] $\mathscr{C}(\mathbf{a}, t|\mathbf{b})$ reduces to the conditional probability $\pi(\mathbf{a}, t|\mathbf{b})$ that $A(\Gamma)$ has the value $\mathbf{a}$ at time t if it had the value $\mathbf{b}$ at time zero when (26) is assumed to hold true. In fact, using Eq. (17), one sees that

$$g(\mathbf{a}, t) = \int d\mathbf{b}\, g(\mathbf{b}, 0)\pi(\mathbf{a}, t|\mathbf{b})$$

where $\pi(\mathbf{a}, t|\mathbf{b})$ is given by Eq. (31).

its component in $H_G(w|\Gamma)$ and its component along the complementary subspace $\tilde{H}_G(w|\Gamma)$. Then

$$G(\mathbf{a}, t) = P_G G(\mathbf{a}, t) + (1 - P_G)G(\mathbf{a}, t) \tag{38}$$

From Eq. (A.9) and the definition of P_G we can rewrite this equation as

$$G(\mathbf{a}, t) = \int d\mathbf{b}\, \mathscr{C}(\mathbf{a}, t|\mathbf{b})G(\mathbf{b}, 0) + \int_0^t ds \int d\mathbf{b}\, \mathscr{C}(\mathbf{a}, t - s|\mathbf{b})F(\mathbf{b}, s) \tag{39}$$

which allows us to express the function $G(\mathbf{a}, t)$ defining the hypercell in phase space in terms of the correlation function $\mathscr{C}(\mathbf{a}, t|\mathbf{b})$.

Next, using $dG(\mathbf{a}, t)/dt$ obtained from Eqs. (37) and (39), one finds, after some rearrangement, that

$$dG(\mathbf{a}, t)/dt = Z(\mathbf{a}, t)G(\mathbf{a}, t) + F(\mathbf{a}, t) \tag{40}$$

This expression is of Langevin type, where the "fluctuating term," which is really the term containing all the irrelevant parts of $G(\mathbf{a}, t)$, satisfies a fluctuation-dissipation theorem as expressed by Eq. (34).

Direct substitution of Eq. (40) back into Eq. (30) yields the desired kinetic equation for $g(\mathbf{a}, t)$. Indeed, using Eq. (17), we find that

$$dg(\mathbf{a}, t)/dt = Z(\mathbf{a}, t)g(\mathbf{a}, t) + (F(\mathbf{a}, t), \nu(\Gamma, 0)) \tag{41}$$

Notice that so far no assumption has been made about the explicit form of the initial distribution, so that Eq. (41) is the most general form of a closed kinetic equation for the function $g(\mathbf{a}, t)$.

The final step in Mori's treatment involves the introduction of the information concerning the initial state of the system. Noticing that the last term in Eq. (41) is the average of $F(\mathbf{a}, t)$ with the initial distribution $\rho(\Gamma, 0)$, namely

$$(F(\mathbf{a}, t), \nu(\Gamma, 0)) = \langle F(\mathbf{a}, t)\rangle^0 \tag{42}$$

and using an analogy with Brownian motion, where this average is set equal to zero, one now assumes that

$$\langle F(\mathbf{a}, t)\rangle^0 = 0 \tag{43}$$

In our formulation this condition is entirely equivalent to our basic assumption expressed by Eq. (26) because

$$(F(\mathbf{a}, t), \nu(\Gamma, 0)) = (F(\mathbf{a}, t), P_G\nu(\Gamma, 0)) = (P_G F(\mathbf{a}, t), \nu(\Gamma, 0)) = 0$$

since $F(\mathbf{a}, t)$ is in $\tilde{H}_g(w|\Gamma)$ due to Eq. (35) and thus $P_G F(\mathbf{a}, t) = 0$. Thus, in Mori's formalism,

$$dg(\mathbf{a}, t)/dt = Z(\mathbf{a}, t)g(\mathbf{a}, t) \tag{44}$$

is the exact kinetic equation satisfied by $g(\mathbf{a}, t)$.

Let us now turn our attention to the derivation of a kinetic equation for $g(\mathbf{a}, t)$ following Zwanzig's scheme. Here we study the time behavior of the function $\nu(\Gamma, t)$, as was pointed out before, whence

$$\frac{dg(\mathbf{a}, t)}{dt} = \left(G(\mathbf{a}, 0), \frac{d\nu(\Gamma, t)}{dt}\right) \tag{45}$$

The whole idea now is to recast Eq. (15), which is the time evolution equation for $\nu(\Gamma, t)$, into the appropriate form. To do this, we write $\nu(\Gamma, t)$ as

$$\nu(\Gamma, t) = P_G\nu(\Gamma, t) + (1 - P_G)\nu(\Gamma, t) \tag{46}$$

in a way similar to that following Eq. (A.9) to calculate $(1 - P_G)\nu(\Gamma, t)$. Letting the operator $-iL$ act on the resulting expression, one finds that

$$\frac{d\nu(\Gamma, t)}{dt} = -\int d\mathbf{b}\, \frac{g(\mathbf{b}, t)}{[G(\mathbf{b}, 0)]}\, iLG(\mathbf{b}, 0) + \int_0^t ds \int d\mathbf{b}\, \frac{g(\mathbf{b}, t - s)}{[G(\mathbf{b}, 0)]}\, iLF(\mathbf{b}, -s) + \phi(\Gamma, t) \tag{47}$$

where

$$\phi(\Gamma, t) = -iL\{\exp[-(1 - P_G)iLt]\}(1 - P_G)\nu(\Gamma, 0) \tag{48}$$

When Eq. (47) is substituted back into Eq. (46), we find the time evolution of $g(\mathbf{a}, t)$, namely,

$$\frac{dg(\mathbf{a}, t)}{dt} = -\int d\mathbf{b}\, \frac{g(\mathbf{b}, t)}{[G(\mathbf{b}, 0)]}\, (G(\mathbf{a}, 0), iLG(\mathbf{b}, 0)) + \int_0^t ds \int d\mathbf{b}\, \frac{g(\mathbf{b}, t - s)}{[G(\mathbf{b}, 0)]} \times (G(\mathbf{a}, 0), iLF(\mathbf{b}, -s)) + (G(\mathbf{a}, 0), \phi(\Gamma, t)) \tag{49}$$

Using the Hermiticity property of L and that of $(1 - P_G)L$ in $\tilde{H}_G(w|\Gamma)$, one obtains the exact kinetic equation for the distribution function $g(\mathbf{a}, t)$, which is identical to Eq. (41).

