

# DYNAMICS OF COARSE GRAINED VARIABLES II. LINEAR NON-MARKOFFIAN PROCESSES

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## ABSTRACT

In this paper we derive an exact kinetic equation for the conditional probability that certain dynamic events occur at a given time in a many body system. This equation is applied to the very specific case of the "slow" decay of spontaneous fluctuations around an equilibrium state. The results are contained in three non-Markoffian equations, one which is of the Fokker-Planck type for the conditional probability itself, one for the coarse grained (mesoscopic) variables that turns out to be of the same structure as the phenomenological generalized regression of fluctuations law and a third one for the transport equations. These results may be regarded as the microscopic basis behind the equations given by Zwanzig some years ago in his generalized treatment of the Green-Kubo formula. We also show explicitly how the transport (Green-Kubo) matrix is related to the microscopic phenomena and discuss the comparison with Zwanzig's results. As a final point we indicate how the linear equations of non-equilibrium thermodynamics are recovered when the process is assumed to be a Markoffian one.

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## RESUMEN

Se deduce una ecuación cinética exacta para la probabilidad condicional de que ciertos eventos dinámicos ocurran en un sistema de muchos cuerpos a un tiempo dado. Esta ecuación se utiliza en el caso específico del "decaimiento lento" de fluctuaciones espontáneas que ocurren alrededor de un estado de equilibrio. Los resultados se expresan en tres ecuaciones no-markoffianas, una del tipo Fokker-Planck para la probabilidad condicional, otra para las variables de grano grueso o mesoscópicas que tiene la forma de una ecuación de regresión fenomenológica generalizada y una tercera para los coeficientes de transporte. Estos resultados pueden considerarse como las bases microscópicas de las ecuaciones propuestas hace varios años por Zwanzig en su tratamiento generalizado de las relaciones de Green y Kubo. También mostramos explícitamente cómo la matriz de transporte (Green y Kubo) está relacionada con fenómenos microscópicos y comparamos los resultados con los obtenidos por Zwanzig. Finalmente indicamos cómo se recuperan las ecuaciones lineales de la termodinámica irreversible cuando los procesos son markoffianos.

## I. INTRODUCTION

The purpose of this work is to give a microscopic basis to the results obtained in a beautiful paper by R. Zwanzig<sup>(1)</sup> and which constitutes an extension of the regression of fluctuations assumption of linear non-equilibrium thermodynamics<sup>(2)</sup> and the well known Green-Kubo time correlation formulas for the transport coefficients<sup>(3,4)</sup> to a non-markoffian process. Further, it was shown in that paper that these results reduce to the ordinary ones for a markoffian process only when the process is "very slow". The full meaning of a slow process is clearly stated in Zwanzig's paper and other sources in the literature<sup>(4)</sup> and we shall come back to it at a later stage of our work.

An exact non-markoffian kinetic equation for the probability distribution of the numerical values of the set of phase space functions chosen to describe the state of the system, has also been derived<sup>(5)</sup>. Furthermore when the phase space functions are assumed to change slowly in time the exact kinetic equation can be approximated by a still non-markoffian equation. Using the concept of a "slowness parameter  $\delta$ " Mori et al.<sup>(6,7)</sup> obtained Zwanzig's kinetic equation<sup>(7)</sup> and found a more systematic way of expanding the relevant quantities in power of  $\delta$ . This expansion has been closely examined recently<sup>(8)</sup> and compared with other approaches to the problem of deriving exact kinetic equations. However, the

precise way in which the non-markoffian regression equation arises from the exact kinetic equation and the subsequent analysis leading, via the kinetic equation, to the slow process approximation has, to our knowledge, never been discussed. This is the main task of this paper.

The general idea that we want to follow is to find the kinetic equation for  $P_{eq}(\vec{a}, t | \vec{b})$ , the conditional probability that the phase space functions  $\vec{A}(\Gamma, t)$  have values between  $\vec{a}$  and  $\vec{a} + d\vec{a}$  at time  $t$  given the initial time values  $\vec{A}(\Gamma, 0) = \vec{b}$ . This equation allows one to obtain an exact form for a law of regression of fluctuations which under well specified conditions it reduces to the linear non-markoffian expression used by Zwanzig. Also, the limiting form for the kinetic equation under the slow process approximation is easily obtained.

For the sake of completeness we shall devote section II of this paper to summarize Zwanzig's analysis. Section III contains the time evolution description for the coarse grained (or mesoscopic) variables of a system from a constrained equilibrium state onto a less constrained equilibrium state. This analysis is extended to the study of the fluctuations in the system around its equilibrium states, and will lead to the aforementioned kinetic equation for  $P_{eq}(\vec{a}, t | \vec{b})$  and to the regression of fluctuations equation. Their particular forms in non-markoffian regimes for linear and slow processes are derived. These results have the same structure as those obtained by Zwanzig. The last section is devoted to a detailed comparison between our results and the ones obtained by Zwanzig. We also point out here what is the structure of mesoscopic dynamics for a very slow process.

## II. RESUME OF ZWANZIG'S ANALYSIS

The essence of Zwanzig's work is to remove the assumption that a process is markoffian in the derivation of the time correlation formulae, the Green-Kubo expressions, for the transport coefficients. This is done through the following steps:

a) A strictly phenomenological linear non-markoffian regression law is proposed to describe the time evolution of well defined mesoscopic quantities,  $\vec{a}(t)$ . This equation reads,



$$\frac{d\vec{a}^b}{dt} = - \int_0^t dt' \underline{Y}(t') \cdot \vec{a}(t-t')^b \quad (1)$$

where  $\underline{Y}(t)$  is the time dependent matrix for the transport coefficients and

$$\vec{a}(t)^b = \int d\vec{a} \vec{a} P_{eq}(\vec{a}, t | \vec{b}) \quad (2)$$

where  $P_{eq}(\vec{a}, t | \vec{b})$  is the quantity defined in the previous section. The variables  $\vec{a}(t)^b$  were first introduced by Onsager<sup>(9)</sup> to characterize the average equilibrium fluctuations in an aged system.

