Stochastic Liouville equation formalism for translational and rotational diffusion[a)]

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Stochastic Liouville equations are used to study the relaxation behavior of position and orientation correlation functions of a fluid particle, if the second-order velocity or angular-velocity correlation is given. Two assumptions for reducing higher-order (angular) velocity correlation functions to two-point correlation functions are compared, the Gaussian assumption and "the assumption of vanishing higher-order G-cumulants." In the case of translation both assumptions predict the same diffusion constant; only the latter one yields a Burnett coefficient that diverges in accordance with microscopic results. For rotational diffusion the second assumption is studied and compared with results obtained by Pomeau and Weber on the basis of the first assumption.

I. INTRODUCTION

The discovery of "long-time tails" for the velocity autocorrelation function of fluid particles has initiated much theoretical study of the long-time decay of correlation functions.[1] One consequence of these long-time tails is that the translational diffusion constant and the Burnett coefficient do not exist in two and three dimensions, respectively.

In this paper, we use stochastic differential equations to determine (a) the decay of position correlation functions if the long-time behavior of the velocity autocorrelation function is given; (b) the decay of orientation correlation functions if the long-time behavior of the angular-velocity autocorrelation function is given.

Our aim is to reproduce the results of the microscopic theories and to present a framework for understanding these microscopic theories. The principal thrust of the analysis is that the stochastic-differential-equation formalism, combined with statistical assumptions about the behavior of certain time derivatives, may be reliably employed to predict the correlation functions of interest and the associated transport coefficients. The question of which assumption is the most appropriate must be decided on the basis of the physics of the system under consideration.

Kubo[2] has presented an analysis of stochastic Liouville equations based on various cumulant expansions. Each expansion involves a different prescription for time ordering and implicitly adopts an assumption about the relevant microscopic physics.

In Sec. II, two ordering prescriptions (F ordering and G ordering) and the corresponding cumulant expansions are defined and discussed. It is stressed that the applicability of F and G orderings depends on a physical assumption about the best approximation for the higher-order correlation functions.

In Sec. III, the Gaussian assumption and the assumption of vanishing higher-order G cumulants are applied to the case of translation. The diffusion constant is the same under both assumptions and agrees with microscopic theories[3] in two and three dimensions; the Burnett coefficient is zero under the former assumption, whereas under the latter assumption it diverges in the way predicted by microscopic theories. In Sec. IV, rotational diffusion is discussed. The two-dimensional case is analogous to the case of one-dimensional translational diffusion. In the three-dimensional case, the F-cumulant expansion under the Gaussian assumption has been discussed at length by Pomeau and Weber.[4] Their result is discussed and compared with the G-cumulant expansion under the assumption of vanishing higher-order G cumulants, which leads to a simpler and physically more attractive result.

II. F ORDERING AND G ORDERING

Our basic stochastic linear differential equation is

$$\dot{\mathbf{u}}(t) = A(t)\mathbf{u}(t) \,, \tag{2.1}$$

where $A(t)$ is a time-dependent stochastic operator, which we assume to be zero on the average

$$\langle A(t)\rangle = 0 \,. \tag{2.2}$$

As the initial condition, we choose $\mathbf{u}(0) = \mathbf{u}_0$, a nonfluctuating quantity. Then the solution of Eq. (2.1) is given by

$$\mathbf{u}(t) = U_1(t)\mathbf{u}_0 \,, \tag{2.3}$$

with

$$U_\lambda(t) \equiv \left[1 + \lambda \int_0^t dt_1 A(t_1) + \lambda^2 \int_0^t dt_1 \int_0^{t_1} dt_2 A(t_1)A(t_2) + \cdots\right]$$

$$\equiv \exp_0 \lambda \int_0^t A(t_1)dt_1 \,. \tag{2.4}$$

This defines the ordered exponential $\exp_0$, which is identical to the usual exponential exp if $A(t_1)$ and $A(t_2)$ commute for arbitrary t_1 and t_2. As has been stressed by Kubo,[2] there are several ways to define cumulants for this problem. In general, a cumulant expansion is given by