In order to follow the way in which the initial conditions are introduced in Zwanzig's scheme, one must remember that in his earlier derivation[2] the kinetic equation is written as

$$\frac{dg(\mathbf{a}, t)}{dt} = \left(G(\mathbf{a}, 0), \frac{dP_G\nu(\Gamma, t)}{dt}\right) \tag{50}$$

and the time evolution for the projected part is

$$\frac{dP_G\,\nu(\Gamma, t)}{dt} = -P_GiLP_G\nu(\Gamma, t) + \int_0^t ds\, P_GiL\{\exp[-i(1 - P_G)Ls]\} \times (1 - P_G)iLP_G\nu(\Gamma, t - s) + P_G\phi(\Gamma, t) \tag{51}$$

Next it is assumed that this equation is closed in $P_G\nu(\Gamma, t)$ by setting $P_G\phi(\Gamma, t) = 0$. This implies that Eq. (26) is valid and that the last term in Eq. (49) vanishes. Hence Eq. (44) follows at once.

It is thus clear that using either formalism one finds the exact kinetic equation (41) and that the assumption given by Eq. (26) is introduced in both of them using arguments which are apparently independent but lead to the same closed kinetic equation for $g(\mathbf{a}, t)$, namely Eq. (44).

As mentioned in footnote 5, preceding Eq. (31), when (26) is introduced $\mathscr{G}(\mathbf{a}, t|\mathbf{b}) = \pi(\mathbf{a}, t|\mathbf{b})$. Thus it follows from Eq. (37) that

$$d\pi(\mathbf{a}, t|\mathbf{b})/dt = Z(\mathbf{a}, t)\pi(\mathbf{a}, t|\mathbf{b}) \tag{52}$$

Zwanzig's kinetic equation[2] is obtained when $w(\Gamma) = 1$ and $g(\mathbf{a}, 0) = \delta(\mathbf{a} - \mathbf{a}_0)$, so that

$$\rho(\Gamma, 0) = \delta(A(\Gamma) - \mathbf{a}_0)/S(\mathbf{a}_0) \tag{53}$$

where $S(\mathbf{a}_0) = \int d\Gamma\, \delta(A(\Gamma) - \mathbf{a}_0)$ is the structure function.

On the other hand, Mori's equation[8] is found when $w(\Gamma) = Z^{-1}e^{-\beta\mathscr{H}}$, so that

$$\rho(\Gamma, 0) = e^{-\beta\mathscr{H}}g(A(\Gamma))/g_{\text{eq}}(A(\Gamma)) \tag{54}$$

where $g_{\text{eq}}(A(\Gamma))$ is the distribution function for the mesoscopic variables when the system is in thermal equilibrium.

These expressions clearly exhibit that the results obtained by Mori and Zwanzig, although identical in structure, correspond to different choices of $\rho(\Gamma)$ at the initial time, i.e., to different ways of physical preparation of the system.

Following the ideas presented here, it is possible to relate Mori's approach to the one followed by Nordholm and Zwanzig[7] to find nonlinear transport equations. It should be kept in mind that although it is linear in the $G(\mathbf{a}, t)$ functions, our treatment is highly nonlinear for the phase functions $\{A_j(\Gamma)\}$. In fact, it can be shown[8] that from Eq. (40) it is possible to derive a time evolution equation for $A_j(\Gamma, t)$, where no term depending on the phase functions is neglected. To prove this statement, we shall proceed in a simpler fashion using Zwanzig's scheme.

Taking the time derivative of Eq. (1) we find that the transport equations are given by

$$\frac{d\alpha_j(t)}{dt} = \left(A_j(\Gamma, 0), \frac{d\nu(\Gamma, t)}{dt}\right) \tag{55}$$

Using Eq. (47), we find after some manipulation that

$$\frac{d\alpha_j(t)}{dt} = \int d\mathbf{b}\, \langle iLA_j(\Gamma, 0); \mathbf{b}\rangle g(\mathbf{b}, t) + \int_0^t ds \int d\mathbf{b}\, \langle iLR_j(\Gamma, s); \mathbf{b}\rangle \times g(\mathbf{b}, t - s) + \langle R_j(\Gamma, t)\rangle^0 \tag{56}$$

where $\langle ...; \mathbf{b}\rangle$ is the average taken over a microcanonical distribution within the hypercell $A(\Gamma) = \mathbf{b}$,[6] $\langle \cdots \rangle^0$ represents the average over the initial distribution, and

$$R_j(\Gamma, t) = \{\exp[(1 - P_G)iLt]\}(1 - P_G)iLA_j(\Gamma, 0) \tag{57}$$

If one now assumes that Eq. (26) is true, then, since $R_j(\Gamma, t)$ does not belong to the space $H_G(w|\Gamma)$, its average over the initial distribution drops out and the resulting equations, namely,

$$d\alpha_j(t)/dt = \int d\mathbf{b}\, \langle iLA_j(\Gamma, 0); \mathbf{b}\rangle g(\mathbf{b}, t) + \int_0^t ds \int d\mathbf{b} \times \langle iLR_j(\Gamma, s); \mathbf{b}\rangle g(\mathbf{b}, t - s) \tag{58}$$

are the nonlinear transport equations derived by Nordholm and Zwanzig.

One can also use this result to find the generalized nonlinear Langevin equations, which are obeyed by the phase functions $\{A_j(\Gamma)\}$. If one furthermore realizes that we may set $\nu(\Gamma, 0) = \delta(\Gamma - \Gamma_0)$ because of the fact that the time evolution implied by (56) corresponds to a single experimental setup, we find that[7]

$$dA_j(\Gamma, t)/dt = \int d\mathbf{b}\, \langle iLA_j(\Gamma, 0); \mathbf{b}\rangle G(\mathbf{b}, t) + \int_0^t ds \int d\mathbf{b} \times \langle iLR_j(\Gamma, s); \mathbf{b}\rangle G(\mathbf{b}, t - s) + R_j(\Gamma, t) \tag{59}$$

This equation is precisely the generalized nonlinear Langevin equation recently derived by Mori *et al.*[8]

Summing up, exact linear kinetic equations can be derived for distribution functions $g(\mathbf{a}, t)$ at the mesoscopic level, each one being characterized by the metric $w(\Gamma)$. Two particular choices of this metric lead directly to the equations first derived by Mori and Zwanzig. Furthermore, it has been shown how the nonlinear transport equations (58) and the nonlinear generalized Langevin equations for the space functions $A_i(\Gamma)$, Eqs. (59), follow directly from the previous results. In the following section we shall discuss various representations of the Zwanzig scheme that have been used in a wide variety of contexts in the recent literature.

