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ON THE VALIDITY OF NON-MARKOV REDUCED EQUATIONS OF MOTION IN NON-EQUILIBRIUM STATISTICAL MECHANICS

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The usefulness of non-Markov reduced equations of motion (REM) for the description of the time evolution of macrovariables is examined. We show that in general one should be very cautious when using such equations since the results may strongly depend on the addition of more variables into the REM. This is in contrast to the use of non-Markov REM in the calculation of equilibrium correlation functions which is always justified.

1. Introduction

One of the basic tools in the theoretical studies of non-equilibrium phenomena is the derivation of reduced equations of motion (REM)[1–5]. REM are often used for the evaluation of equilibrium correlation functions[6]), line shapes[7]), transport coefficients[8,9]) and for the description of the time evolution of macrovariables[4a,5,10–12]). The derivation of the REM is most often accomplished using the projection operator techniques of Zwanzig and Mori. A crucial step in any such derivation involves the identification of a "relevant" set of macrovariables whose values approximately specify the macroscopic non-equilibrium state[4a]). It is well established that if we are successful in defining a "complete set of relevant variables" then the resulting equations assume a particularly simple form in which the coefficients in the REM are independent of time. In this case, the amount of microscopic information relevant for the evaluation of our chosen set of variables is reduced to few coefficients, which sometimes can be evaluated by perturbative methods. This is the Markov limit. When the resulting equations are not Markov we may in principle try to add more variables into our description, with the hope of

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obtaining a Markov set of equations[8,11]). Since a systematic method for the choice of the relevant variables does not exist, it is difficult to know whether we have included all of them in our description. It should be noted that non-Markov equations are often used in the calculation of equilibrium correlation functions, such as those found in line-shape problems or in generalized hydrodynamics.

In this paper, we explore the applicability of non-Markov REM for macrovariables. To that end we compare the dynamics of a set of variables A_ν as obtained from two sets of REM denoted REM I and REM II. REM I are constructed for the variables A_ν. REM II are obtained by extending the set A_ν by including more variables B_ν, writing REM for the combined set $\{A_\nu, B_\nu\}$, and then eliminating B_ν formally. We are then able to investigate under what conditions the results of REM I and REM II are practically identical. The derivation of REM I and REM II is done in section 2. In section 3 we analyze and compare the results of both REM. Section 4 contains illustrative examples and section 5 analyzes the calculation of equilibrium correlation functions and finally section 6 contains a short summary.

2. Derivation of REM for macrovariables

We consider a macroscopic system characterized by a Hamiltonian H and a density matrix ρ. At time $t = 0$ we prepare the system by fixing the values of a certain set of dynamical variables $\tilde{A}_\nu$,

$$\tilde{a}_\nu \equiv \mathrm{Tr}(\rho(0)\tilde{A}_\nu). \tag{1}$$

The initial density matrix may be taken to be "microcanonical":

$$\rho(0) = \rho_{\mathrm{eq}} \prod_\nu \delta(\tilde{a}_\nu - \tilde{A}_\nu)/\mathrm{Tr}\left(\prod_\nu \delta(\tilde{a}_\nu - \tilde{A}_\nu)\rho_{\mathrm{eq}}\right), \tag{2a}$$

where ρ_{eq} is the equilibrium density matrix.

Alternatively, we may choose a maximum entropy canonical distribution function

$$\rho(0) = \rho_{\mathrm{eq}} \exp\left(-\sum_\nu \lambda_\nu \tilde{A}_\nu\right)\bigg/\mathrm{Tr}\left(\exp\left(-\sum_\nu \lambda_\nu \tilde{A}_\nu\right)\rho_{\mathrm{eq}}\right), \tag{2b}$$

where λ_ν are chosen so that relations (1) are satisfied. In either case, $\rho(0)$ may be written as a linear superposition of all possible products of $\tilde{A}_\nu$, i.e., $\tilde{A}_\nu\tilde{A}_\mu$, $\tilde{A}_\nu\tilde{A}_\mu\tilde{A}_\lambda$, etc. For the sake of convenience let us define an extended set of operators $\{A_\nu\}$ which includes $\tilde{A}_\nu$ as well as all their products[8,11]), i.e.

$$\{A_\nu\} \equiv \{\tilde{A}_\nu, \tilde{A}_\nu\tilde{A}_\mu, \tilde{A}_\nu\tilde{A}_\mu\tilde{A}_\lambda \ldots\}. \tag{3}$$

We may now write eqs. (2a) and (2b) in the form

$$\rho(0) = \left(1 + \sum_\nu \sigma_\nu A_\nu\right)\rho_{eq}, \tag{4}$$

where σ_ν are numerical constants.

We are interested in the expectation values

$$a_\nu(t) \equiv \mathrm{Tr}(A_\nu \rho(t)), \tag{5}$$

where $\rho(t)$ satisfies the Liouville equation

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\mathrm{i}L\rho \equiv \begin{cases} -\mathrm{i}[H, \rho] & \text{(quantum mechanics),} \quad (6a) \\ \{H, \rho\} & \text{(classical mechanics),} \quad (6b) \end{cases}$$

L being the Liouville operator for the entire system. Using eqs. (4) and (6) we have

$$\rho(t) = \exp(-\mathrm{i}Lt)\rho(0) = \sum_\nu \sigma_\nu \rho_{eq} \exp(-\mathrm{i}Lt)A_\nu. \tag{7a}$$

Upon taking the time-derivative of eq. (7a) we have

$$\dot{\rho}(t) = -\mathrm{i} \sum_\nu \sigma_\nu \rho_{eq} \exp(-\mathrm{i}Lt)LA_\nu. \tag{7b}$$

Multiplying eqs. (7) by A_μ from the left and taking a trace, we get

$$a_\mu(t) = \sum_\nu \langle A_\mu(t)A_\nu\rangle\sigma_\nu, \tag{8a}$$

and

$$\dot{a}_\mu(t) = \sum_\nu \langle \dot{A}_\mu(t)\dot{A}_\mu\rangle\sigma_\nu, \tag{8b}$$

where the time-correlation functions are defined as

$$\langle A_\mu(t)A_\mu\rangle \equiv \mathrm{Tr}(\rho_{eq}A_\mu \exp(-\mathrm{i}Lt)A_\nu), \tag{9a}$$

$$\langle \dot{A}_\mu(t)A_\nu\rangle \equiv -\mathrm{i}\,\mathrm{Tr}(\rho_{eq}A_\mu L \exp(-\mathrm{i}Lt)A_\nu) \tag{9b}$$

and

$$A_\mu(t) \equiv \exp(\mathrm{i}Lt)A_\mu \equiv \exp(\mathrm{i}Ht)A_\mu \exp(-\mathrm{i}Ht) \tag{10}$$

(note that $A_\mu \equiv A_\mu(0)$).