The correlation matrix  $\underline{C}$  is now defined as,

$$\underline{C}(t) = \int d\vec{b} g_{eq}(\vec{b}) \vec{a}(t)^b \vec{b} \quad (3)$$

where  $g_{eq}(\vec{b})$  is the equilibrium distribution of the coarse grained variables  $\{\vec{b}\}$ . Multiplication of Eq. (1) by  $g_{eq}(\vec{b}) \vec{b}$  and integration over  $d\vec{b}$  leads at once to the time evolution equation for  $\underline{C}(t)$ , namely,

$$\frac{d\underline{C}(t)}{dt} = - \int_0^t ds \underline{Y}(s) \cdot \underline{C}(t-s) \quad (4)$$

from which  $\underline{C}(t)$  is readily obtained,

$$\frac{d^2 \underline{C}(t)}{dt^2} = -\underline{Y}(t) \cdot \underline{C}(0) + \int_0^t dt_1 \int_0^{t-t_1} dt_2 \underline{Y}(t_1) \cdot \underline{Y}(t_2) \cdot \underline{C}(t-t_1-t_2) \quad (5)$$

b) The microscopic equation for the matrix  $\underline{C}$  is found in terms of the time derivatives of the phase space functions  $\{A(\Gamma)\}$  and from it a corresponding equation for  $\underline{C}(t)$  is obtained. This is accomplished starting with the definition of a time correlation function, namely<sup>(10)</sup>,

$$\underline{C}(t) = \int d\Gamma \rho_{eq}(\Gamma) \vec{A}(\Gamma, 0) \vec{A}(\Gamma, t) \equiv \left\{ \vec{A}(\Gamma, t), \vec{A}(\Gamma, 0) \right\} \quad (6)$$

where the scalar product  $(A, B)$  is defined in the usual way,

$$(A,B) = \int d\Gamma \rho_{\text{eq}}(\Gamma) A(\Gamma) B(\Gamma) \quad (7)$$

Then,

$$\dot{C}(t) = \left[ \dot{\vec{A}}(\Gamma, t), \vec{A}(\Gamma, 0) \right] = \left[ \dot{\vec{A}}(\Gamma, 0), \vec{A}(\Gamma, -t) \right] \quad (8)$$

since because of Eq. (7), Eq. (6) is invariant under time inversions. If we denote by  $\Pi$  the time inversion operator  $\Pi f(\Gamma, t) = f(\Gamma', -t)$  where  $\Gamma = (\vec{q}, \vec{p})$  and  $\Gamma' = (\vec{q}, -\vec{p})$ , then  $\Pi \vec{A}(\Gamma, t) = \underline{\varepsilon} \cdot \vec{A}(\Gamma', +t)$  where  $\varepsilon_{ij} = \varepsilon_i \delta_{ij}$  and  $\varepsilon_i = \pm 1$  the plus sign corresponding to even functions and the minus sign to odd functions of time. Since  $\dot{C}(t)$  is invariant under time inversions,

$$\dot{C}(t) = \left[ \Pi \dot{\vec{A}}(\Gamma, 0), \Pi \vec{A}(\Gamma, -t) \right] = -\underline{\varepsilon} \cdot \left[ \dot{\vec{A}}(\Gamma, 0), \vec{A}(\Gamma, t) \right] \cdot \underline{\varepsilon} \quad (9)$$

and hence

$$\ddot{C}(t) = -\underline{\varepsilon} \cdot \left[ \dot{\vec{A}}(\Gamma, 0), \dot{\vec{A}}(\Gamma, t) \right] \cdot \underline{\varepsilon} = -\underline{\varepsilon} \cdot \underline{g}(t) \cdot \underline{\varepsilon} \quad (10)$$

where  $\underline{g}$  is referred to as the time correlation matrix. If one further assumes that all the components of the vector  $\vec{A}(\Gamma, t)$  are of the same parity under time inversions

$$\ddot{C}(t) = -\underline{g}(t) \quad (11)$$

and  $C(t=0) = 0$  according to Eq. (9)

c) The matrix for the transport coefficients is obtained by simply setting the two expressions for  $\ddot{C}(t)$  in (a) and (b) equal to each other. This relates  $\underline{Y}(t)$  to  $\underline{g}(t)$ . If one takes the Laplace transforms of Eqs. (5) and (11) one gets immediately that

$$\hat{\underline{g}}(p) = \left[ \hat{\underline{Y}}(p) - \frac{\hat{\underline{Y}}^2(p)}{p \mathbf{1} + \underline{Y}(p)} \right] \cdot \underline{C}(0) \quad , \quad (12)$$

where  $\hat{\underline{f}}(p) = \int dt e^{-pt} f(t)$  and  $\mathbf{1}$  the unit matrix.

d) The next step consists in studying the conditions under which the Green-Kubo formulae are valid by assuming that  $\underline{y}(t)$  is governed by a "slowness parameter". Then the idea of a very slow process may be set forth in a precise language. This leads also to the behaviour of  $\underline{c}(t)$  for slow processes when the microscopic behaviour of  $\underline{g}(t)$  is extracted from its macroscopic counterpart.

To do this one introduces the "slowness parameter  $\zeta$ " in such a way that

$$\hat{\underline{y}}(\underline{p}) = \zeta \underline{\mu}(\zeta, \underline{p}) \quad (13)$$

and  $\underline{\mu}(\zeta, \underline{p})$  is a continuous function at  $\underline{\mu}(0, 0)$ . Further, the Laplace transform of Eq. (4) gives that

$$\underline{c}(\underline{p}) = [\underline{p}\underline{1} + \underline{y}(\underline{p})]^{-1} \cdot \underline{c}(0) \quad . \quad (14)$$

Substitution of Eq. (13) into Eq. (14) and inversion of the Laplace transform leads at once to

$$\underline{c}(t) = \frac{1}{2\pi i} \int dx e^{x\tau} [\underline{x}\underline{1} + \underline{\mu}(\zeta, \zeta x)]^{-1} \cdot \underline{c}(0) \quad , \quad (15)$$

where  $x = \zeta^{-1} p$  and  $\tau = \zeta t$  .

A very slow process is now defined as one in which the limit of  $\zeta \rightarrow 0$  keeping  $\tau$  constant. Then,

$$\lim_{\substack{\zeta \rightarrow 0 \\ \tau = \text{const.}}} \underline{c}(t) = e^{-\underline{\mu}(0,0)\tau} \cdot \underline{c}(0) \quad . \quad (16)$$

If the behaviour of  $\underline{c}(t)$  for long times,  $\underline{c}_{\text{macro}}(t)$ , is now identified with the limit expressed by Eq. (16), then it implies that

$$\frac{d\underline{c}_{\text{macro}}(t)}{dt} = -\underline{\mu}(0,0) \zeta \underline{c}_{\text{macro}}(t) \quad , \quad (17)$$

which is nothing else than the equation for the time correlation matrix which one obtains when Onsager's linear regression assumption is used.