4. ALTERNATIVE EXPRESSIONS FOR THE ZWANZIG OPERATOR

The importance of the Zwanzig operator has been made apparent in the previous section. Here we show that its explicit expression given by Eq. (36) is equal to the complex conjugate of the original operator found by Zwanzig and furthermore that this form leads in a more or less direct fashion to a

[6] $\langle f(\Gamma); \mathbf{b}\rangle = \int d\Gamma\, f(\Gamma)\rho_{\text{micro}}(\mathbf{b}, 0) = [G(b, 0)]^{-1}(f(\Gamma), G(\mathbf{b}, 0))$.

series of operators, the generalized Fokker–Planck operator, the modified Fokker–Planck operator, and the Mori–Fujisaka–Shigematsu (MFS) form, all of which have played important roles in various treatments of this subject.

Let us begin by proving our first statement. Taking the complex conjugate of Eq. (36) and using Eqs. (A.11) and (A.12), one finds that

$$Z^*(\mathbf{a}, t)f(\mathbf{a}, t) = [G(\mathbf{a}, 0)]\Big\{ -\int d\mathbf{b}\, i\Omega(\mathbf{b}, \mathbf{a}) \frac{f(\mathbf{b}, t)}{[G(\mathbf{b}, 0)]} - \int_0^t ds \int d\mathbf{b}\, K(\mathbf{b}, \mathbf{a}, -s) \frac{f(\mathbf{b}, t-s)}{[G(\mathbf{b}, 0)]} \Big\} \tag{60}$$

where we have considered that $f(\mathbf{a}, t)$ is a real function. Defining an average over the hypercell assuming a microcanonical distribution function [see footnote 6, following Eq. (56)] and using Eqs. (33) and (34), we find that

$$i\Omega(\mathbf{a}, \mathbf{b}) = \langle iLG(\mathbf{a}, 0); \mathbf{b} \rangle \tag{61}$$

and

$$K(\mathbf{a}, \mathbf{b}, t) = -\langle iLF(\mathbf{a}, t); \mathbf{b} \rangle \tag{62}$$

where $\langle \ldots; \mathbf{b} \rangle$ is the average defined over a microcanonical distribution. Equation (60) takes the form

$$Z^*(\mathbf{a}, t)f(\mathbf{a}, t) = [G(\mathbf{a}, 0)]\Big\{ -\int d\mathbf{b} \langle iLG(\mathbf{b}, 0); \mathbf{a} \rangle \frac{f(\mathbf{b}, t)}{[G(\mathbf{b}, 0)]} + \int_0^t ds \int d\mathbf{b} \langle iLF(\mathbf{b}, -s); \mathbf{a} \rangle \frac{f(\mathbf{b}, t-s)}{[G(\mathbf{b}, 0)]} \Big\} \tag{63}$$

Since $\pi(\mathbf{a}, t|\mathbf{b})$ is real, Eq. (52) also may be expressed as

$$d\pi(\mathbf{a}, t|\mathbf{b})/dt = Z^*(\mathbf{a}, t)\pi(\mathbf{a}, t|\mathbf{b}) \tag{64}$$

which, with the use of Eq. (63), may be rewritten as

$$\frac{d\pi(\mathbf{a}, t|\mathbf{b})}{dt} = [G(\mathbf{a}, 0)]\Big\{ -\int d\mathbf{c} \langle iLG(\mathbf{c}, 0); \mathbf{a} \rangle \frac{\pi(\mathbf{c}, t|\mathbf{b})}{[G(\mathbf{c}, 0)]} + \int_0^t ds \int d\mathbf{c} \langle iL\{\exp[-(1 - P_G)iLs]\}(1 - P_G)iLG(\mathbf{c}, 0); \mathbf{a} \rangle \times \frac{\pi(\mathbf{c}, t-s|\mathbf{b})}{[G(\mathbf{c}, 0)]} \Big\} \tag{65}$$

When $w(\Gamma) = 1$, Eq. (65) reduces to Eq. (24) of Zwanzig's paper.[2] Thus, we shall call Eq. (36) for ZO its fundamental form. Notice that it is the complex conjugate of Zwanzig's expression, but it is more general in the sense that it has been defined for an arbitrary metric $w(\Gamma)$ satisfying Eq. (13).

We now proceed to calculate the generalized Fokker–Planck form for ZO. To do so, use is made of the following identities:

$$iLG(\mathbf{a}, 0) = -\sum_k \dot{A}_k(0)\, \partial G(\mathbf{a}, 0)/\partial a_k \tag{66}$$

and

$$P_G\{f(\Gamma)G(\mathbf{a}, 0)\} = \{P_G f(\Gamma)\}G(\mathbf{a}, 0) \tag{67}$$

Using Eq. (66), we can rewrite the form for $i\Omega(\mathbf{a}, \mathbf{b})$ given by Eq. (33) as

$$i\Omega(\mathbf{a}, \mathbf{b}) = -\sum_k \frac{\partial}{\partial a_k}[v_k(\mathbf{a})\, \delta(\mathbf{a} - \mathbf{b})] \tag{68}$$

where $v_k(\mathbf{a})$ is the average of $\dot{A}_k(0)$ over the hypercell characterized by $A(\Gamma) = \mathbf{a}$, or

$$v_k(\mathbf{a}) = \langle \dot{A}_k(\Gamma, 0); \mathbf{a} \rangle \tag{69}$$

We now proceed in a manner similar to that used by Mori[8] to cast the kernel $K(\mathbf{a}, \mathbf{b}; s)$ in a more convenient way. Thus, using Eqs. (35) and (66) one arrives at

$$F(\mathbf{a}, t) = -\sum_k \frac{\partial}{\partial a_k} X_k(\mathbf{a}, t) \tag{70}$$

where

$$X_k(\mathbf{a}, t) = U(t)\{R_k(0)G(\mathbf{a}, 0)\} \tag{71}$$

$R_k(t)$ is defined in Eq. (57) and $U(t)$ is the time evolution operator in the subspace $\tilde{H}_G(w|\Gamma)$, namely,

$$U(t) = \exp[(1 - P_G)iLt] \tag{72}$$

Clearly, $R_k(0)$ is the part of $\dot{A}_k(\Gamma, 0)$ that lies in $\tilde{H}_G(w|\Gamma)$. Thus, separating $\dot{A}_k(\Gamma, 0)$ into its components, one has that

$$\dot{A}_k(\Gamma, 0) = \int d\mathbf{b}\, v_k(\mathbf{b})G(\mathbf{b}, 0) + R_k(0) \tag{73}$$