To simplify the subsequent manipulations we introduce a matrix notation and define column vectors $\boldsymbol{\sigma}$, $\boldsymbol{a}$ and $\mathbf{A}$, whose components are σ_ν, a_ν and A_ν, respectively. We further introduce the matrices

$$\langle \mathbf{A}(t)\mathbf{A}\rangle_{\nu\mu} \equiv \langle A_\nu(t)A_\mu\rangle, \tag{11a}$$

$$\langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle_{\nu\mu} = \mathrm{i}\langle LA_\nu(t)A_\mu\rangle, \tag{11b}$$

and define

$$\langle \mathbf{A}(t)\dot{\mathbf{A}}\rangle_{\nu\mu} = \mathrm{i}\langle A_\nu(t)LA_\mu\rangle, \tag{12}$$

so that

$$\langle \mathbf{A}(t)\dot{\mathbf{A}}\rangle = -\langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle. \tag{13}$$

Eq. (13) defines the "dot switching" operation which will be used later. Using the notation of eqs. (11a) and (11b), eqs. (8a) and (8b) assume the form

$$\boldsymbol{a}(t) = \langle \mathbf{A}(t)\mathbf{A}\rangle\boldsymbol{\sigma}, \tag{14a}$$

$$\dot{\boldsymbol{a}}(t) = \langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle\boldsymbol{\sigma}. \tag{14b}$$

Eq. (14a) may be formally solved for $\boldsymbol{\sigma}$ and the solution substituted in (14b), resulting in our basic REM for $\boldsymbol{a}$, denoted hereafter as REM I*

$$\frac{\mathrm{d}\boldsymbol{a}(t)}{\mathrm{d}t} = \langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1}\boldsymbol{a}(t). \tag{15a}$$

Alternatively, REM I may be written in the form

$$\frac{\mathrm{d}\boldsymbol{a}(t)}{\mathrm{d}t} = \langle \dot{\mathbf{A}}\mathbf{A}\rangle\langle \mathbf{A}\mathbf{A}\rangle^{-1}\boldsymbol{a}(t) - \int_0^t \mathrm{d}\tau\langle \dot{\mathbf{A}}^{\neq}(\tau)\dot{\mathbf{A}}\rangle\langle \mathbf{A}(\tau)\mathbf{A}\rangle^{-1}\cdot\boldsymbol{a}(t), \tag{15b}$$

where we have defined

$$\dot{\mathbf{A}}^{\neq}(t) \equiv \dot{\mathbf{A}}(t) - \langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1}\mathbf{A}(t). \tag{16}$$

The form (15b) is obtained by splitting the kernel of (15a) into its value at $t = 0$ resulting in the first term of (15b), and the rest. The equivalence of (15b) and (15a) is easily verified by noting that

$$\frac{\mathrm{d}}{\mathrm{d}\tau}[\langle \dot{\mathbf{A}}(\tau)\mathbf{A}\rangle\langle \mathbf{A}(\tau)\mathbf{A}\rangle^{-1}] = \langle \dot{\mathbf{A}}^{\neq}(\tau)\dot{\mathbf{A}}\rangle\langle \mathbf{A}(\tau)\mathbf{A}\rangle^{-1}. \tag{17}$$

Let us now add another group of variables $\boldsymbol{B}$ to our set $\mathbf{A}$. We then derive a

* Eq. (15a) is local in time. In the more conventional approach, a momory equation of the form $\dot{\boldsymbol{a}}(t) = \mathrm{i}\underline{\boldsymbol{\Omega}}\cdot\boldsymbol{a}(t) + \int_0^t \mathrm{d}t_1\underline{\boldsymbol{K}}(t-t_1)\cdot\boldsymbol{a}(t_1)$ is obtained, the function $\underline{\boldsymbol{K}}$ being the memory function. Both types of equations can be derived in an essentially exact fashion and more importantly, they yield exactly the same solution for $\boldsymbol{a}(t)$, i.e., eq. (8)[1,5]).

new REM, denoted by REM II, for the combined set of variables **A** and **B**

$$\frac{d}{dt}\begin{pmatrix} a(t) \\ b(t) \end{pmatrix} = \begin{pmatrix} \langle \dot{A}(t)A \rangle & \langle \dot{A}(t)B \rangle \\ \langle \dot{B}(t)A \rangle & \langle \dot{B}(t)B \rangle \end{pmatrix} \cdot \begin{pmatrix} \langle A(t)A \rangle & \langle A(t)B \rangle \\ \langle B(t)A \rangle & \langle B(t)B \rangle \end{pmatrix}^{-1} \cdot \begin{pmatrix} a(t) \\ b(t) \end{pmatrix}, \tag{18}$$

where the notation is as before, b are the expectation values of B, etc. The b variables may be formally eliminated from eq. (18) and after some manipulations which are carried out in the appendix we may bring REM II to the form

$$\frac{da}{dt} = \langle \dot{A}(t)A \rangle \cdot \langle A(t)A \rangle^{-1} \cdot a(t) + \langle \dot{A}^{\neq}(t)B \rangle \cdot \langle B^{\neq}(0)B \rangle^{-1} \cdot b^{\neq}(0) \tag{19a}$$

and

$$\frac{db^{\neq}(t)}{dt} = \left[\frac{d}{dt}\langle B^{\neq}(t)B \rangle\right] \cdot \langle B^{\neq}(t)B \rangle^{-1} \cdot b^{\neq}(t). \tag{19b}$$