Thus  $\zeta \underline{\mu}(0,0)$  is the time independent transport correlation matrix,

e) The last step is to calculate the time independent correlation matrix  $\underline{\mu}(0,0)$  in terms of the microscopic quantities and thus obtain the Green-Kubo formulae. To do this one uses the "slowness" assumption as given by Eq. (13) in Eq. (12) relating the micro and macroscopic matrices. Thus,

$$\zeta^{-1} \hat{\zeta}(\underline{p}) \cdot \zeta(0)^{-1} = \underline{\mu}(\zeta, \underline{p}) - \frac{\zeta \underline{\mu}^2(\zeta, \underline{p})}{\underline{p} \mathbf{1} + \zeta \underline{\mu}(\zeta, \underline{p})} \quad . \quad (18)$$

Now take first the limit as  $\zeta \rightarrow 0$  and next the limit when  $\underline{p} \rightarrow 0$ . Then,

$$\underline{\mu}(0,0) = \lim_{\underline{p} \rightarrow 0} \lim_{\zeta \rightarrow 0} \zeta^{-1} \hat{\zeta}(\underline{p}) \cdot \zeta^{-1}(0) \quad . \quad (19)$$

Using now the fact that<sup>(2)</sup>

$$g_{\text{eq}}(\underline{a}) = c \exp \left( - \frac{1}{2k_B} \underline{g} : \vec{\underline{a}} \vec{\underline{a}} \right) \quad , \quad (20)$$

where  $g_{ij} = \left( \frac{\partial^2 S}{\partial a_i \partial a_j} \right)$ ,  $S$  being the equilibrium entropy and  $k_B$  Boltzmann's constant, we get that  $\zeta^{-1}(0) = k_B^{-1} \underline{g}$ . Finally,

$$\underline{\mu}(0,0) = \frac{1}{k_B} \lim_{\underline{p} \rightarrow 0} \lim_{\zeta \rightarrow 0} \zeta^{-1} \int_0^{\infty} e^{-\underline{p}t} \left( \dot{\vec{\underline{A}}}(\Gamma, 0), \dot{\vec{\underline{A}}}(\Gamma, t) \right) dt \cdot \underline{g} \quad , \quad (21)$$

which is the Green-Kubo expression for the transport coefficients.

### III. MESOSCOPIC DYNAMICS

Using the projector operator method introduced by Mori<sup>(11)</sup> we shall derive an exact kinetic equation for the conditional probability  $P(\vec{\underline{a}}, t | \vec{\underline{b}})$  as well as the equation of motion for the variables  $\vec{\underline{a}}(t)$ . In the latter case only a brief outline of the calculation is given since the full details have been published elsewhere<sup>(12)</sup>. Let  $\{\underline{A}_j(\Gamma, t)\} \equiv \vec{\underline{A}}(\Gamma, t)$  denote the vector formed by all the phase space functions associated to the macroscopic observables of the system  $\vec{\underline{a}}(t)$ . Clearly,



$$\vec{\alpha}(t) = \int d\Gamma \rho(\Gamma, 0) \vec{A}(\Gamma, t) \quad (22)$$

Assuming that the initial state of the system is a constrained equilibrium state described by  $\vec{A}(\Gamma, 0)$ , we have that

$$\rho(\Gamma, 0) = W(\Gamma) v\left(\vec{A}(\Gamma, 0)\right) \quad (23)$$

where  $W(\Gamma)$  is a real function of the system's invariants and  $v\left(\vec{A}(\Gamma, 0)\right)$  an arbitrary function of  $\vec{A}(\Gamma, 0)$ .

Each time we observe the state of the system, the vector  $\vec{A}(\Gamma)$  takes a numerical value  $\vec{a}$ , which is taken to be a stochastic process. Thus one is interested in the probability distribution  $g(\vec{a}, t) d\vec{a}$  representing the probability that at time  $t$  the numerical value of  $\vec{A}$  lies in the range  $\vec{a}, \vec{a} + d\vec{a}$ . Also<sup>(5)</sup>,

$$g_n(\vec{a}_1 t_1, \dots, \vec{a}_n t_n) = \int d\Gamma \rho(\Gamma, 0) G(\vec{a}_1, t_1) \dots G(\vec{a}_n, t_n) \quad , \quad (24)$$

where  $G(\vec{a}, t) = \int \delta\left[A_i(\Gamma, t) - a_i\right] = \delta\left[\vec{A}(\Gamma, t) - \vec{a}\right]$  is the well known characteristic function for the hypercell in phase space at time  $t$ .

The quantity that is of our interest here is the conditional probability  $P(\vec{a}, t | \vec{b})$  which is in general defined as<sup>(10)</sup>

$$P(\vec{a}, t | \vec{b}) = g_1^{-1}(\vec{b}, 0) g_2(\vec{a}, t; \vec{b}, 0) \quad (25)$$

and may also be written in a more compact way using Eq. (7) but with  $W(\Gamma)$  as a weight function instead of  $\rho_{eq}(\Gamma)$ . Then, calling  $[G(\vec{b}, 0)] = [1, G(\vec{b}, 0)] = \int d\Gamma W(\Gamma) G(\vec{b}, 0)$  and using the expression for the average of any phase space function  $f(\Gamma)$  over the hypercell,

$$\langle f(\Gamma); \vec{b} \rangle = [G(\vec{b}, 0)]^{-1} \left[ f(\Gamma), G(\vec{b}, 0) \right] \quad (26)$$

we get that

$$P(\vec{a}, t | \vec{b}) = \langle G(\vec{a}, t); \vec{b} \rangle \quad (27)$$



Furthermore, the exact equation of motion for the characteristic function  $G(\vec{a}, t)$  has been shown to be given by<sup>(8)</sup>

$$\frac{dG(\vec{a}, t)}{dt} = Z(\vec{a}, t) G(\vec{a}, t) + F(\vec{a}, t) \quad (28)$$

where  $Z(\vec{a}, t)$ , Zwanzig's operator (20), is a kinetic operator whose explicit form is at present irrelevant (see Eq. (36) in Ref. 8) and  $F(\vec{a}, t)$  is a function satisfying the property that

$$\langle F(\vec{a}, t); b \rangle = 0 \quad (29)$$

From Eqs. (27) and (28) it follows at once, using Eq. (29), that

$$\frac{dP(\vec{a}, t | \vec{b})}{dt} = Z(\vec{a}, t) P(\vec{a}, t | \vec{b}) \quad (30)$$

Equation (30) is similar in structure to the kinetic equation derived by Zwanzig who obtains the time evolution equation for  $g_1(\vec{a}, t)$  when Eq. (28) is averaged with  $\rho(\Gamma, 0)$ <sup>(5)</sup>. For future purposes, we shall choose, among the various possible expressions for  $ZO$ <sup>(8)</sup>, its Generalized Kramers Moyal (GKM) form which is given by<sup>(7,8,14)</sup>

$$Z(\vec{a}, t) f(\vec{a}, t) = \sum_{n=0}^{\infty} \sum_{k_0} \dots \sum_{k_n} \left[ -\frac{\partial}{\partial a_{k_0}} \right] \dots \left[ -\frac{\partial}{\partial a_{k_n}} \right] \int ds K_{k_0 \dots k_n}(\vec{a}, s) f(\vec{a}, t-s) \quad (31)$$

where the functions  $K_{k_0 \dots k_n}(\vec{a}, s)$  are summarized in the appendix. Equations (30) and (31) constitute our sought kinetic equation for the probability function  $P(\vec{a}, t | \vec{b})$ .