Furthermore, by definition, the time evolution equations for $F(\mathbf{a}, t)$, $X_k(\mathbf{a}, t)$, and $R_k(t)$ are of the form

$$dB(t)/dt = (1 - P_G)iLB(t) \tag{74}$$

and they are related through the set of equalities

$$R_k(t) = \int d\mathbf{a}\, a_k F(\mathbf{a}, t) = \int d\mathbf{a}\, X_k(\mathbf{a}, t) \tag{75}$$

as may be easily verified. Introducing Eq. (70) into Eq. (34), we get

$$K(\mathbf{a}, \mathbf{b}, t) = [G(\mathbf{b}, 0)]^{-1} \sum_k \sum_l \frac{\partial}{\partial a_k} \frac{\partial}{\partial b_l^*} \{[G(\mathbf{b}, 0)] K_{kl}(\mathbf{a}, \mathbf{b}, t)\} \tag{76}$$

where now

$$K_{kl}(\mathbf{a}, \mathbf{b}, t) = \frac{(X_k(\mathbf{a}, t), X_l(\mathbf{b}, 0))}{[G(\mathbf{b}, 0)]} = \langle R_l^*(0) X_k(\mathbf{a}, t); \mathbf{b} \rangle \tag{77}$$

Substitution of Eqs. (68) and (76) into Eq. (36) leads, after an integration by parts, to the final expression

$$Z(\mathbf{a}, t) f(\mathbf{a}, t) = - \sum_k \frac{\partial}{\partial a_k} [v_k(\mathbf{a}) f(\mathbf{a}, t)] + \int_0^t ds \int d\mathbf{b} \sum_k \sum_l \frac{\partial}{\partial a_k} \times \{[G(\mathbf{b}, 0)] K_{kl}(\mathbf{a}, \mathbf{b}, s)\} \frac{\partial}{\partial b_l^*} \frac{f(\mathbf{b}, t - s)}{[G(b, 0)]} \tag{78}$$

This result is the generalized Fokker–Planck form of ZO. It consists of two parts, one which is Markovian and yields a "convective" contribution to $f(\mathbf{a}, t)$, and a memory term which is in essence a measure of the correlation between vectors $R_l^*(0)$ and $X_k(\mathbf{a}, t)$ in the hypercell characterized by $A(\Gamma) = \mathbf{b}$.

The modified Fokker–Planck form for $Z(\mathbf{a}, t)$ may be easily found from Eq. (78). The underlying idea is to separate Eq. (77) in such a way that the correlation between $R_l^*(0)$ and $R_k(t)$ appears in an explicit manner. This is accomplished if we write

$$X_k(\mathbf{a}, t) = R_k(t) G(a, 0) + Y_k(\mathbf{a}, t) \tag{79}$$

which is essentially a definition for the quantity $Y_k(\mathbf{a}, t)$. Substitution into Eq. (77) yields

$$K_{kl}(\mathbf{a}, \mathbf{b}, t) = L_{kl}(\mathbf{b}, t)\, \delta(\mathbf{a} - \mathbf{b}) + K'_{kl}(\mathbf{a}, \mathbf{b}, t) \tag{80}$$

where

$$L_{kl}(\mathbf{b}, t) = \langle R_k(t) R_l^*(0); \mathbf{b} \rangle \tag{81}$$

and

$$K'_{kl}(\mathbf{a}, \mathbf{b}, t) = \langle Y_k(\mathbf{a}, t) R_l^*(0); \mathbf{b} \rangle \tag{82}$$

Combination of Eqs. (80) and (78) leads to the modified Fokker–Planck form for ZO, namely

$$\begin{aligned} Z(\mathbf{a}, t) f(\mathbf{a}, t) &= - \sum_k \frac{\partial}{\partial a_k} [v_k(\mathbf{a}) f(\mathbf{a}, t)] + \sum_k \sum_l \frac{\partial}{\partial a_k} \int_0^t ds\, [G(\mathbf{a}, 0)] \\ &\quad \times L_{kl}(\mathbf{a}, s) \frac{\partial}{\partial a_l^*} \frac{f(\mathbf{a}, t - s)}{[G(\mathbf{a}, 0)]} \\ &\quad + \sum_k \sum_l \frac{\partial}{\partial a_k} \int_0^t ds \int d\mathbf{b}\, [G(\mathbf{b}, 0)] K'_{kl}(\mathbf{a}, \mathbf{b}, s) \frac{\partial}{\partial b_l^*} \frac{f(\mathbf{b}, t - s)}{[G(\mathbf{b}, 0)]} \end{aligned} \tag{83}$$

The main reason for rewriting $Z(\mathbf{a}, t)$ in this form is that it easily lends itself to the introduction of approximations. These will be discussed in another paper.

Continuing within the context of this work with regard to exact kinetic equations, we shall finally derive the MFS form for ZO. It consists essentially in writing the correlation appearing in (82) as a power series expansion of all its diagonal terms in a space. Thus, one can approach the problem by thinking of the diagonalization of a matrix whose elements are $K'_{kl}(\mathbf{a}, \mathbf{b}; t)$. To do this, one proceeds in a systematic way: first, $Y_k(\mathbf{a}, t)$ is written in terms of $X_k(\mathbf{a}, s)$ with $0 \leqslant s \leqslant t$. Second, one obtains an integral equation for $X_k(\mathbf{a}, t)$ and writes its solution in terms of a power series expansion. Third and last, one calculates $K_{kl}(\mathbf{a}, \mathbf{b}; s)$.

Taking the time derivative of Eq. (79) and using Eq. (74), one gets

$$dY_k(\mathbf{a}, t)/dt = (1 - P_G)iLX_k(\mathbf{a}, t) - [(1 - P_G)iLR_k(t)]G(\mathbf{a}, 0) \tag{84}$$

Defining iL_a and its complement iL_a' through the relations

$$iL_a = -\sum_k \dot{A}_k(0)\, \partial/\partial a_k \tag{85}$$

$$iL_a' = iL - iL_a \tag{86}$$

and introducing them in (84), one finds, with the aid of Eqs. (67) and (79) that

$$dY_k(\mathbf{a}, t)/dt = (1 - P_G)iL_a' Y_k(\mathbf{a}, t) + (1 - P_G)iL_a X_k(\mathbf{a}, t) \tag{87}$$

By definition, $Y_k(\mathbf{a}, 0) = 0$, so that the solution to Eq. (87) is

$$Y_k(\mathbf{a}, t) = \int_0^t ds\, \{\exp[(1 - P_G)iL_a'(t - s)]\}(1 - P_G)iL_a X_k(\mathbf{a}, s) \tag{88}$$