The new variables appearing in eqs. (19a) and (19b) are related to the old ones by

$$B^{\neq}(t) \equiv B(t) - \langle B(t)A \rangle \cdot \langle A(t)A \rangle^{-1} \cdot A(t) \tag{20a}$$

and

$$b^{\neq}(t) \equiv \mathrm{Tr}(\rho(0)B^{\neq}(t)) = b(t) - \langle B(t)A \rangle \cdot \langle A(t)A \rangle^{-1} \cdot a(t). \tag{20b}$$

Before continuing, it should be noted that the quantities with the "$\neq$" superscripts are orthogonal to the variables A, in the sense that

$$\langle B^{\neq}(t)A \rangle = 0 \tag{21}$$

for any B. This property is very important for what follows in the later sections.

Redefining the B variable has led to an exact decoupling of the equation of motion for $b^{\neq}$ from a (the latter still depends on $b^{\neq}(0)$). What is the physical significance of $b^{\neq}(t)$? To answer this, consider the second term on the r.h.s. of eq. (20b). Using eqs. (4) and (14a), it is easy to show that this term is the average of $B(t)$ using the initial density matrix defined in terms of the A's alone, i.e., the REM I distribution. Hence, $b^{\neq}(t)$ is the difference between the nonequilibrium averages of B computed in REM I and II. In general, there is no good reason to expect that $b^{\neq}(0)$ vanishes. Nonetheless, if the set of variables A describes the nonequilibrium "state" of the system, then it would be reasonable to expect that the REM II value of $b(t)$ would quickly approach the value computed in terms of $a(t)$, i.e., the REM I value. Equivalently, $b^{\neq}(t)$ should decay quickly. This discussion will be made more precise below.

The equations of motion, eqs. (19a) and (19b), can be solved exactly by noting that

$$\langle \dot{A}^{\neq}(t)B\rangle = \langle A(t)A\rangle \frac{d}{dt}[\langle A(t)A\rangle^{-1}\langle A(t)B^{\neq}\rangle] \tag{22}$$

which when used in eqs. (19a) and (19b) gives

$$b^{\neq}(t) = \langle B^{\neq}(t)B\rangle \cdot \langle B^{\neq}(0)B\rangle^{-1} \cdot b^{\neq}(0) \tag{23a}$$

and

$$a(t) = \langle A(t)A\rangle \cdot \langle A(0)A\rangle^{-1} \cdot a(0) + \langle A(t)B^{\neq}\rangle \cdot \langle B^{\neq}(0)B\rangle^{-1} \cdot b^{\neq}(0). \tag{23b}$$

Although the set defined by eq. (3) contains infinite order products of the linear variables, the nonlinear elements are important only in systems that are far from equilibrium. In the examples presented in section 4 we consider only systems close to equilibrium and drop the nonlinear terms. The connection between the multilinear variables and nonlinear deviations from equilibrium is discussed in ref. 4a. The method used in ref. 4a, if applied in the derivation of the REM, will result in eq. (18) to linear order in the deviations from equilibrium.

As far as a is concerned, the differences between REM I and II are contained in the terms proportional to $b^{\neq}(0)$ in eqs. (19a) and (23b). In order that the two descriptions be equivalent, BOTH of these terms should become small. Stated another way, REM II must reduce to REM I after some time AND any transient effects associated with $b^{\neq}(0)$ must decay.

In the next section, the differences between REM I and II are examined.

3. Analysis of REM I and REM II

Upon comparing REM I (eqs. (15a) and (15b)) with REM II (eqs. (19a) and (19b)) we note that in general they are not the same and they differ by the addition of an extra term, proportional to $b^{\neq}(0)$, in the latter. The problem is now to find the conditions under which the solutions for $a(t)$ obtained from REM I and REM II are identical or practically identical. To that end we shall distinguish between three cases, and analyze each one separately.

3.1. *Case I* – $b^{\neq}(0) = 0$

The condition $b^{\neq}(0) = 0$ implies that

$$b(0) = \langle BA\rangle\langle AA\rangle^{-1} a(0). \tag{24}$$

For this special set of initial conditions, REM I and REM II are identical.

As was discussed above, the vanishing of $b^{\neq}(0)$ is equivalent to having an initial distribution appropriate to REM I. Thus it is not surprising that the inclusion of additional variables is irrelevant to the evolution of $\boldsymbol{a}$. As will be shown in section 5, this trivial case is the appropriate one for equilibrium time-correlation functions.

We note that in general, any solution of REM I also solves REM II by taking $\boldsymbol{b}^{\neq}(0) = 0$. The reverse however, is not necessarily true. Since REM II provides us with a more detailed description of our system (which includes also the $\boldsymbol{B}$ variables), they allow for a broader class of solutions which do not satisfy eq. (24) and as a result there is a family of solutions of REM II which do not satisfy REM I.

3.2. *Case II – separation of time scales*

In general, $\boldsymbol{b}^{\neq}(0)$ is nonzero and thus in the strict mathematical sense REM I and II are not equivalent. On the other hand, experience tells us that many systems have sets of variables, **A**, which admit REM I descriptions. These hold under a variety of experimental conditions and in particular, they are valid for a wide class of initial conditions. Some simple examples where this seems to occur are Brownian motion[13]), hydrodynamics[6]) and T_1 and T_2 processes in spectroscopy[5,7,14]). It is highly unlikely that $\boldsymbol{b}^{\neq}(0)$ is zero for all choices of $\boldsymbol{B}$ or every experiment and thus something else must be happening in order that REM I and II give equivalent pictures. This is the separation of time scales between the evolution of $\boldsymbol{a}$ and $\boldsymbol{b}^{\neq}$.