In order to obtain the microscopic form for Eq. (1), we start from the definition of a coarse grained variable as the first moment of the function  $P(\vec{a}, t | \vec{b})$ , namely<sup>(10)</sup>,

$$\overline{\vec{a}(t)}^b = \int d\vec{a} \vec{a} P(\vec{a}, t | \vec{b}) = \langle \vec{A}(\Gamma, t); b \rangle \quad (32)$$

where the last equality follows from Eq. (27) and the obvious identity  $\vec{A}(\Gamma, t) = \int d\vec{a} \vec{a} G(\vec{a}, t)$ . It also shows that the coarse grained variables are given as averages taken over the hypercell in phase space of the phase space functions  $\vec{A}(\Gamma, t)$ . From Eqs. (30), (31) and (32) it follows at once that

$$\frac{d\overline{\vec{a}(t)}^b}{dt} = \int_0^t ds \int d\vec{a} \vec{K}(\vec{a}, s) P(\vec{a}, t-s | \vec{b}) \quad , \quad (33)$$

where  $\vec{K}(\vec{a}, s)$  is the vector whose components are the functions  $K_{k_0}(\vec{a}, s)$  appearing in Eq. (31). Equation (33) is our desired goal, it gives the microscopic form of the time evolution of the coarse grained variables  $\overline{\vec{a}(t)}^b$ .

Finally, if we substitute Eq. (23) into Eq. (22), we make use of Eq. (32) and recognize that  $v[\vec{A}(\Gamma, 0)] = \int d\vec{b} v(\vec{b}) G(\vec{b}, 0)$ , we find that

$$\vec{\alpha}(t) = \int d\vec{b} v(\vec{b}) [G(\vec{b}, 0)] \overline{\vec{a}(t)}^b \quad (34)$$

is a useful relationship between the macroscopic variables  $\vec{\alpha}(t)$  and the coarse grained variables  $\overline{\vec{a}(t)}^b$ . Indeed the time evolution equation for the former ones is now easily derived using Eq. (33) obtaining that

$$\frac{d\vec{\alpha}(t)}{dt} = \int_0^t ds \int d\vec{a} \vec{K}(\vec{a}, s) \int d\vec{b} v(\vec{b}) [G(\vec{b}, 0)] P(\vec{a}, t-s | \vec{b}) \quad . \quad (35)$$

Recalling that from Eq. (24)  $g_1(\vec{b}, 0) = v(\vec{b}) [G(\vec{b}, 0)]$  and carrying over the last integral, Eq. (35) reduces to

$$\frac{d\vec{\alpha}(t)}{dt} = \int_0^t ds \int d\vec{a} \vec{K}(\vec{a}, s) g_1(\vec{a}, t-s) \quad . \quad (36)$$

This result is the non linear transport equation describing the time evolution of the macroscopic set  $\vec{\alpha}(t)$ . As we shall show later on, it will reduce under suitable approximations to the ordinary linear equation of irreversible thermodynamics for a non-markoffian process.

## IV. FLUCTUATIONS AROUND AN EQUILIBRIUM STATE

The results derived in the previous section are used here to study the decay of spontaneous fluctuations around an equilibrium state. For such a state,  $\rho(\Gamma, 0)$  is now chosen to be the equilibrium distribution function corresponding to the choice  $W(\Gamma) = \rho_{\text{eq}}(\Gamma)$  and  $v[\vec{A}(\Gamma, 0)] = 1$ . In this case the stochastic process describing the behaviour of the a's is a stationary one, namely,

$$g_n^{\text{eq}}(\vec{a}_1, t_1; \dots; \vec{a}_n, t_n) = g_n^{\text{eq}}(\vec{a}_1, t_1 + \tau; \dots; \vec{a}_n, t_n + \tau) \quad (37)$$

as it follows at once from Eq. (24). This means that  $g_1^{\text{eq}}(\vec{a})$  is a time independent function which describes the distribution function of the fluctuations around equilibrium. Also  $[G(\vec{b}, 0)] = g_{\text{eq}}(\vec{b})$  and  $g_2^{\text{eq}}(\vec{a}, t_1; \vec{b}, t_2) = g_2^{\text{eq}}(\vec{a}, t_1 - t_2; \vec{b}, 0)$  so that  $P_{\text{eq}}(\vec{a}, t | \vec{b})$  given by Eq. (27) involves now an average over the hypercell but with  $\rho_{\text{eq}}(\Gamma)$  as the weight function and its time evolution equation is given by Eq. (30). Equation (32) for the coarse grained variables involves now  $P_{\text{eq}}(\vec{a}, t | \vec{b})$  and is identical to Eq. (2), the variables defined by Onsager. Equation (33) becomes then the generalized regression of fluctuations equation which is exact in the sense that the full microscopic dynamics is contained in the vector  $\vec{K}(\vec{a}, s)$ .

We shall now analyze the dynamics of fluctuations for the case in which the time rate of change of the dynamical variables  $\vec{A}(\Gamma, 0)$  is controlled by a slowness parameter  $\delta$ , namely,  $\dot{\vec{A}}(\Gamma, 0) \sim \delta$ ,  $\delta < 1$ . Also we shall only consider all terms which are at most of order  $\delta^2$  both in the kinetic equation and in the regression of fluctuations expressions. In the Appendix we show in full detail that the functions that appear in the GKM form for  $Z(\vec{a}, t)$  satisfy the property that  $K_{k_0 \dots k_n}(\vec{a}, t) \sim \delta^{n+1}$ . Thus only  $K_{k_0}(\vec{a}, t)$  and  $K_{k_0, k_1}(\vec{a}, t)$  give relevant contributions to the process when it is slow. Further it is explicitly shown that

$$K_{k_0}^{(s)}(\vec{a}, t) = 2v_{k_0}(\vec{a})\delta(t) + C_{k_0}^{(2)}(\vec{a}, t) \quad , \quad (38a)$$

$$K_{k_0, k_1}^{(s)}(\vec{a}, t) = L_{k_0, k_1}^{(2)}(\vec{a}, t) \equiv \delta^2 \lim_{\delta \rightarrow 0} \left\langle \frac{1}{\delta^2} \langle \dot{A}_{k_0}(\Gamma, t) \dot{A}_{k_1}(\Gamma, 0); a \rangle \right\rangle - v_{k_0}(\vec{a}) v_{k_1}(\vec{a}) \quad (38b)$$

where

$$v_{k_0}(\vec{a}) = \langle \dot{A}_{k_0}(\Gamma, 0); a \rangle \quad (39)$$

and

$$C_{k_0}^{(2)}(\vec{a}, t) = \sigma_{\text{eq}}^{-1}(\vec{a}) \sum_{\ell} \frac{\partial}{\partial a_{\ell}} g_{\text{eq}}(\vec{a}) L_{k_0, \ell}^{(2)}(\vec{a}, t) \quad (40)$$