To obtain an integral equation for $X_k(\mathbf{a}, t)$, we substitute Eq. (88) back into Eq. (79) to get

$$X_k(\mathbf{a}, t) = R_k(t)G(\mathbf{a}, 0) + \int_0^t ds\, \{\exp[(1 - P_G)iL_a'(t - s)]\}(1 - P_G)iL_a X_k(\mathbf{a}, s) \tag{89}$$

In Appendix B it is shown that the solution to this equation is

$$X_k(\mathbf{a}, t) = \sum_{n=0}^{\infty} Q_n(\mathbf{a}, t) \tag{90}$$

where $Q_0(\mathbf{a}, t)$ is just equal to the inhomogeneous term of Eq. (89) and $Q_n(\mathbf{a}, t)$ is given by Eq. (B.9). This is a rather complicated expression due to the presence of the operators $(1 - P_G)iL_a$ and $(1 - P_G)iL_a'$. It is thus con-

venient to transform it into another form in which the more familiar operator $(1 - P_G)iL$ shows up. This is done in Appendix B, where, after some algebraic manipulations, one finds finally

$$X_k(\mathbf{a}, t) = \sum_{n=0}^{\infty} (-1)^n \sum_{k_1} \cdots \sum_{k_n} \left[\frac{\partial}{\partial a_{k_1}} \cdots \frac{\partial}{\partial a_{k_n}} G(\mathbf{a}, 0) \right] S(k, k_1, \ldots, k_n; t) \quad (91)$$

where $S(k, k_1, \ldots, k_n; t)$ is given by Eq. (B.23).

When substituted into Eq. (77) this finally yields

$$K_{kl}(\mathbf{a}, \mathbf{b}; t) = \sum_{n=0}^{\infty} (-1)^n \sum_{k_1} \cdots \sum_{k_n} \frac{\partial}{\partial a_{k_1}} \cdots \frac{\partial}{\partial a_{k_n}} \langle R_l^*(0) S(k, k_1, \ldots, k_n; t); \mathbf{b} \rangle \, \delta(\mathbf{a} - \mathbf{b}) \quad (92)$$

which shows that this quantity has been diagonalized in a space. Introducing Eq. (92) into the generalized Fokker–Planck form for ZO, Eq. (98), and performing the **b** integration, one gets

$$\begin{aligned} Z(\mathbf{a}, t) f(\mathbf{a}, t) &= -\sum_k \frac{\partial}{\partial a_k} [v_k(\mathbf{a}) f(\mathbf{a}, t)] + \sum_{n=0}^{\infty} (-1)^n \sum_{k_0} \sum_{k_1} \cdots \sum_{k_n} \\ &\quad \times \frac{\partial}{\partial a_{k_0}} \frac{\partial}{\partial a_{k_1}} \cdots \frac{\partial}{\partial a_{k_n}} \sum_l \int_0^t dt' \\ &\quad \times [G(\mathbf{a}, 0)] \langle S(k_0, k_1, \ldots, k_n; t') R_l^*(0); \mathbf{a} \rangle \frac{\partial}{\partial a_l^*} \frac{f(\mathbf{a}, t - t')}{[G(\mathbf{a}, 0)]} \end{aligned} \quad (93)$$

which is the MFS form for ZO. It is important to emphasize the fact that the first term of the series ($n = 0$) is the second term appearing in the modified Fokker–Planck form of the operator, so that the whole series, except for that term, is nothing else than the last term of Eq. (83).

Summing up, we have shown how, starting from the fundamental form for $Z(\mathbf{a}, t)$ given by Eq. (36) it is possible to derive its equivalent expressions, namely, from Eq. (65) found by Zwanzig, one obtains the generalized Fokker–Planck form given in Eq. (78), the modified Fokker–Planck form given in Eq. (83), and the MFS form given in Eq. (94). All of these expressions are exact and lend themselves to finding equivalent time evolution equations for the hypercell given in Eq. (40), for the correlation function $\mathscr{C}(\mathbf{a}, t|\mathbf{b})$ given in (37), and for the kinetic equation (44). As a final remark, we should mention that, although Eq. (93) was found by essentially the same technique used by Mori *et al.*,[8] our results are more general, being valid for any arbitrary choice of the metric $w(\Gamma)$.

In forthcoming publications we shall show how one can obtain approximate Markovian and non-Markovian kinetic equations for the relevant variables and the transport equations as well.

APPENDIX A

In this appendix we outline the steps leading to Eqs. (32) and (40), namely the time evolution equation for the hypercell in phase space. Starting with the definition of $\mathscr{C}(\mathbf{a}, t|\mathbf{b})$, one has

$$\frac{d\mathscr{C}(\mathbf{a}, t|\mathbf{b})}{dt} = \frac{(dG(\mathbf{a}, t)/dt, G(\mathbf{b}, 0))}{[G(\mathbf{b}, 0)]} = \frac{(iLG(\mathbf{a}, t), G(\mathbf{b}, 0))}{[G(\mathbf{b}, 0)]} \tag{A.1}$$

where use has been made of the equation of motion for $G(\mathbf{a}, t)$. Moreover, since the Liouville operator is Hermitian, we also have

$$\frac{d\mathscr{C}(\mathbf{a}, t|\mathbf{b})}{dt} = -\frac{(G(\mathbf{a}, t), iLG(\mathbf{b}, 0))}{[G(\mathbf{b}, 0)]} = -\frac{(G(\mathbf{a}, t), \dot{G}(\mathbf{b}, 0))}{[G(\mathbf{b}, 0)]} \tag{A.2}$$

The vector $G(\mathbf{b}, 0)$ can be separated into its component on the space $H_G(w|\Gamma)$ and its component in the complementary space, namely

$$\dot{G}(\mathbf{b}, 0) = P_G iLG(\mathbf{b}, 0) + (1 - P_G)iLG(\mathbf{b}, 0) \tag{A.3}$$

Applying the explicit form for the operator P_G given by Eq. (18), one is led to

$$\dot{G}(\mathbf{b}, 0) = \int d\mathbf{c}\, i\Omega(\mathbf{b}, \mathbf{c})G(\mathbf{c}, 0) + (1 - P_G)iLG(\mathbf{b}, 0) \tag{A.4}$$

where $i\Omega(\mathbf{b}, \mathbf{c})$ is given by (33).