The variables **A** must be chosen such that *all* slow quantities are included. By slow, we mean

$$\dot{A}(t)/A(t) \sim \mathcal{O}(\lambda), \quad \lambda \ll 1. \tag{25}$$

Examples of the slowness parameter, λ, are the light to heavy particle mass ratio in Brownian motion, the wavevector, k, of the mode in hydrodynamics, or a weak coupling parameter in lineshape studies. The other variables in the system, $\boldsymbol{B}$ are fast which implies

$$\dot{B}/B \sim \mathcal{O}(1), \quad \lambda \ll 1. \tag{26}$$

Note that eqs. (25) and (26) may be consequences of the underlying microscopic dynamics (e.g. conservation laws or weak coupling) or may be valid only in average sense, as is the case in broken symmetry systems[15]) or line shape problems[7]).

What we are interested in knowing are the conditions under which the behavior of $\boldsymbol{a}(t)$ found from REM I and II agree (at least approximately). The transient effects associated with $\boldsymbol{b}^{\neq}(0)$ can be expected to disappear only after some time. We, on the other hand, will measure $\boldsymbol{a}(t)$ on the time scale which characterizes its "slow" motion.

In order to discuss this more quantitatively we will rewrite eq. (23b). Defining

$$\langle \mathbf{A}(t)\mathbf{A}\rangle \equiv \exp[-\mathbf{\Phi}(t)]\cdot\langle \mathbf{A}\mathbf{A}\rangle \tag{27}$$

implies

$$\langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle\cdot\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1} = -\dot{\mathbf{\Phi}}(t). \tag{28}$$

Upon substitution of eq. (28) in eq. (16) and "solving" for $\mathbf{A}(t)$ we get

$$\mathbf{A}(t) = \exp[-\mathbf{\Phi}(t)]\cdot\left\{\mathbf{A}(0) + \int_0^t \mathrm{d}t_1 \exp[\mathbf{\Phi}(t_1)]\cdot\dot{\mathbf{A}}^{\neq}(t_1)\right\}. \tag{29}$$

Eq. (29) can be used in eq. (23b) to give

$$\boldsymbol{a}(t) = \exp[-\mathbf{\Phi}(t)]\cdot\left\{\boldsymbol{a}(0) + \int_0^t \mathrm{d}\tau \exp[\mathbf{\Phi}(\tau)]\cdot\langle\dot{\mathbf{A}}^{\neq}(\tau)\boldsymbol{B}^{\neq}\rangle\cdot\langle \boldsymbol{B}^{\neq}(0)\boldsymbol{B}\rangle^{-1}\cdot\boldsymbol{b}^{\neq}(0)\right\}. \tag{30}$$

The first term on the r.h.s. of eq. (30) is the REM I result, and thus the agreement between REM I and II is given by the relative magnitude of the two terms on this side of the equation. Of course, this is meaningful only if the factor $\exp[-\mathbf{\Phi}(t)]$ is not too small. Should the opposite be true, then the system has relaxed and the question is moot. The matrix $\mathbf{\Phi}(t)$ has eigenvalues whose real parts we denote by $\Gamma_i(t)$. For a stable system these diverge as $t\to\infty$. Moreover, as $\mathbf{\Phi}$ characterizes the motion of the $\boldsymbol{A}$ variables, Γ_i will vanish as $\lambda\to 0$ for fixed t. We thus have

$$\Gamma_i \to 0 \quad \text{as } \lambda\to 0, \quad t \text{ fixed}, \tag{31a}$$

$$\Gamma_i \to \infty \quad \text{as } t\to\infty, \quad \lambda \text{ fixed}. \tag{31b}$$

For example in hydrodynamics ($\lambda\equiv k$), $\Gamma_i(t)\sim\lambda^2 t$. We wish to compare REM I and REM II on a time scale in which the relaxation is still in progress, i.e.

$$\Gamma_i(t) \leqslant 1, \quad \text{for small } \lambda. \tag{31c}$$

Clearly this imposes a connection between t and λ (cf. eqs. (31a) and (31b)), since the relevant range of t will depend on λ. In order to make this explicit we introduce the scaled time defined by

$$t = \lambda^{-\alpha} t^*, \quad t^* \leqslant 1, \tag{32}$$

where the exponent α is chosen such that

$$\lim_{\substack{\lambda\to 0\\ t^* \text{ fixed} \leqslant 1}} \Gamma_i(t^*\lambda^{-\alpha}) \leqslant \mathcal{O}(1). \tag{33}$$

In general this imposes an upper bound on α (eq. 32). In hydrodynamics $\Gamma_i(t^*\lambda^{-\alpha}) \sim \lambda^{2-\alpha}t^*$ and thus $\alpha \leq 2$. The above limiting procedure defines the $\boldsymbol{a}$ timescale.

Returning to eq. (30) we see that the REM II contribution will be unimportant on the $\boldsymbol{a}$ timescale if

$$\left|\int_0^{t^*} \frac{\mathrm{d}\tau}{\lambda^\alpha} \exp[\boldsymbol{\Phi}(\tau/\lambda^\alpha)]\langle \dot{\boldsymbol{A}}^{\neq}(\tau/\lambda^\alpha)\boldsymbol{B}^{\neq}\rangle \cdot \langle \boldsymbol{B}^{\neq}\boldsymbol{B}\rangle^{-1} \cdot \boldsymbol{b}^{\neq}(0)\right| < f(\lambda), \quad f \to 0 \text{ as } \lambda \to 0, \tag{34}$$

where f gives the magnitude of the error made by using REM I.

If a $\boldsymbol{B}$ is found for which eq. (33) does not hold, then REM I and II are not equivalent and thus the $\boldsymbol{a}$ set of variables must be expanded. Moreover, implicit in this discussion is the restriction that the $\boldsymbol{b}^{\neq}(0)$ do not depend on λ in a singular fashion; a reasonable physical requirement. Since $\exp(\boldsymbol{\Phi}(\tau)/\lambda^\alpha)$, is $\mathcal{O}(1)$ for τ's appearing in eq. (34), eq. (34) implies that

$$\langle \dot{\boldsymbol{A}}^{\neq}(t^*/\lambda)\boldsymbol{B}^{\neq}\rangle \cdot \langle \boldsymbol{B}^{\neq}(0)\boldsymbol{B}\rangle^{-1} \cdot \boldsymbol{b}^{\neq}(0)/\lambda^\alpha = \mathcal{O}(\lambda^\epsilon); \quad \epsilon > 0. \tag{35}$$

This should not come as a surprise, since eq. (35) simply states that the REM II correction be negligible in eq. (19a) on the $\lambda^{-\alpha}$ time scale. Eq. (35) is interesting in that it gives a precise meaning to statements concerning the time decay of "fast" variables. An important example is obtained by letting $B = \dot{A}$, thereby yielding the type of correlation function commonly found in the definitions of dissipative coefficients.