Use of Eqs. (31), (38a) and (38b) in Eq. (30) leads to the kinetic equation in the slow process approximation, namely,

$$\begin{aligned} \frac{\partial P_{\text{eq}}(\vec{a}, t | \vec{b})}{\partial t} &= \sum_{k_0} \left[ - \frac{\partial}{\partial a_{k_0}} \right] \int_0^t ds K_{k_0}^{(s)}(\vec{a}, s) P_{\text{eq}}(\vec{a}, t-s | \vec{b}) + \\ &+ \sum_{k_0} \sum_{k_1} \left[ \frac{\partial}{\partial a_{k_0}} \right] \left[ \frac{\partial}{\partial a_{k_1}} \right] \int_0^t ds K_{k_0, k_1}^{(s)}(\vec{a}, s) P_{\text{eq}}(\vec{a}, t-s | \vec{b}) \end{aligned} \quad (41)$$

The regression law, Eq. (33) with  $\vec{K}^{(s)}(\vec{a}, s)$  whose only components are  $K_{k_0}^{(s)}(\vec{a}, t)$  defined in Eq. (38a), is clearly seen to be a non linear equation in the  $a$ 's since both the drift term  $\vec{v}(\vec{a})$  defined in Eq. (39) and the term  $\vec{C}^{(2)}(\vec{a}, t)$  defined in Eq. (40) contain contributions to all orders in  $\vec{a}$ .

We now introduce another approximation, namely, that a slow process is also a linear one. To accomplish this we define a mesoscopic linear projector  $P_b$  <sup>(6,13)</sup>,

$$P_b = \langle\langle \cdot, \vec{b} \rangle\rangle \cdot \langle\langle \vec{b}, \vec{b} \rangle\rangle^{-1} \cdot \vec{b} \quad , \quad (42)$$

where  $\vec{b} = \overline{\vec{a}(t=0)}^b$  and an inner product defined by

$$\langle\langle f(\vec{b}), h(\vec{b}) \rangle\rangle = \int d\vec{b} g_{\text{eq}}(\vec{b}) f(\vec{b}) h(\vec{b}) \quad (43)$$



for arbitrary functions  $h(\vec{b})$  and  $f(\vec{b})$ .

Using Eqs. (32) and (43) it is easy to see that

$$\langle\langle \overline{\vec{a}(t)}^b, \vec{b} \rangle\rangle = \left[ \vec{A}(\Gamma, t), \vec{A}(\Gamma, 0) \right] = \underline{C}(t) \quad (44)$$

is the time correlation matrix (see Eq. (6)) in the coarse grained language. With the aid of Eq. (44), Eq. (42) may be also written as

$$P_b = \langle\langle \cdot, b \rangle\rangle \cdot \underline{C}^{-1}(0) \cdot \vec{b} \quad (45)$$

A slow linear process is now defined as one in which only the linear part of  $K_{k_0}^{(s)}(\vec{a}, t)$  is retained and  $K_{k_0, k_1}^{(s)}(\vec{a}, t)$  is substituted by its equilibrium average.

Formally,

$$K_{k_0}^{(L)}(\vec{a}, t) = P_a K_{k_0}^{(s)}(\vec{a}, t) \quad (46)$$

and

$$K_{k_0, k_1}^{(L)}(t) = \int d\vec{a} K_{k_0, k_1}^{(s)}(\vec{a}, t) g_{\text{eq}}(\vec{a}) \quad (47)$$

The effect of applying the linear operator  $P_a$  on Eq. (38a) is readily calculated. In fact, using Eqs. (39) and (43) find that

$$\langle\langle \vec{v}(\vec{a}), \vec{a} \rangle\rangle = \left[ \dot{\vec{A}}(\Gamma, 0), \vec{A}(\Gamma, 0) \right] = \dot{\underline{C}}(0) \quad (48)$$

and also from Eqs. (40) and (43) we find that

$$\langle\langle \vec{C}^{(2)}(\vec{a}, t), \vec{a} \rangle\rangle = - \int d\vec{a} \underline{L}^{(2)}(\vec{a}, t) g_{\text{eq}}(\vec{a}) \equiv - \overset{\circ}{\underline{L}}^{(2)}(t). \quad (49)$$

Hence, Eqs. (48) and (49) show that

$$P_a \vec{K}^{(s)}(\vec{a}, t) = [2\dot{\underline{C}}(0) \delta(t) - \overset{\circ}{\underline{L}}^{(2)}(t)] \cdot \underline{C}^{-1}(0) \cdot \vec{a} \quad (50)$$

Also Eqs. (38b) and (47) yield that

$$\underline{K}^{(L)}(t) = + \underline{L}^{(2)}(t) = \delta^2 \lim_{\delta \rightarrow 0} \frac{1}{\delta^2} \underline{\tilde{g}}(t) - \left[ d\vec{a} \sigma_{\text{eq}}(\vec{a}) \left[ P_a \vec{v}(\vec{a}) \right] \left[ P_a \vec{v}(\vec{a}) \right] \right], \quad (51)$$

where  $\underline{g}(t)$  is defined in Eq. (10). The last term in Eq. (51) arises from the fact that we are only interested in keeping those terms in  $\vec{v}(\vec{a})$  which are linear in the  $\vec{a}$ 's.