Substitution of Eq. (A.4) into Eq. (A.2) yields

$$\frac{d\mathscr{C}(\mathbf{a}, t|\mathbf{b})}{dt} = \int d\mathbf{c}\, \frac{i\Omega^*(\mathbf{b}, \mathbf{c})}{[G(\mathbf{b}, 0)]}\, [G(\mathbf{c}, 0)]\mathscr{C}(\mathbf{a}, t|\mathbf{c}) - \frac{(G(\mathbf{a}, t), (1 - P_G)\dot{G}(\mathbf{b}, 0))}{[G(\mathbf{b}, 0)]} \tag{A.5}$$

The second term on the rhs of this expression in turn can be related to the correlation function $\mathscr{C}(\mathbf{a}, t|\mathbf{b})$. Indeed, using the fact that $(1 - P_G)$ is idempotent and Hermitian, one gets

$$\frac{(G(\mathbf{a}, t), (1 - P_G)iLG(\mathbf{b}, 0))}{[G(\mathbf{b}, 0)]} = \frac{((1 - P_G)G(\mathbf{a}, t), (1 - P_G)iLG(\mathbf{b}, 0))}{[G(\mathbf{b}, 0)]} \tag{A.6}$$

Since the time evolution equation for $(1 - P_G)G(\mathbf{a}, t)$ is

$$\frac{d(1 - P_G)G(\mathbf{a}, t)}{dt} = (1 - P_G)iLP_G(\mathbf{a}, t) + (1 - P_G)iL(1 - P_G)G(\mathbf{a}, t) \tag{A.7}$$

whose solution is

$$(1 - P_G)G(\mathbf{a}, t) = \int_0^t ds \{\exp[(1 - P_G)iLs]\}(1 - P_G)iLP_GG(\mathbf{a}, t - s) \quad \text{(A.8)}$$

this may be cast, after application of the projector operator to $G(\mathbf{a}, t - s)$, in the form

$$(1 - P_G)G(\mathbf{a}, t) = \int d\mathbf{c} \int_0^t ds\, \mathscr{C}(\mathbf{a}, t - s|\mathbf{c})F(\mathbf{c}, s) \quad \text{(A.9)}$$

where $F(\mathbf{c}, t)$ is defined by Eq. (35).

Substituting Eq. (A.9) back into Eq. (A.6) and using the resulting expression in Eq. (A.5), we obtain

$$\frac{d\mathscr{C}(\mathbf{a}, t|\mathbf{b})}{dt} = \int d\mathbf{c}\, \frac{i\Omega^*(\mathbf{b}, \mathbf{c})[G(\mathbf{c}, 0)]}{[G(\mathbf{b}, 0)]} \mathscr{C}(\mathbf{a}, t|\mathbf{c}) - \int d\mathbf{c} \int_0^t ds\, \mathscr{C}(\mathbf{a}, t - s|\mathbf{c})K(\mathbf{c}, \mathbf{b}, s) \quad \text{(A.10)}$$

where $K(\mathbf{c}, \mathbf{b}, s)$ is defined by Eq. (34).

On the other hand, from Eqs. (33) and (34) one gets the following relations:

$$i\Omega(\mathbf{b}, \mathbf{c})[G(\mathbf{c}, 0)] = i\Omega^*(\mathbf{c}, \mathbf{b})[G(\mathbf{b}, 0)] \quad \text{(A.11)}$$

$$K(\mathbf{c}, \mathbf{b}, s)[G(\mathbf{b}, 0)] = K(\mathbf{b}, \mathbf{c}, -s)[G(\mathbf{c}, 0)] \quad \text{(A.12)}$$

To obtain the former, use has been made of the Hermitian property of L, and for the second, the fact that $(1 - P_G)L$ is Hermitian on the subspace $\tilde{H}_G(w|\Gamma)$. Furthermore, from Eq. (31) it is easy to see that $\mathscr{C}(\mathbf{a}, t|\mathbf{b})$ satisfies

$$\mathscr{C}(\mathbf{a}, t|\mathbf{b})[G(\mathbf{b}, 0)] = \mathscr{C}^*(\mathbf{b}, -t|\mathbf{a})[G(\mathbf{a}, 0)] \quad \text{(A.13)}$$

Now, from direct substitution of Eq. (A.11) into Eq. (A.10) we obtain

$$\frac{d\mathscr{C}(\mathbf{a}, t|\mathbf{b})}{dt} = \int d\mathbf{c}\, \mathscr{C}(\mathbf{a}, t|\mathbf{c})i\Omega(\mathbf{c}, \mathbf{b}) - \int_0^t ds \int d\mathbf{c}\, \mathscr{C}(\mathbf{a}, t - s|\mathbf{c})K(\mathbf{c}, \mathbf{b}, s) \quad \text{(A.14)}$$

To find Eq. (32) we take the complex conjugate of this expression, interchange indices **a** and **b**, and, use Eqs. (A.11) and (A.12), obtain

$$d\mathscr{C}(\mathbf{a}, -t|\mathbf{b})/dt = -\int d\mathbf{c}\, i\Omega(\mathbf{a}, \mathbf{c})\mathscr{C}(\mathbf{c}, -t|\mathbf{b}) + \int_0^t ds \int d\mathbf{c}\, K(\mathbf{a}, \mathbf{c}, -s)\mathscr{C}(\mathbf{c}, -t + s|\mathbf{b}) \quad \text{(A.15)}$$

which, after the change of t to $-t$, leads finally to the desired result.

In order to find the equation of motion for the hypercell we again split $G(\mathbf{a}, t)$ into its projected and unprojected components, namely

$$G(\mathbf{a}, t) = P_G G(\mathbf{a}, t) + (1 - P_G)G(\mathbf{a}, t) \tag{A.16}$$

Use of the definitions of P_G and $\mathscr{C}(\mathbf{a}, t|\mathbf{b})$ leads to

$$P_G G(\mathbf{a}, t) = \int d\mathbf{b}\, \mathscr{C}(\mathbf{a}, t|\mathbf{b}) G(\mathbf{b}, 0) \tag{A.17}$$

which, combined with Eqs. (A.8) and (A.16), yields

$$G(\mathbf{a}, t) = \int d\mathbf{b}\, \mathscr{C}(\mathbf{a}, t|\mathbf{b}) G(\mathbf{b}, 0) + \int d\mathbf{b} \int_0^t ds\, \mathscr{C}(\mathbf{a}, t - s|\mathbf{b}) F(\mathbf{b}, s) \tag{A.18}$$

Taking the Laplace transform of Eq. (A.18), we have

$$\hat{G}(\mathbf{a}, \epsilon) = \int d\mathbf{b}\, \hat{\mathscr{C}}(\mathbf{a}, \epsilon|\mathbf{b})[G(\mathbf{b}, 0) + \hat{F}(\mathbf{b}, \epsilon)] \tag{A.19}$$

where

$$\hat{f}(\epsilon) = \int_0^\infty e^{-\epsilon t} f(t)\, dt \tag{A.20}$$

On the other hand, the Laplace transform of Eq. (A.14) leads to

$$\int d\mathbf{c}\, \mathscr{C}(\mathbf{a}, \epsilon|\mathbf{c})[-i\Omega(\mathbf{c}, \mathbf{b}) + \hat{K}(\mathbf{c}, \mathbf{b}, \epsilon) + \epsilon\, \delta(\mathbf{b} - \mathbf{c})] = \delta(\mathbf{a} - \mathbf{b}) \tag{A.21}$$

noticing that $\mathscr{C}(\mathbf{a}, 0|\mathbf{b}) = \delta(\mathbf{a} - \mathbf{b})$.