The fact that the time dependence is carried by $\dot{\boldsymbol{A}}^{\neq}(t)$, a quantity orthogonal to the slow variables, motivates the usual assumption that this correlation function decays on the fast (i.e., λ-independent) time scale. If this is true, then it can easily be shown that eq. (34) holds for any $\alpha > 0$ (provided eq. (33) is satisfied). In fact, by letting $\tau \to \tau/\lambda^\alpha$ in the integral in eq. (34) we find that $f(\lambda) \approx \lambda$ when the separation of time scales is assumed. Thus, even if the assumption of separation of time scales is justified, REM I and II in general agree only to $\mathcal{O}(\lambda)$.

The limit of separation of time scales is sometimes referred to as the Markov limit, since the coefficients in REM I will be independent of time on the '$\boldsymbol{a}$' time scale (cf. eq. (15b)).

3.3. *Case III – non-Markov behavior*

If there is no separation of time scales, then correlation functions of the tyep $\langle \dot{A}^{\neq}(t)B^{\neq}\rangle$ will vary on the '$\boldsymbol{a}$' time scale or a longer one. In this case, we cannot in general neglect the $\boldsymbol{b}^{\neq}(0)$ term in eq. (31) since it varies on the '$\boldsymbol{a}$'

time scale. It may however be small, implying that for some non-Markov REM, differences between REM I and II are unimportant for small λ. We expect that here λ must be much smaller than in the Markov case, if the two descriptions are ever equivalent. Another way of stating this is as follows: The non-Markovian REM I is an indication that other variables $\boldsymbol{B}$, not included in our $\boldsymbol{A}$ set, are relevant for the evolution of $\boldsymbol{a}$. As a result their initial conditions $\boldsymbol{b}(0)$ are also relevant. Since we have no way of incorporating that information in REM I, it is very unlikely that they will be valid, unless we are lucky and condition (24) holds for all relevant variables not included in our $\boldsymbol{A}$ set. We should thus be very cautious when using non-Markovian REM for the time evolution of macrovariables. This will be demonstrated very clearly in the next section.

4. Illustrative examples

In order to clarify some of the ideas presented above, we consider the case where $\boldsymbol{A}$ is a single variable A and where REM II is obtained by including the time derivative of A. Thus

$$b(0) = b^*(0) = \dot{a}(0), \tag{36}$$

This follows from the fact that $\langle \dot{A}(0)A \rangle$ vanishes. Using eqs. (23b), (19a) and (28), REM II can be written as

$$\frac{\mathrm{d}a(t)}{\mathrm{d}t} = -\dot{\Phi}(t)a(t) + \exp[-\Phi(t)]\ddot{\Phi}(t)/\ddot{\Phi}(0) \cdot \dot{a}(0), \tag{37a}$$

with the solution

$$a(t) = \exp[-\Phi(t)]\left\{a(0) + \frac{\dot{\Phi}(t)}{\ddot{\Phi}(0)}\dot{a}(0)\right\}. \tag{37b}$$

Eq. (37a) clearly shows the close connection between the REM II correction and non-Markovness. When $\dot{\Phi}$ = constant then $\ddot{\Phi} = 0$, and the REM I and REM II equations agree. The second term in eq. (37b) merely reflects the initial non-Markovness.

A simple example is found by taking the variable A to have the Brownian motion correlation function, i.e.,

$$\Phi(t) = \frac{\Delta^2}{\gamma^2}[\mathrm{e}^{-\gamma t} - 1 + \gamma t], \tag{38a}$$

with

$$\dot{\Phi}(t) = \frac{\Delta^2}{\gamma}[1 - \mathrm{e}^{-\gamma t}]. \tag{38b}$$

Then it follows (cf. eq. (28)) that

$$\ddot{\Phi}(0) = \langle \dot{A}^2 \rangle / \langle A^2 \rangle = \Delta^2. \tag{38c}$$

Combining these results with eq. (37b) gives

$$a(t) = \exp[-\Phi(t)]\left\{a(0) + \frac{1}{\gamma}[1 - e^{-\gamma t}]\dot{a}(0)\right\}. \tag{39}$$

The REM II correction is now quite simple. In the large friction case (i.e., $\gamma \gg \Delta$), $a(t)$ evolves on a time scale given by Δ^2/γ. The relaxation is exponential (i.e., Markov) and for $t \approx \gamma/\Delta^2$, the relative importance of the REM II part is given by $(\gamma^2/\Delta^2 \gg 1)$

$$\frac{1}{\gamma}\dot{a}(0)/a(0); \tag{40}$$

since γ is large, this term will be small in general.

The opposite limit $(\Delta \gg \gamma)$ gives a Gaussian relaxation; i.e.,

$$a(t) \approx \exp\left[-\frac{\Delta^2 t^2}{2}\right]\{a(0) + t\dot{a}(0)\}. \tag{41}$$

What is striking is the fact that the REM II correction increases with time. If $\dot{a}(0)/a(0) \approx \mathcal{O}(\Delta)$, then the second term on the r.h.s. of eq. (41) will not be negligible on the time scale of the relaxation. Thus in the Gaussian limit REM I and II are not equivalent. If we try to rectify this by including both A and $\dot{A}$ in our REM I description, then we will encounter analogous difficulties if $\ddot{A}$ is incorporated in REM II. Hence, the simplest model of a non-Markov process fails to meet the restrictions discussed here. At best, this process describes only those experiments for which

$$(\dot{a}(0)/\Delta a(0)) \ll 1.$$

As a second example, consider the generalized hydrodynamics of diffusion, where A is a concentration. In this case, we may write

$$\Phi(t) - Dk^2 t = Dk^2\zeta \begin{Bmatrix} 2t^{1/2} & (3-d) \\ t(\ln t - 1) & (2-d) \\ \frac{2}{3}t^{3/2} & (1-d) \end{Bmatrix}, \quad \ddot{\Phi}(t) \propto t^{-d/2}, \tag{42}$$

where k is the mode wavevector, while D and ζ are constants. The terms on the r.h.s. of the equation arise from long-time tails and should be considered only for asymptotically long times. From eq. (42) we see that $\dot{\Phi}(t)$ diverges for less than two dimensions, thus causing a divergence in the diffusion coefficient.