If all the phase space functions have the same parity  $\underline{g}(t) = \underline{\tilde{g}}(t)$  and  $\underline{\dot{C}}(0) = 0$  so that Eqs. (46) and (47) are further reduced to the expressions,

$$\underline{\vec{K}}^{(L)}(\vec{a}, t) = - \underline{L}^{(2)}(t) \cdot \underline{C}^{-1}(0) \cdot \vec{a} \quad (52)$$

and

$$\underline{K}^{(L)}(\vec{a}, t) = \underline{L}^{(2)}(t) = \delta^2 \lim_{\delta \rightarrow 0} \frac{1}{\delta^2} \underline{g}(t) \quad , \quad (53)$$

since the last term in (51) vanishes. Substituting Eqs. (52) and (53) into Eq. (41) yields the kinetic equation for a slow linear process when the phase variables all have the same parity, namely,

$$\frac{\partial P_{\text{eq}}(\vec{a}, t | \vec{b})}{\partial t} = \int_0^t \left\{ \underline{\tilde{M}}(t') : \frac{\partial}{\partial \vec{a}} P_{\text{eq}}(\vec{a}, t-t' | \vec{b}) \vec{a} + \underline{Q}(t') : \frac{\partial^2 P_{\text{eq}}(\vec{a}, t-t' | \vec{b})}{\partial \vec{a} \partial \vec{a}} \right\} \quad , \quad (54)$$

where

$$\underline{\tilde{M}}(t) = \left\{ \delta^2 \lim_{\delta \rightarrow 0} \frac{\underline{g}(t)}{\delta^2} \right\} \cdot \underline{C}^{-1}(0) \quad (55)$$

and

$$\underline{Q}(t) = \frac{1}{2} [\underline{\tilde{M}}(t) \cdot \underline{C}(0) + \underline{C}(0) \cdot \underline{\tilde{M}}(t)] \quad . \quad (56)$$

Notice that Eq. (54) is a Fokker-Planck type of equation but with a memory. Thus it does not correspond to a markoffian process. The regression

law on the other hand for slow linear processes is obtained from Eqs. (33), (52) and (55), and is simply given by

$$\frac{d\vec{a}(t)}{dt} = - \int_0^t ds \underline{M}(s) \vec{a}(t-s) \quad , \quad (57)$$

which is precisely of the same formal structure as Eq. (1), the form postulated by Zwanzig. It remains now to show in detail how Eq. (57) leads to the results predicted in section I and this is done in the following section.

It is pertinent to mention here that the transport equation for the macroscopic variables  $\vec{\alpha}(t)$  (c.f. Eq. (36)) has the same structure of Eq. (57). This is readily seen if we use Eq. (34), the facts that  $[\underline{G}(\vec{b}, 0)] = g_{eq}(\vec{b})$  and that  $g_{eq}(\vec{b})$  is properly normalized. Then,

$$\frac{d\vec{\alpha}(t)}{dt} = - \int_0^t ds \underline{M}(s) \cdot \vec{\alpha}(t-s) \quad (58)$$

which allows us to identify  $\underline{M}(s)$  with the time dependent transport matrix.

## V. COMPARISON OF THE RESULTS

The essential result of Zwanzig's approach to the derivation of the time correlation formulas for the transport coefficients is Eq. (12) which relates the Laplace transforms for the transport matrix  $\hat{Y}(\rho)$  with the correlation matrix  $\hat{G}(\rho)$ . Thus we want to compare

$$\hat{Y}(\rho) = [\underline{D} - \hat{G}(\rho) \cdot \underline{C}^{-1}(0)]^{-1} \cdot \rho \hat{G}(\rho) \cdot \underline{C}^{-1}(0) \quad (59)$$

with Eq. (55) which gives the corresponding relationship but in terms of the dynamics of slow linear processes. The comparison has to be made exercising a great deal of care because Eq. (59) is so far free from any assumptions concerning the slowness of the process involved and only when we extract from it those terms which are at most of order  $\delta^2$ , the two results will turn out to be identical.

From Eqs. (10) and (26) it follows that

$$\sigma_{ij}(t) = \left\langle \dot{A}_i(0), \dot{A}_j(t) \right\rangle = \left\langle d\vec{a} \cdot \underline{g}_{eq}(\vec{a}) \langle \dot{A}_i(0) \dot{A}_j(t); a \rangle \right\rangle, \quad (60)$$

which shows explicitly that  $\sigma_{ij}$  is of order  $\delta^2$  since  $\langle \dot{A}_i(0) \dot{A}_j(t); a \rangle \sim O(\delta^2)$ . Thus, Eq. (59) has terms which contribute to  $\hat{\underline{g}}(p)$  of order  $\delta^3$  and higher which must be consistently neglected. To do this we expand its r.h.s. in powers of  $\hat{\underline{g}}(p)$ ,

$$\begin{aligned} \hat{\underline{y}}(p) &= \hat{\underline{g}}(p) \cdot \underline{C}^{-1}(0) \left\{ \underline{1} + \frac{1}{\delta} \hat{\underline{g}}(p) \cdot \underline{C}^{-1}(0) + \dots \right\} \\ &= \delta^2 \sum_{n=1}^{\infty} \delta^{2(n-1)} \hat{\underline{y}}^{(2n)}(\delta, p) \end{aligned} \quad (61)$$

where

$$\hat{\underline{y}}^{(2n)}(\delta, p) = \frac{1}{p^{n-1}} \left[ \frac{\hat{\underline{g}}(p)}{\delta^2} \cdot \underline{C}^{-1}(0) \right]^n \quad (62)$$

Equation (61) is just a formal way of expressing the property of  $\hat{\underline{g}}(p)$  indicated in Eq. (A-20). If we now compare Eqs. (13) and (61) we see that  $\zeta \equiv \delta^2$  and that

$$\underline{\mu}(\delta^2, p) = \sum_{n=1}^{\infty} \delta^{2(n-1)} \hat{\underline{y}}^{(2n)}(\delta, p) \quad (63)$$

Hence to lowest order in  $\delta$ ,  $\underline{\mu}(\delta^2, p) = \hat{\underline{y}}^{(2)}(\delta, p)$ . Using this result together with Eqs. (61) and (62) we find that for slow processes,

$$\hat{\underline{y}}(p) = \delta^2 \lim_{\delta \rightarrow 0} \frac{\hat{\underline{g}}(p)}{\delta^2} \cdot \underline{C}^{-1}(0) = \hat{\underline{M}}(p) \quad (64)$$

where use has been also made of the Laplace transform of Eq. (55). Equation (64) shows explicitly that for slow linear processes the transport matrix  $\underline{M}(t)$  is identical to the phenomenological matrix  $\underline{y}(t)$  if only the terms of order up to  $\delta^2$  are kept in the latter one. If we now use the macroscopic definition for  $\underline{M} = \delta^2 \underline{\mu}(0,0)$ , Eqs. (10), (21) and (64), we finally arrive at the result that



$$\underline{M} = \delta^2 \lim_{p \rightarrow 0} \int_0^{\infty} e^{-pt} \frac{\underline{M}(t)}{\delta^2} dt \quad , \quad (65)$$

where  $\underline{M}$  is now the time independent transport matrix. It is important to stress here that the evaluation of  $\underline{M}$  is explicitly dependent on the microscopic dynamics of a slow linear process as it is shown by Eqs. (53) and (55).