The inverse of the correlation $\hat{\mathscr{C}}^{-1}(\mathbf{a}, \epsilon|\mathbf{b})$ is expressed as

$$\hat{\mathscr{C}}^{-1}(\mathbf{c}, \epsilon|\mathbf{b}) = -i\Omega(\mathbf{c}, \mathbf{b}) + \hat{K}(\mathbf{c}, \mathbf{b}, \epsilon) + \epsilon\, \delta(\mathbf{b} - \mathbf{c}) \tag{A.22}$$

Multiplying Eq. (A.19) by Eq. (A.22), integrating over $\mathbf{a}$, and using Eq. (A.21), we obtain

$$-G(\mathbf{c}, 0) + \epsilon \hat{G}(\mathbf{c}, \epsilon) = \int d\mathbf{a}\, [i\Omega(\mathbf{c}, \mathbf{a}) - K(\mathbf{c}, \mathbf{a}, \epsilon)]\hat{G}(\mathbf{a}, \epsilon) + \hat{F}(\mathbf{c}, \epsilon) \tag{A.23}$$

which, after its inverse Laplace transform is taken, yields the desired result, Eq. (40) for the hypercell, where the term $Z(\mathbf{a}, t)G(\mathbf{a}, t)$ is given by Eq. (36) when $f = G$.

APPENDIX B

In this appendix we outline the steps leading to Eqs. (90) and (91). We begin by taking the Laplace transform of Eq. (89) to obtain

$$\hat{X}_k(\mathbf{a}, \epsilon) = \hat{R}_k(\epsilon) G(\mathbf{a}, 0) + \frac{1}{\epsilon - (1 - P_G) iL_a'} (1 - P_G) iL_a X_k(\mathbf{a}, \epsilon) \tag{B.1}$$

From this expression we obtain

$$\hat{X}_k(\mathbf{a}, \epsilon) = \left[1 - \frac{(1 - P_G)iL_a}{\epsilon - (1 - P_G)iL_a'}\right]^{-1} \hat{R}_k(\epsilon)G(\mathbf{a}, 0) \tag{B.2}$$

Using the binomial expansion of $(1 - \alpha)^{-1}$, one has

$$\hat{X}_k(\mathbf{a}, \epsilon) = \sum_{n=0}^{\infty} [\hat{Q}(\mathbf{a}, \epsilon)]^n \hat{R}_k(\epsilon)G(\mathbf{a}, 0) \tag{B.3}$$

where we introduce the operator

$$\hat{Q}(\mathbf{a}, \epsilon) = \frac{(1 - P_G)iL_a}{\epsilon - (1 - P_G)iL_a'} \tag{B.4}$$

Taking the inverse Laplace transform of Eq. (B.2) leads to

$$X_k(\mathbf{a}, t) = \sum_{n=0}^{\infty} Q_n(\mathbf{a}, t) \tag{B.5}$$

where

$$Q_n(\mathbf{a}, t) = \mathscr{L}^{-1}|[\hat{Q}(\mathbf{a}, \epsilon)]^n R_k(\epsilon)G(\mathbf{a}, 0)\} \tag{B.6}$$

Furthermore,

$$Q(\mathbf{a}, t) = \mathscr{L}^{-1}\hat{Q}(\mathbf{a}, \epsilon) = \{\exp[(1 - P_G)iL_a't]\}(1 - P_G)iL_a \tag{B.7}$$

so that

$$\begin{aligned} Q_n(\mathbf{a}, t) = \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n\, Q(\mathbf{a}, t - t_1) \\ \times Q(\mathbf{a}, t_1 - t_2) \cdots Q(\mathbf{a}, t_n - t_{n-1})R_k(t_n)G(\mathbf{a}, 0) \end{aligned} \tag{B.8}$$

which, after repetitive application of Eq. (B.7), yields

$$\begin{aligned} Q_n(\mathbf{a}, t) = \int_0^t dt_1 \cdots \int_0^{t_{n-1}} \{\exp[(1 - P_G)iL_a'(t - t_1)]\} \\ \times (1 - P_G)iL_a \cdots \{\exp[(1 - P_G)iL_a'(t_n - t_{n-1})]\} \\ \times (1 - P_G)iL_aR_k(t_n)G(\mathbf{a}, 0) \end{aligned} \tag{B.9}$$

which is the general term in Eq. (90).

We now express Eq. (B.9) in terms of the operator iL to obtain the desired equation. To do this, we first consider the effect of $\hat{Q}(\mathbf{a}, \epsilon)$ on $\hat{R}_k(\epsilon)G(\mathbf{a}, 0)$, namely

$$\hat{Q}(\mathbf{a}, \epsilon)\hat{R}_k(\epsilon)G(\mathbf{a}, 0) = \frac{1}{\epsilon - (1 - P_G)iL_a'}(1 - P_G)iL_a\hat{R}_k(\epsilon)G(\mathbf{a}, 0) \tag{B.10}$$

and recalling that iL_a is defined through Eq. (85), we find

$$(1 - P_G)iL_a\hat{R}_k(\epsilon)G(\mathbf{a}, 0) = -(1 - P_G)\sum_{k_n}\hat{R}_k(\epsilon)\dot{A}_{k_n}(0)\frac{\partial G(\mathbf{a}, 0)}{\partial a_{k_n}} \quad \text{(B.11)}$$