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$$\langle U_\lambda(t)\rangle = \exp_P\left[\sum_{n=1}^{\infty}\lambda^n \int_{t\geq t_1\geq t_2\geq\cdots\geq t_n\geq 0} dt_1 dt_2\cdots dt_n \times\langle 1\ 2\cdots n\rangle_P\right], \tag{2.5}$$

where P denotes a certain ordering prescription for the exponential. The cumulants $\langle 1\ 2\cdots n\rangle_P$ (which depend on $t_1, t_2, \ldots, t_n$) are found by expanding the ordered exponentials and equating terms of the same order in λ. We shall concentrate on two of Kubo's ordering prescriptions, which we call F ordering and G ordering:
(a) If we write

$$\frac{\partial}{\partial t}\langle \mathbf{u}(t)\rangle = F(t)\langle \mathbf{u}(t)\rangle\ , \tag{2.6}$$

the average of $\mathbf{u}(t)$ is given by

$$\langle \mathbf{u}(t)\rangle = \left[1 + \int_0^t dt_1 F(t_1) + \int_0^t dt_1 \int_0^{t_1} dt_2 F(t_1)F(t_2) + \cdots\right]\mathbf{u}_0 \equiv \left[\exp_F \int_0^t F(t')dt'\right]\mathbf{u}_0\ , \tag{2.7}$$

which defines $\exp_F$. This ordered exponential reduces to the usual exponential exp if $F(t_1)$ and $F(t_2)$ commute for arbitrary t_1 and t_2, respectively. The associated cumulants are found by [cf. Eq. (2.4)]

$$\langle U_\lambda(t)\rangle = \exp_F\left[\sum_{n=1}^{\infty}\lambda^n \int_{t\geq t_1\geq\cdots\geq t_n\geq 0} dt_1 dt_2\cdots dt_n \times\langle 1\ 2\cdots n\rangle_F\right]. \tag{2.8}$$

For example [cf. Eq. (2.2)],

$$\langle 1\rangle_F = \langle 1\rangle = 0\ ,\quad \langle 1\ 2\rangle_F = \langle 1\ 2\rangle\ ,\quad \langle 1\ 2\ 3\rangle_F = \langle 1\ 2\ 3\rangle\ ,$$
$$\langle 1\ 2\ 3\ 4\rangle_F = \langle 1\ 2\ 3\ 4\rangle - \langle 1\ 2\rangle_F\langle 3\ 4\rangle_F - \langle 1\ 3\rangle_F\langle 2\ 4\rangle_F - \langle 1\ 4\rangle_F\langle 2\ 3\rangle_F\ , \tag{2.9}$$

where $\langle 1\ 2\cdots n\rangle = \langle A(t_1)A(t_2)\cdots A(t_n)\rangle$ and $t\geq t_1\geq\cdots\geq t_n\geq 0$.
(b) If the differential equation for $\langle u(t)\rangle$ is written as

$$\frac{\partial}{\partial t}\langle \mathbf{u}(t)\rangle = \int_0^t dt'\, G(t,t')\langle \mathbf{u}(t')\rangle\ , \tag{2.10}$$

the average of $\mathbf{u}(t)$ is given by

$$\langle \mathbf{u}(t)\rangle = \left[1 + \int_{t\geq t_1\geq t_2\geq 0} dt_1 dt_2\, G(t_1,t_2) + \int_{t\geq t_1\geq\cdots\geq t_4\geq 0} dt_1 dt_2 dt_3 dt_4\, G(t_1,t_2)G(t_3,t_4) + \cdots\right]\mathbf{u}_0, \equiv \left[\exp_G \int_0^t dt_1 \int_0^{t_1} dt_2\, G(t_1,t_2)\right]\mathbf{u}_0\ , \tag{2.11}$$

where $\exp_G$ is by definition the G-ordered exponential which does *not* reduce to the usual exponential if $G(t_1,t_2)$ commutes with $G(t_3,t_4)$. The G cumulants up to fourth order are

$$\langle 1\rangle_G = \langle 1\rangle\ ,\quad \langle 1\ 2\rangle_G = \langle 1\ 2\rangle\ ,\quad \langle 1\ 2\ 3\rangle_G = \langle 1\ 2\ 3\rangle\ ,$$
$$\langle 1\ 2\ 3\ 4\rangle_G = \langle 1\ 2\ 3\ 4\rangle - \langle 1\ 2\rangle_G\langle 3\ 4\rangle_G\ . \tag{2.12}$$