It is also pertinent to point out here that in the markoffian approximation defined by

$$\underline{M}(t) = 2\underline{M} \delta(t) \quad , \quad (66)$$

Eq. (57) reduces to the ordinary linear regression law and Eq. (54) is just the Fokker-Planck equation for a stationary, linear, markoffian process<sup>(2)</sup>, namely,

$$\frac{\partial P_{eq}(\vec{a}, t | \vec{b})}{\partial t} = \tilde{M} : \frac{\partial}{\partial \vec{a}} P_{eq}(\vec{a}, t | \vec{b}) \vec{a} + Q : \frac{\partial^2 P_{eq}(\vec{a}, t | \vec{b})}{\partial \vec{a} \partial \vec{a}} \quad , \quad (67)$$

where

$$Q = \frac{1}{2} \left[ \underline{M} \cdot \underline{C}(0) + \underline{C}(0) \cdot \tilde{M} \right] \quad . \quad (68)$$

#### APPENDIX

Here we consider in detail the steps leading to the main results of section IV using the GKM of ZO which is given in Eq. (31). The coefficients  $K_{k_0 \dots k_n}(\vec{a}, t)$  have been obtained elsewhere<sup>(7, 14)</sup> and for convenience we only list here the results.

Thus,

$$K_{k_0}(\vec{a}, t) = 2v_{k_0}(\vec{a}) \delta(t) + C_{k_0}(\vec{a}, t) \quad , \quad (A-1)$$

$$K_{k_0 \dots k_n}(\vec{a}, t) = L_{k_0 \dots k_{n-1}; k_n}(\vec{a}, t) + C_{k_0 \dots k_n}(\vec{a}, t) \quad , \quad (A-2)$$

where

$$C_{k_0 \dots k_n}(\vec{a}, t) = g_{\text{eq}}^{-1}(\vec{a}) \int_{\ell} \frac{\partial}{\partial \vec{a}_{\ell}} \sigma_{\text{eq}}(\vec{a}) L_{k_0 \dots k_n; \ell}(\vec{a}, t) \quad (\text{A-3})$$

and

$$L_{k_0 \dots k_n; \ell}(\vec{a}, t) = \langle S(k_0 \dots k_n; t) R_{\ell}(0); \vec{a} \rangle \quad (\text{A-4})$$

Here,

$$S(k_0 \dots k_n, t) = \int_0^t dt_1 \dots \int_0^{t_{n-1}} dt_n U(t-t_1) (1-P_G) \dot{A}_{k_1}(0) \dots U(t_n-t_{n-1}) (1-P_G) \cdot \dot{A}_{k_n}(0) R_{k_0}(t_n) \quad (\text{A-5})$$

with  $U(t) = e^{(1-P_G) iLt}$  and

$$R_k(t) = U(t) (1-P_G) \dot{A}_k(0) \quad (\text{A-6})$$

$P_G$  being the generalized projection operator defined as

$$P_G = \int d\vec{b} \langle \cdot ; \vec{b} \rangle G(\vec{b}, 0) \quad (\text{A-7})$$

and  $v_{k_0}(\vec{a})$  being defined in Eq. (39) in the text.

To study the slow process approximation we start by inquiring on the dependence in the slowness parameter  $\delta$  of the quantities defined in Eqs. (A-3) and (A-4). Clearly, if  $I(\Gamma)$  is a phase space function that changes as  $\delta^r$ , then

$$[i L P_G]^n I(\Gamma) \sim O(\delta^{n+r}) \quad (\text{A-8})$$

Choose first the quantity  $S(k_0 \dots k_n; t)$ . Since  $\dot{A}_k(0) \sim \delta$  then by Eqs. (A-8) and (A-6)  $R_k(t)$  is at least of  $O(\delta)$ . Inspection of Eq. (A-5) then shows that

$$S(k_0, \dots, k_n, t) \sim O(\delta^{n+1}) \quad , \quad (A-9)$$

When this result and the behavior of  $R_\ell(0)$  are used in Eq. (A-4) we find that

$$L_{k_0 \dots k_n; \ell}(\vec{a}, t) \sim O(\delta^{n+2}) \quad (A-10)$$

so that Eqs. (A-10) and (A-3) also show that

$$C_{k_0 \dots k_n}(\vec{a}, t) \sim O(\delta^{n+2}) \quad . \quad (A-11)$$

From Eqs. (A-2), (A-10) and (A-11) we see that of the two terms that appear in  $K_{k_0 \dots k_n}(\vec{a}, t)$  the lowest in  $\delta$  is  $L_{k_0 \dots k_{n-1}; k_n}$  so that

$$K_{k_0 \dots k_n}(\vec{a}, t) \sim O(\delta^{n+1}) \quad . \quad (A-12)$$

In the slow process approximation we want to retain only those contributions up to order  $\delta^2$  so that, as Eq. (A-12) indicates, we need only to keep the first two functions  $K_{k_0}(\vec{a}, t)$  and  $K_{k_0 k_1}(\vec{a}, t)$ . However both terms are not per se of order  $\delta$  and  $\delta^2$  respectively but contain contributions of order higher in  $\delta$ . We now show how to extract from them the terms linear and quadratic in  $\delta$ .

For  $n=1$ , Eq. (A-11) shows that the only relevant contribution to  $K_{k_0 k_1}(\vec{a}, t)$  comes from  $L_{k_0 k_1}(\vec{a}, t)$  which in view of Eqs. (A-4) and (A-5) is just given by,

$$L_{k_0, k_1}(\vec{a}, t) = \langle R_{k_0}(t) R_{k_1}(0); a \rangle \quad . \quad (A-13)$$

On the other hand from Eq. (A-6),

$$\begin{aligned} R_{k_0}(t) &= e^{(1-P_G) i L t} (1-P_G) \dot{A}_{k_0}(0) = [1 + (1-P_G) i L t \\ &+ \frac{t^2}{2} (1-P_G) i L (1-P_G) i L + \dots] (1-P_G) \dot{A}_{k_0}(0) \end{aligned}$$

and using Eq. (A-8) it reduces to

$$R_{k_0}(\mathbf{t}) = (1-P_G) \dot{A}_{k_0}(\mathbf{t}) + O(\delta^2) \quad (\text{A-14})$$