The static correlation functions in eq. (37) typically satisfy

$$\ddot{\Phi} = \frac{\langle \dot{A}^2 \rangle}{\langle A^2 \rangle} \approx k^2 k_B T/m, \tag{43}$$

where m is a mass, k_B is Boltzmann's constant and T is temperature (this is exact for self-diffusion). Thus

$$a(t) \approx e^{-\Phi(t)} a(0) \left\{ 1 + \frac{\dot{\Phi}(t)}{k^2 m k_B T} \frac{\dot{a}(0)}{a(0)} \right\}. \tag{44}$$

For three dimensions, the effect of the long-time tail becomes less important for long times and the importance of the REM II correction is characterized by

$$\frac{Dk}{mk_B T}, \quad \text{with } \frac{\dot{a}}{a} \approx k. \tag{45}$$

This is typical Markov behavior. We remark, that the relative importance of the long-time tail is even smaller and therefore long-time tail effects should not be included if REM I/II paradoxes are to be neglected consistently.

In one dimension, the long-time tail part of Φ is more important for long times. Hence, $\alpha \leq 4/3$, which is clearly not characteristic of normal hydrodynamics ($\alpha = 2$). From eq. (44), it follows that the REM II correction is $\mathcal{O}(k^{1-(\alpha/2)})$. This is larger than the correction in three dimensions. Thus if one is satisfied with a larger error, REM I (non-Markov) will suffice.

The case of two dimensions is interesting because the divergences associated with long-time tails are extremely weak (logarithmic). Thus a hydrodynamic time scale makes sense for all but extremely long times. If we choose such a scale (i.e., $\alpha \leq 2$) then the REM II correction is $\mathcal{O}(k \ln k)$ which goes to zero for $k \to 0$.

In summary, then, we have shown that extreme caution must be used in interpreting reduced equatons of motion for nonequilibrium processes. In the best situation (i.e., Markov) there is still some error, this error becoming worse as the system becomes more non-Markov.

5. REM for equilibrium correlation functions

An equilibrium correlation function $U_{\nu\mu}(\tau)$ is defined as[1-6])

$$U_{\nu\mu}(\tau) \equiv \mathrm{Tr}(A_\nu^\dagger(\tau) A_\mu \rho_{eq}), \tag{46}$$

where ρ_{eq} is the equilibrium density matrix of our system which commutes with the Hamiltonian H, i.e.

$$L\rho_{eq} = [H, \rho_{eq}] = 0. \tag{47}$$

Reduced equations of motion are often used as a method of getting useful approximations for equilibrium correlation functions. In this case, one often uses non-Markov equations. We shall now show that here, unlike the evolution of macrovariables, REM I is equivalent to REM II even in the non-Markov case. Let us define a matrix of correlation functions $\mathbf{U}_{AA}(\tau)$ whose components are $U_{\nu\mu}(\tau)$. One can easily repeat the manipulations of the previous sections to derive REM for $\mathbf{U}_{AA}$. The resulting REM are

$$\frac{\mathrm{d}\mathbf{U}_{AA}(t)}{\mathrm{d}t} = \langle \mathbf{AA}\rangle\langle \mathbf{AA}\rangle^{-1}\mathbf{U}_{AA}(t) - \int_0^t \mathrm{d}\tau \langle \dot{\mathbf{A}}^{\neq}(\tau)\dot{\mathbf{A}}\rangle\langle \mathbf{A}(\tau)\mathbf{A}\rangle^{-1}\mathbf{U}_{AA}(t). \tag{48}$$

Upon adding the B variables we define a new extended $\mathbf{U}$ matrix

$$\mathbf{U} = \begin{pmatrix}\mathbf{U}_{AA}\\ \mathbf{U}_{BA}\end{pmatrix} = \begin{pmatrix}\langle \mathbf{A}(t)\mathbf{A}\rangle\\ \langle \boldsymbol{B}(t)\mathbf{A}\rangle\end{pmatrix}. \tag{49}$$

We may now proceed as before to derive REM for $\mathbf{U}$, and eliminate $\mathbf{U}_{BA}$. The final result will be REM II.

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{pmatrix}\mathbf{U}_{AA}\\ \mathbf{U}_{BA}\end{pmatrix} = \begin{pmatrix}\langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle & \langle \dot{\mathbf{A}}(t)\boldsymbol{B}\rangle\\ \langle \dot{\boldsymbol{B}}(t)\mathbf{A}\rangle & \langle \dot{\boldsymbol{B}}(t)\boldsymbol{B}\rangle\end{pmatrix}\begin{pmatrix}\langle \mathbf{A}(t)\mathbf{A}\rangle & \langle \mathbf{A}(t)\boldsymbol{B}\rangle\\ \langle \boldsymbol{B}(t)\mathbf{A}\rangle & \langle \boldsymbol{B}(t)\boldsymbol{B}\rangle\end{pmatrix}^{-1}\begin{pmatrix}\mathbf{U}_{AA}\\ \mathbf{U}_{BA}\end{pmatrix}. \tag{50}$$

Proceeding along the same lines which led from eq. (18) to eq. (19), we may rewrite (50) in the form

$$\frac{\mathrm{d}\mathbf{U}_{AA}}{\mathrm{d}t} = \langle \dot{\mathbf{A}}\mathbf{A}\rangle\langle \mathbf{AA}\rangle^{-1}\mathbf{U}_{AA} - \int_0^t \mathrm{d}\tau\langle \dot{\mathbf{A}}^{\neq}(\tau)\mathbf{A}\rangle\langle \mathbf{A}(\tau)\mathbf{A}\rangle^{-1}\mathbf{U}_{AA}(t) + \langle \dot{\mathbf{A}}^{\neq}(t)\boldsymbol{B}\rangle \times \langle \boldsymbol{B}^{\neq}\boldsymbol{B}\rangle^{-1}\mathbf{U}^{\neq}_{BA}(0), \tag{51}$$

where $\dot{\mathbf{A}}^{\neq}$ is defined in (16) and $B^{\neq}$ is given by eq. (20a).