The applicability of F and G orderings depends on what is the best approximation for the higher-order correlation functions. The answer to this question cannot be obtained from mathematics, but must be found in the physics of the problem. If $A(t_1)$ and $A(t_2)$ commute for all times t_1 and t_2, the assumption of a Gaussian process implies that the F-cumulant expansion breaks off after the second cumulant; in such a case, one must use Eq. (2.6). If one assumes all higher-order G cumulants vanish [$\langle 1\ 2\ 3\cdots(2n-1)\rangle = 0$; $\langle 1\ 2\ 3\cdots 2n\rangle = \langle 1\ 2\rangle \times\langle 3\ 4\rangle\cdots\langle(2n-1)(2n)\rangle$], one must use Eq. (2.10) with $G(t_1,t_2) = \langle A(t_1)A(t_2)\rangle$.

The two orderings differ in the way "overlapping" pairs, triplets, etc., are dealt with. For example,

$$\int_{t\geq t_1\geq\cdots\geq t_4\geq 0} dt_1\cdots dt_4\left(\langle 1\ 2\ 3\ 4\rangle_G - \langle 1\ 2\ 3\ 4\rangle_F\right) = \int_{t\geq t_1\geq\cdots\geq t_4\geq 0} dt_1\cdots dt_4\left(\langle 1\ 3\rangle\langle 2\ 4\rangle + \langle 1\ 4\rangle\langle 2\ 3\rangle\right)\ . \tag{2.13}$$

If we define τ_c as the correlation time of the pair correlation function and α as the typical size of a fluctuation $A(t)$, then it is easy to see that, because of the time ordering, the integral on the right-hand side of Eq. (2.13) is of the order $\alpha(\alpha\tau_c)^3$. This has to be compared with the integral over the first nonvanishing cumulant

$$\int_{t\geq t_1\geq t_2\geq 0} dt_1 dt_2\,\langle 1\ 2\rangle = \mathcal{O}[\alpha(\alpha\tau_c)]\ . \tag{2.14}$$

Since $\alpha\tau_c$ may be taken as a smallness parameter in many situations, the difference between the fourth-order G cumulant and F cumulant is often very small. Some care must be taken, however, in the generalization of this argument to the whole cumulant expansion because the number of terms on the right-hand side of the equivalent of Eq. (2.13) for cumulants of order n increases very rapidly as n increases.[4] Van Kampen[5] argues that Eqs. (2.6) and (2.10) cannot be distinguished unless there is specific knowledge about terms of order $\alpha(\alpha\tau_c)^3$.

III. TRANSLATION

The theory of stochastic Liouville equations is discussed by Kubo.[2] Here we look at the simple case of a particle whose movement is totally determined by a stochastic velocity $\mathbf{v}(t)$, which has a zero average. The Liouville equation for such a system is

$$\frac{\partial}{\partial t}f(\mathbf{r},t) = -\mathbf{v}(t)\cdot\nabla f(\mathbf{r},t)\ , \tag{3.1}$$

where $f(\mathbf{r},t)$ is the distribution function. The stochastic operator $A(t)$ consists of a stochastic part $-\mathbf{v}(t)$ and an operator part (the gradient operator ∇). For symmetry reasons, odd moments of the velocity and hence odd moments of A vanish. Because of the fact that $A(t)$ and $A(t')$ commute for every t and t', the ordered exponentials $\exp_0$ and $\exp_F$ reduce to the usual exponential exp. Therefore, the structure factor

$$S(\mathbf{k},t) \equiv \langle\exp\{i\mathbf{k}\cdot[\mathbf{r}(t)-\mathbf{r}(0)]\}\rangle = \left\langle\exp\left[i\mathbf{k}\cdot\int_0^t \mathbf{v}(t')dt'\right]\right\rangle \tag{3.2}$$

is the Fourier transform of $\langle U_1(\mathbf{r},t)\rangle$ [cf. Eqs. (2.3) and (2.4)]. The discussion in Sec. II suggests the following

two approximations for the higher-order correlation functions:

(a) All F cumulants vanish except $\langle 1\ 2\rangle_F$. This is the usual Gaussian approximation. It leads to

$$\frac{\partial}{\partial t}\langle f(\mathbf{r}, t)\rangle = \int_0^t dt'\, \psi(t')\nabla^2\langle f(\mathbf{r}, t)\rangle \ , \tag{3.3}$$

where $\psi(t) \equiv \langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle/d$ for a d-dimensional system. If we define

$$\Delta^{(2)}(t) \equiv \int_0^t dt'\, \psi(t') \ , \tag{3.4}$$

then the (lowest-order) diffusion constant is given by the limit of $\Delta^{(2)}(t)$ for $t\to\infty$, if this limit exists. In three dimensions, the velocity autocorrelation function decays like $t^{-3/2}$ so that the limit exists. In two dimensions, $\Delta^{(2)}(t)$ diverges for large t; the exact form of the predicted divergence depends on the theory one uses for the long-time behavior of $\psi(t)$. According to hydrodynamic theory, $\psi(t)\sim t^{-1}$, so that $\Delta^{(2)}(t)\sim \ln t$; according to trilinear mode-coupling theory,[6] $\psi(t)\sim(t\ln t)^{-1}$ so that $\Delta^{(2)}(t)\sim \ln\ln t$; finally, if one includes all multilinear modes,[7] $\psi(t)\sim(t\sqrt{\ln t})^{-1}$ so that $\Delta^{(2)}(t)\sim\sqrt{\ln t}$ (all for long times). Higher-order diffusion coefficients, like the Burnett and super-Burnett coefficients, are zero in the Gaussian approximation.

(b) Let us now assume that all G cumulants vanish except $\langle 1\ 2\rangle_G$. Then [cf. Eq. (2.10)]

$$\frac{\partial}{\partial t}\langle f(\mathbf{r}, t)\rangle = \int_0^t dt'\, \psi(t-t')\nabla^2\langle f(\mathbf{r}, t')\rangle \ . \tag{3.5}$$

After a Fourier transformation in space and a Laplace transformation in time, we find

$$S(k, s) = [s + \psi(s)k^2]^{-1} \ . \tag{3.6}$$

The generalized diffusion coefficient $\psi(s)$ in Eq. (3.6), i.e., $\psi(s)$, is only a function of s and not of $\mathbf{k}$. Nevertheless, as has been stressed by Keyes and Oppenheim,[3] the Burnett coefficient is not necessarily zero in this case. We calculate the diffusion constant and Burnett coefficient from the second and fourth moments of the displacement $x(t)$, defined by

$$x(t) \equiv \int_0^t f(\mathbf{r}, t)\, x d\mathbf{r} \ . \tag{3.7}$$

From Eq. (3.7), one easily checks that $(\partial/\partial t)x(t) = v_x(t)$, so that

$$\frac{\partial}{\partial t}x^2(t) = 2\int_0^t v_x(t)v_x(t')dt' \tag{3.8}$$

and consequently

$$\frac{\partial}{\partial t}\langle x^2(t)\rangle = 2\Delta^{(2)}(t) \ . \tag{3.9}$$

This result does not depend on any assumption about correlation functions and therefore holds as well in the case of vanishing higher-order F cumulants as in the case of higher-order G cumulants. Note that, only in the former case, is $\Delta^{(2)}(t)$ equal to $F(t)$ and that only in the latter case is $\Delta^{(2)}(t)$ equal to $\int_0^t G(t-t')dt'$, so that in general $F(t=\infty)\neq G(s=0)$.[2]

In the calculation of the fourth moment, we use the fact that the fourth-order G cumulant vanishes ($\langle 1\ 2\ 3\ 4\rangle = \langle 1\ 2\rangle\langle 3\ 4\rangle$) to derive

$$\frac{\partial}{\partial t}\langle x^4(t)\rangle = 12\int_0^t dt'\, \psi(t-t')\langle x^2(t')\rangle \ . \tag{3.10}$$

If the Burnett coefficient exists, it is found as the limit for infinite time of

$$\Delta^{(4)}(t) = [3\langle x^2(t)\rangle^2 - \langle x^4(t)\rangle]/(24t) \ . \tag{3.11}$$