Notice that in Eq. (A-14) only the first term is of order  $\delta$  and not linear in  $\delta$ . Use of Eqs. (A-14) and (A-8) back in Eq. (A-13) leads to:

$$L_{k_0 k_1}(\vec{\mathbf{a}}, \mathbf{t}) = \langle [(1-P_G) \dot{A}_{k_0}(\mathbf{t})] [(1-P_G) \dot{A}_{k_1}(0)]; \mathbf{a} \rangle + O(\delta^3) \quad (\text{A-15})$$

Explicit evaluation of the quantities in square brackets, by applying  $P_G$  given in Eq. (A-7) reduces Eq. (A-15) to the form:

$$L_{k_0 k_1}(\vec{\mathbf{a}}, \mathbf{t}) = \langle \dot{A}_{k_0}(\mathbf{t}) \dot{A}_{k_1}(0); \mathbf{a} \rangle - \langle \dot{A}_{k_0}(\mathbf{t}); \mathbf{a} \rangle v_{k_1}(\mathbf{a}) + O(\delta^3) \quad (\text{A-16})$$

where use has been made of Eq. (39) and two obvious identities,

$$\langle \dot{A}_k(\mathbf{t}) G(\vec{\mathbf{b}}, 0); \mathbf{a} \rangle = \langle \dot{A}_k(\mathbf{t}); \mathbf{a} \rangle \delta(\vec{\mathbf{a}} - \vec{\mathbf{b}}) \quad \text{and} \quad \langle G(\vec{\mathbf{b}}, 0) G(\vec{\mathbf{b}'}, 0); \mathbf{a} \rangle = \delta(\vec{\mathbf{b}} - \vec{\mathbf{b}'}) \\ \delta(\vec{\mathbf{b}} - \vec{\mathbf{a}}).$$

Now, we have to extract from Eq. (A-16) those terms which are at most, quadratic in  $\delta$ . First consider the second term. Since  $v_{k_1}(\vec{\mathbf{a}}) \sim \delta$  we must find the linear term in  $\delta$  from  $\langle \dot{A}_{k_0}(\mathbf{t}); \vec{\mathbf{a}} \rangle$ . From Eq. (26) it follows that

$$\langle \dot{A}_{k_0}(\mathbf{t}); \mathbf{a} \rangle = g_{\text{eq}}^{-1}(\vec{\mathbf{a}}) \left[ e^{iL\mathbf{t}} \dot{A}_{k_0}(0), G(\vec{\mathbf{a}}, 0) \right] = g_{\text{eq}}^{-1}(\vec{\mathbf{a}}) \left[ \dot{A}_{k_0}(0), G(\vec{\mathbf{a}}, -\mathbf{t}) \right] \quad (\text{A-17})$$

Using the identity

$$\Delta A(\Gamma, -\mathbf{t}) = A(\Gamma, -\mathbf{t}) - A(\Gamma, 0) = \int_0^{-\mathbf{t}} \dot{A}(\Gamma, s) ds$$

we may write that

$$G(\vec{\mathbf{a}}, -\mathbf{t}) = \delta [A(\Gamma, -\mathbf{t}) - \vec{\mathbf{a}}] = \delta [A(\Gamma, 0) - \mathbf{a} + \Delta A(\Gamma, -\mathbf{t})] \quad ,$$



which upon expansion around  $t=0$  yields that

$$G(\vec{a}, -t) = G(\vec{a}, 0) + \sum_{\ell} \frac{\partial}{\partial a_{\ell}} \int_0^t ds \dot{A}_{\ell} \Gamma, -s) G(a, 0) + O(\dot{A}^2) \quad . \quad (A-18)$$

Introducing Eq. (A-18) into Eq. (A-17) we arrive at the following expression,

$$\langle \dot{A}_{k_0} (t); a \rangle = v_{k_0}(\vec{a}) + g_{\text{eq}}^{-1}(\vec{a}) \sum_{\ell} \frac{\partial}{\partial a_{\ell}} g_{\text{eq}}(\vec{a}) \int_0^t \langle \dot{A}_{k_0} (0) \dot{A}_{\ell}(-s); a \rangle ds + O(\dot{A}^3) \quad , \quad (A-19)$$

so that  $v_{k_0}(\vec{a})$  is the linear contribution of this term.

The first term in Eq. (A-16) is easy to deal with, since we may always write that

$$\langle \dot{A}_{k_0} (t) \dot{A}_{k_1} (0); a \rangle = \delta^2 \sigma_{k_0 k_1}^{(0)}(\vec{a}, t) + \delta^3 \sigma_{k_0 k_1}^{(1)}(\vec{a}, t) + \dots \quad (A-20)$$

where  $\sigma_{k_0, k_1}^{(n)}(\vec{a}, t)$  does not depend on  $\delta$ . Hence the relevant contribution is simply given by

$$\sigma_{k_0, k_1}(\vec{a}, t) = \lim_{\delta \rightarrow 0} \frac{1}{\delta^2} \langle \dot{A}_{k_0} (t) \dot{A}_{k_1} (0); a \rangle \quad . \quad (A-21)$$

When Eqs. (A-19) and (A-21) are substituted back into Eq. (A-16) keeping only the relevant terms, we find that

$$L_{k_0 k_1}(\vec{a}, t) = L_{k_0 k_1}^{(2)}(\vec{a}, t) + O(\delta^3) \quad (A-22)$$

and  $L_{k_0 k_1}^{(2)}(\vec{a}, t)$  is defined by Eq. (38b) in the text.

Finally, to find the part of  $K_{k_0}(\vec{a}, t)$  which contributes to the slow process we notice from Eq. (A-1) that, on one hand  $v_{k_0}(\vec{a}) \sim \delta$  and on the other hand Eqs. (A-3) and (A-22) show that

$$C_{k_0}(\vec{a}, t) = C_{k_0}^{(2)}(\vec{a}, t) + O(\delta^3) = g_{\text{eq}}^{-1}(\vec{a}) \sum_{\ell} \frac{\partial}{\partial a_{\ell}} g_{\text{eq}}(\vec{a}) L_{k_0; \ell}^{(2)}(\vec{a}, t) \quad (A-23)$$

whence,

$$K_{k_0}^{(s)}(\vec{a}, t) = 2v_{k_0}(\vec{a}) \delta(t) + C_k^{(2)}(\vec{a}, t) \quad (\text{A-24})$$

which is Eq. (38a) in the text.

Note: Equation (41) in the text is not identical to Zwanzig's equation for slow processes (see Eq. (33) Ref. 5). The difference arises because he takes Eq. (A-16) for  $L_{k_0 k_1}^{(2)}(\vec{a}, t)$  and as we have shown here, that expression still includes terms of order higher than  $\delta^2$ .

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