$U^{\neq}_{BA}(0)$ is the analogue of $b^{\neq}(0)$ (eq. (20b)) and is given by

$$\mathbf{U}^{\neq}_{BA}(0) = \mathrm{Tr}(\boldsymbol{B}^{\neq}\mathbf{A}\rho) = \langle \boldsymbol{B}\mathbf{A}\rangle - \langle \boldsymbol{B}\mathbf{A}\rangle\langle \mathbf{AA}\rangle^{-1}\langle \mathbf{AA}\rangle = 0. \tag{52}$$

Thus this falls within the category of case (I) of section 3 and thus REM II is identical with REM I!

We note that there is a basic difference between REM for macrovariables and REM for correlation functions. In both cases, non-Markov equations mean that there are more relevant variables $\boldsymbol{B}$ not included initially in our set A. REM I do not allow us to use the information about the initial values of $\boldsymbol{B}(\boldsymbol{b}(0))$ but rather fix them automatically, whereas REM II allow us to use that information. REM for equilibrium correlation functions are means of resummation (getting good approximations for correlation functions) and they have to be solved with a fixed set of initial conditions; $\mathbf{U}(0)$ is a well-defined matrix and is not a matter of preparation. In this case, the choice of the relevant variables is just a matter of convenience and the non-Markov equations are in principle exact. A given set of REM may be improved by adding more variables or by calculating the kernels in higher order, but this is a technical matter and there is no fundamental limitation to the usage of non-Markov REM for the evaluation of equilibrium correlation functions.

6. Summary

In this paper we have considered the usefulness and ranges of validity of Markov and non-Markov REM in non-equilibrium statistical mechanics. In particular we have given a precise criterion for checking the choice of the state variables $\boldsymbol{a}(t)$ (cf. eqs. (34) and (35)). In fact, should eq. (34) not hold for some choice of $\boldsymbol{B}$, then REM I/II are inconsistent, implying that the set $\boldsymbol{A}$ is incomplete. In sections 3 and 4 we have given estimates for the differences between REM I and II. In the case of a Markov process, the differences between REM I/II was smallest, but even here it was not zero. For non-Markov processes, as is clearly shown by eqs. (37a) and (37b), the magnitude of the differences between REM I/II increases with the degree of non-Markovness. Surprisingly this was most severe in the Gaussian limit (cf. eq. (41)). For the examples taken from long-time tail phenomena, the differences between REM I/II were larger than in the Markov limit, although the error could still be made small. Note that in the context of this discussion it was crucial that the comparison was made on the relevant time scale, which may not be hydrodynamic.

Finally we have shown (cf. section 5) that all of the above-mentioned problems completely disappear when REM are used to compute equilibrium time-correlation functions.

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Appendix A

The basic reduced equations of motion (eq. (8)) for the variables $C = \begin{pmatrix} a \\ b \end{pmatrix}$ are

$$\dot{C} = \dot{\mathbf{S}}\mathbf{S}^{-1}C, \tag{A.1}$$

where

$$\mathbf{S} = \begin{pmatrix} \langle A(t)A\rangle & \langle A(t)B\rangle \\ \langle B(t)A\rangle & \langle B(t)B\rangle \end{pmatrix} \tag{A.2}$$

and

$$\dot{\mathbf{S}} = \begin{pmatrix} \langle \dot{A}(t)A\rangle & \langle \dot{A}(t)B\rangle \\ \langle \dot{B}(t)A\rangle & \langle \dot{B}(t)B\rangle \end{pmatrix}. \tag{A.3}$$

Let us define a new variable

$$b^{\neq}(t) = b(t) - \langle B(t)A\rangle\langle A(t)A\rangle^{-1}a(t), \tag{A.4}$$

so that we get a new set $C' \equiv \begin{pmatrix} a \\ b^{\neq} \end{pmatrix}$. We may thus write

$$C' = \mathbf{T}^{-1}C, \tag{A.5}$$

where

$$\mathbf{T}^{-1} = \begin{pmatrix} 1 & 0 \\ -\langle B(t)A\rangle\langle A(t)A\rangle^{-1} & 1 \end{pmatrix}. \tag{A.6}$$

We shall now derive REM for C'. To that end we substitute eq. (A.5) in (A.1) resulting in

$$\frac{\mathrm{d}}{\mathrm{d}t}(\mathbf{T}C') = \dot{\mathbf{S}}\mathbf{S}^{-1}\mathbf{T}C', \tag{A.7}$$

where

$$\mathbf{T} = \begin{pmatrix} 1 & 0 \\ \langle B(t)A\rangle\langle A(t)A\rangle^{-1} & 1 \end{pmatrix}. \tag{A.8}$$

Upon performing the derivative on the l.h.s. of (A.7) and rearranging terms we finally get

$$\dot{C}' = \mathbf{K}(t)C', \tag{A.9a}$$

where

$$\mathbf{K}(t) = -\mathbf{T}^{-1}\dot{\mathbf{T}} + \mathbf{T}^{-1}\dot{\mathbf{S}}(\mathbf{T}^{-1}\mathbf{S})^{-1}. \tag{A.9b}$$