In a straightforward way, it is found that, in three dimensions, $[\psi(t)\sim t^{-3/2}]\,\Delta^{(4)}(t)$ is given by

$$\Delta^{(4)}(t) = C_1\sqrt{t} \quad (t \text{ large}) \ , \tag{3.12}$$

with $C_1 > 0$. This result agrees with Ref. 3, though the near cancellation does not occur, because in the theory presented here, the generalized diffusion coefficient does not depend on $\mathbf{k}$, so that the contribution to the Burnett coefficient from the k dependence of the diffusion coefficient $D(k, s)$ is equal to zero. Thus, the diffusion constant in three dimensions is finite whereas the Burnett coefficient does not exist. In two dimensions, hydrodynamic theory $[\psi(t)\sim t^{-1}]$ leads to

$$\Delta^{(4)}(t) = -C_2 t\ln t + C_3 t \quad (t \text{ large}) \ , \tag{3.13}$$

with $C_2, C_3 > 0$. The term proportional to t does not occur in the mode-coupling calculation by Keyes and Oppenheim; in their result, a similar term is cancelled by a contribution from the $\mathbf{k}$-dependent part of the generalized diffusion coefficient. As explained above, the present theory cannot reproduce $\mathbf{k}$ dependence.

IV. ROTATION

In the theory of rotational diffusion, there is an essential difference between two and three dimensions. As we shall see, the operators $A(t_1)$ and $A(t_2)$ commute in two dimensions whereas they do not in three.

A. Rotational diffusion in two dimensions

In two dimensions, the stochastic rotation of a disk around a fixed axis is formally equivalent to stochastic translation in one dimension. The Liouville equation for the distribution function $f(\phi, t)$ is

$$\frac{\partial}{\partial t}f(\phi, t) = -\omega(t)\frac{\partial}{\partial\phi}f(\phi, t) \ , \tag{4.1}$$

where ϕ is the orientation angle of the disk (in the plane of the disk) and where $\omega(t)$ is the fluctuating angular velocity which we assume to be zero on the average. Introducing the correlation function $\psi(t) \equiv \langle\omega(t)\omega(0)\rangle$, we find

$$\frac{\partial}{\partial t}\langle f(\phi, t)\rangle = \int_0^t dt'\, \psi(t')\frac{\partial^2}{\partial\phi^2}\langle f(\phi, t)\rangle \tag{4.2}$$

if all F cumulants except $\psi(t)$ vanish, and

$$\frac{\partial}{\partial t}\langle f(\phi, t)\rangle = \int_0^t dt'\, \psi(t-t')\frac{\partial^2}{\partial\phi^2}\langle f(\phi, t')\rangle dt' \tag{4.3}$$

if all G cumulants except $\psi(t)$ vanish. For two-dimensional rotational diffusion, two predictions of the long-time behavior of $\psi(t)$ have appeared in the literature. From Messenger's[8] calculations for a cylinder rotating

about a fixed axis, one would conclude $\psi(t) \sim t^{-1}$. This would lead to a logarithmically diverging $\Delta^{(2)}(t)$, so that the rotational diffusion constant does not exist. Berne[9] reports $\psi(t) \sim t^{-5/2}$ for rotational diffusion of a disk in a two-dimensional fluid. If that is the case, the diffusion constant is finite.

B. Rotational diffusion in three dimension

In three dimensions, the Liouville equation for rotational diffusion is

$$\frac{\partial}{\partial t} f(\mathbf{\Omega}, t) = -\boldsymbol{\omega}(t) \cdot \mathbf{L} f(\mathbf{\Omega}, t) , \tag{4.4}$$

where $\mathbf{\Omega}$ is a unit vector fixed to the sphere and where $\mathbf{L} \equiv \mathbf{\Omega} \times (\partial/\partial \mathbf{\Omega})$ is the angular-momentum operator. Now the operators $A(t_1)$ and $A(t_2)[A(t) \equiv \boldsymbol{\omega}(t) \cdot \mathbf{L}]$ do *not* commute at different times t_1 and t_2, so that the F-cumulant expansion does not break off after the second cumulant if one assumes the Gaussian approximation for higher-order velocity autocorrelation functions. For example,

$$\langle 1\ 2\ 3\ 4 \rangle_F = \overbrace{1\ 2\ 3\ 4} + \overbrace{1\ 2\ 3\ 4} - \overbrace{1\ 3}\ \overbrace{2\ 4} - \overbrace{1\ 4}\ \overbrace{2\ 3} , \tag{4.5}$$

where the horizontal brackets indicate the pairs that are correlated. Because of rotational invariance,[4] F cumulants do commute, so that we may replace $\exp_F$ by exp.