Furthermore it is easy to show that the following holds:

$$P_G\left\{f(\Gamma)\frac{\partial}{\partial a_{k_1}}\cdots\frac{\partial}{\partial a_{k_n}}G(\mathbf{a}, 0)\right\} = \frac{\partial}{\partial a_{k_1}}\cdots\frac{\partial}{\partial a_{k_n}}G(\mathbf{a}, 0)\{P_G f(\Gamma)\} \quad \text{(B.12)}$$

for an arbitrary function $f(\Gamma)$ which does not depend on the set $\{a_k\}$. Using Eqs. (B.11) and (B.12) in Eq. (B.10), we obtain

$$\hat{Q}(a, \epsilon)\hat{R}_k(\epsilon)G(\mathbf{a}, 0) = \frac{1}{\epsilon - (1 - P_G)iL_a'}\left[-\sum_{k_n}\frac{\partial G(\mathbf{a}, 0)}{\partial a_{k_n}}(1 - P_G)\hat{R}_k(\epsilon)\dot{A}_{k_n}(0)\right] \quad \text{(B.13)}$$

The explicit application of the operator $[\epsilon - (1 - P_G)iL_a']^{-1}$ in this equation is done through its power series representation, whence

$$\hat{Q}(a, \epsilon)\hat{R}_k(\epsilon)G(\mathbf{a}, 0) = -\frac{1}{\epsilon}\sum_{l=0}^{\infty}\left(\frac{(1 - P_G)iL_a'}{\epsilon}\right)^l\sum_{k_n}\frac{\partial G(\mathbf{a}, 0)}{\partial a_{k_n}} \times (1 - P_G)\hat{R}_k(\epsilon)\dot{A}_{k_n}(0) \quad \text{(B.14)}$$

Since it is immediate to prove that

$$iL_a'\left[f(\Gamma)\frac{\partial G(\mathbf{a}, 0)}{\partial a_k}\right] = \frac{\partial G(\mathbf{a}, 0)}{\partial a_k}iLf(\Gamma) \quad \text{(B.15)}$$

then

$$\frac{(1 - P_G)iL_a'}{\epsilon}\sum_k\frac{\partial G(\mathbf{a}, 0)}{\partial a_{k_n}}(1 - P_G)\hat{R}_k(\epsilon)\dot{A}_{k_n}(0) = \sum_{k_n}\frac{\partial G(\mathbf{a}, 0)}{\partial a_{k_n}}\frac{1 - P_G}{\epsilon}iL\hat{R}_k(\epsilon)\dot{A}_{k_n}(0)$$

a result which, after use of Eq. (B.14), leads to

$$\hat{Q}(\mathbf{a}, \epsilon)\hat{R}_k(\epsilon)G(\mathbf{a}, 0) = -\sum_{k_n}\frac{\partial G(\mathbf{a}, 0)}{\partial a_{k_n}}\frac{1}{\epsilon - (1 - P_G)iL}(1 - P_G)\hat{R}_k(\epsilon)\dot{A}_{k_n}(0) \quad \text{(B.16)}$$

Thus, repeated applications of $\hat{Q}(\mathbf{a}, \epsilon)$ gives

$$\hat{Q}^2(\mathbf{a}, \epsilon)\hat{R}_k(\epsilon)G(\mathbf{a}, 0) = \frac{1}{\epsilon - (1 - P_G)iL_a'}(1 - P_G) \times \left[(-1)^2\sum_{k_{n-1}}\sum_{k_n}\frac{\partial}{\partial a_{k_{n-1}}}\frac{\partial G(\mathbf{a}, 0)}{\partial a_{k_n}} \times \dot{A}_{k_{n-1}}(0)\frac{1}{\epsilon - (1 - P_G)iL}(1 - P_G)\hat{R}_k(\epsilon)\dot{A}_{k_n}(0)\right]$$

and therefore

$$\hat{Q}^2(\mathbf{a}, \epsilon)\hat{R}_k(\epsilon)G(\mathbf{a}, 0)$$
$$= (-1)^2 \sum_{k_{n-1}} \sum_{k_n} \frac{\partial}{\partial a_{k_{n-1}}} \frac{\partial G(\mathbf{a}, 0)}{\partial a_{k_n}} \frac{1}{\epsilon - (1 - P_G)iL} (1 - P_G)\dot{A}_{k_{n-1}}(0)$$
$$\times \frac{1}{\epsilon - (1 - P_G)iL} (1 - P_G)\dot{A}_{k_n}(0)\hat{R}_k(\epsilon) \tag{B.17}$$

By induction one can easily verify that

$$[\hat{Q}(\mathbf{a}, \epsilon)]^n \hat{R}_k(\epsilon)G(\mathbf{a}, 0)$$
$$= (-1)^n \sum_{k_n} \cdots \sum_{k_1} \frac{\partial}{\partial a_{k_1}} \cdots \frac{\partial G(\mathbf{a}, 0)}{\partial a_{k_n}}$$
$$\times \left[\prod_{r=1}^{n} \frac{1}{\epsilon - (1 - P_G)iL} (1 - P_G)\dot{A}_{k_r}(0)\right]\hat{R}_k(\epsilon) \tag{B.18}$$

Substitution of Eq. (B.18) back into Eq. (B.3) yields

$$\hat{X}_k(\mathbf{a}, \epsilon) = \sum_{n=0}^{\infty} (-1)^n \sum_{k_1} \cdots \sum_{k_n} \frac{\partial}{\partial a_{k_1}} \cdots \frac{\partial G(\mathbf{a}, 0)}{\partial a_{k_n}} \hat{S}(k, k_1, \ldots, k_n, \epsilon) \tag{B.19}$$

where the quantity $\hat{S}(k, k_1, \ldots, k_n, \epsilon)$ is defined by

$$\hat{S}(k, k_1, \ldots, k_n, \epsilon) = \left[\prod_{r=1}^{n} \frac{1}{\epsilon - (1 - P_G)iL} (1 - P_G)\dot{A}_{k_r}(0)\right]\hat{R}_k(\epsilon) \tag{B.20}$$

Since

$$\hat{R}_k(\epsilon) = \frac{1}{\epsilon - (1 - P_G)iL} R_k(0) \tag{B.21}$$

we have that

$$\hat{S}(k, k_1, \ldots, k_n, \epsilon) = \prod_{r=1}^{n} \left[\frac{1}{\epsilon - (1 - P_G)iL} R_{k_r}(0)\right] \frac{1}{\epsilon - (1 - P_G)iL} R_k(0) \tag{B.22}$$

which after the inverse Laplace transform is taken, leads precisely to Eq. (91), where $S(k, k_1, \ldots, k_n, t)$ is the inverse Laplace function of $\hat{S}$ defined in Eq. (B.22). Thus,

$$S(k, k_1, \ldots, k_n, t)$$
$$= \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \, U(t - t_1)R_{k_1}(0) \cdots U(t_n - t_{n-1})R_{k_n}(0)U(t_n)R_k(0) \tag{B.23}$$

where $U(t) = \exp[(1 - P_G)iLt]$.

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