Let us now evaluate $\mathbf{T}^{-1}\mathbf{S}$. Using eqs. (A.2) and (A.6) we have

$$\mathbf{T}^{-1}\mathbf{S} = \begin{pmatrix} \langle A(t)A\rangle & \langle A(t)B\rangle \\ 0 & \langle B^{\neq}(t)B\rangle \end{pmatrix}, \tag{A.10}$$

where we have defined

$$B^{\neq}(t) \equiv B(t) - \langle B(t)A\rangle\langle A(t)A\rangle^{-1}A(t). \tag{A.11}$$

Upon inverting the matrix (A.10) we get

$$(\mathbf{T}^{-1}\mathbf{S})^{-1} = \begin{pmatrix} \langle A(t)A\rangle^{-1} & -\langle A(t)A\rangle^{-1}\langle A(t)B\rangle\langle B^{\neq}(t)B\rangle^{-1} \\ 0 & \langle B^{\neq}(t)B\rangle^{-1} \end{pmatrix}. \tag{A.12}$$

From (A.8) we have

$$\dot{\mathbf{T}} = \begin{pmatrix} 0 & 0 \\ -\langle \boldsymbol{B}^{\neq}(t)\dot{\mathbf{A}}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1} & 0 \end{pmatrix}, \tag{A.13}$$

where we have used the dot switching relation

$$\langle \dot{A}A\rangle = -\langle A\dot{B}\rangle. \tag{A.14}$$

Upon substitution of (A.3), (A.6), (A.12) and (A.13) in (A.9) we get

$$\mathbf{K}(t) = \mathbf{T}^{-1}\left\{\begin{pmatrix} 0 & 0 \\ \langle \boldsymbol{B}^{\neq}(t)\dot{\mathbf{A}}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1} & 0 \end{pmatrix} + \begin{pmatrix} \langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle & \langle \dot{\mathbf{A}}(t)\boldsymbol{B}\rangle \\ \langle \dot{\boldsymbol{B}}(t)\mathbf{A}\rangle & \langle \dot{\boldsymbol{B}}(t)\boldsymbol{B}\rangle \end{pmatrix}\begin{pmatrix} \langle \mathbf{A}(t)\mathbf{A}\rangle^{-1} & -\langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle\langle \mathbf{A}(t)\boldsymbol{B}\rangle\langle \boldsymbol{B}^{\neq}(t)\boldsymbol{B}\rangle^{-1} \\ 0 & \langle \boldsymbol{B}^{\neq}(t)\boldsymbol{B}\rangle^{-1} \end{pmatrix}\right\} \tag{A.15}$$

so that

$$\mathbf{K}(t) = \mathbf{T}^{-1}\begin{pmatrix} \langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1} & -\langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1}\langle \mathbf{A}(t)\boldsymbol{B}\rangle\langle \boldsymbol{B}^{\neq}(t)\boldsymbol{B}\rangle^{-1} + \langle \dot{\mathbf{A}}(t)\boldsymbol{B}\rangle\langle \boldsymbol{B}^{\neq}(t)\boldsymbol{B}\rangle^{-1} \\ \langle \boldsymbol{B}^{\neq}(t)\dot{\mathbf{A}}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1} + \langle \dot{\boldsymbol{B}}(t)\mathbf{A}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1} & -\langle \dot{\boldsymbol{B}}(t)\mathbf{A}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1}\langle \mathbf{A}(t)\boldsymbol{B}\rangle\langle \boldsymbol{B}^{\neq}(t)\boldsymbol{B}\rangle^{-1} + \langle \dot{\boldsymbol{B}}(t)\boldsymbol{B}\rangle\langle \boldsymbol{B}^{\neq}(t)\boldsymbol{B}\rangle^{-1} \end{pmatrix}$$

$$\equiv \begin{pmatrix} \boldsymbol{\beta}_{11} & \boldsymbol{\beta}_{12} \\ \boldsymbol{\beta}_{21} & \boldsymbol{\beta}_{22} \end{pmatrix}. \tag{A.16}$$

We thus have

$$\boldsymbol{\beta}_{11} = \langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1}, \tag{A.17}$$

$$\boldsymbol{\beta}_{12} = \langle \dot{\mathbf{A}}^{\neq}(t)\boldsymbol{B}\rangle\langle \boldsymbol{B}^{\neq}(t)\boldsymbol{B}\rangle^{-1} \tag{A.18}$$

where

$$\dot{\mathbf{A}}^{\neq}(t) = \dot{\mathbf{A}}(t) - \langle \dot{\mathbf{A}}(t)\mathbf{A}\rangle\langle \mathbf{A}(t)\mathbf{A}\rangle^{-1}\mathbf{A}(t), \tag{A.19}$$

$$\beta_{21} = 0, \tag{A.20}$$

and

$$\beta_{22} = \left[\frac{\mathrm{d}}{\mathrm{d}t}\langle \boldsymbol{B}^{\neq}(t)\boldsymbol{B}\rangle\right]\langle \boldsymbol{B}^{\neq}(t)\boldsymbol{B}\rangle^{-1}. \tag{A.21}$$

The REM (A.9) thus assume the form

$$\frac{\mathrm{d}\boldsymbol{a}}{\mathrm{d}t} = \boldsymbol{\beta}_{11}\boldsymbol{a} + \boldsymbol{\beta}_{12}\boldsymbol{b}^{\neq}, \tag{A.22a}$$

$$\frac{\mathrm{d}\boldsymbol{b}^{\neq}}{\mathrm{d}t} = \boldsymbol{\beta}_{22}\boldsymbol{b}^{\neq}, \tag{A.22b}$$

The solution of eq. (A.22b) is

$$b^{\neq}(t) = \langle B^{\neq}(t)B\rangle\langle B^{\neq}B\rangle^{-1}b^{\neq}(0). \tag{A.23}$$

Upon substitution of (A.23) in (A.22a) we finally get our final form of REM II (eq. (19a)):

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \langle \dot{A}(t)A\rangle\langle A(t)A\rangle^{-1}a + \langle \dot{A}^{\neq}(t)B\rangle\langle B^{\neq}B\rangle^{-1}b^{\neq}(0). \tag{A.24}$$

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