The F-cumulant expansion for rotation has been studied extensively by Poneau and Weber.[4] They show that the terms in this expansion are finite if the angular velocity correlation function $\psi(t)$ $[\psi(t) \equiv \langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0) \rangle / d]$ decays faster than t^{-2} for large t. They calculate orientation autocorrelation functions for both small and large $\alpha \tau_c$. They find a correction to the Debye equation of diffusion on the unit sphere which is due to F cumulants of order 8 (and higher). The Debye law for the correlation function of the autocorrelation function of associated Legendre polynomials is

$$\langle Y_{lm}[\mathbf{\Omega}(0)] Y^*_{l'm'}(\mathbf{\Omega}(t)) \rangle = \delta_{ll'} \delta_{mm'} \exp[-tl(l+1)D] , \quad t \gg \tau_c , \tag{4.6}$$

where the rotational diffusion coefficient may depend on $(\alpha \tau_c)^2$ but not on l. Pomeau and Weber do find an l-dependent term in a calculation where $\psi(t)$ is assumed to be of the form $\psi(t) = \alpha^2 \exp(-t/\tau_c)$. Their result is

$$g_l(t) \equiv \langle Y_{lm}[\mathbf{\Omega}(0)] Y^*_{lm}[\mathbf{\Omega}(t)] \rangle = \exp\left\{ -tl(l+1) \left[(\alpha\tau_c)^2 + \tfrac{1}{2}(\alpha\tau_c)^4 + \frac{7}{12}(\alpha\tau_c)^6 + \frac{17}{18}(\alpha\tau_c)^8 - \frac{1}{8}(\alpha\tau_c)^8 l(l+1) + \cdots \right] \right\} , \quad t \gg \tau_c . \tag{4.7}$$

Here we shall investigate the consequences of the assumption of vanishing higher-order G cumulants. This assumption leads to

$$\frac{\partial}{\partial t} \langle f(\mathbf{\Omega}, t) \rangle = \int_0^t dt' \, \psi(t - t') L^2 \langle f(\mathbf{\Omega}, t') \rangle . \tag{4.8}$$

From Eq. (4.8), one finds that $g_l(t)$ obeys a similar equation, which after Laplace transformation reads

$$g_l(s) = [s + \psi(s) l(l+1)]^{-1} . \tag{4.9}$$

Thus, the Debye result is generalized to allow for frequency dependence of the rotational diffusion coefficient and no anomalous l dependence occurs. A similar generalization to frequency dependence was found in the case of translational diffusion.

It is useful to point out that the assumption of vanishing higher-order G cumulants implies, for example,

$$\langle A(t_1)A(t_2)A(t_3)A(t_4) \rangle = \langle A(t_1)A(t_2) \rangle \langle A(t_3)A(t_4) \rangle \quad (\text{for } t_1 \geq t_2 \geq \cdots \geq t_4) , \tag{4.10}$$

which does not affect the order of the operators $A(t_1), \ldots, A(t_4)$ and hence is independent of commutation properties. The assumption of vanishing higher-order F cumulants would imply that higher-order correlation functions, when reduced to pair correlations, are cancelled by pair terms where noncommuting operators occur in a different order. Therefore, in the case of a noncommuting stochastic operator, the assumption of vanishing higher-order F cumulants is not physically acceptable. If the Gaussian assumption is employed in conjunction with F ordering and a noncommuting stochastic operator, the F expansion does not terminate after the second-order F cumulant.

V. CONCLUDING REMARKS

We have shown how the formalism of stochastic differential equations combined with assumptions about the properties of the random operator may be employed to relate conveniently the long-time behavior of (angular) position correlation functions to the associated velocity correlation functions. The stochastic assumptions are formulated in terms of cumulant expansions accompanied by different ordering prescriptions as suggested by Kubo. The formalism is simple and reproduces the essential results of previous analyses for the correlation functions pertinent to both translational and rotational diffusion.

Most importantly, our analysis of three-dimensional rotational diffusion demonstrates that the discrepancy with the Debye law found by Pomeau and Weber for $\langle Y_{lm}(t) Y_{lm}(0) \rangle$ is a consequence of F ordering combined with the Gaussian approximation. If one adopts G ordering, the conventional Debye law is found at long times. Which ordering is correct depends upon a specific microscopic physical model and the issue cannot be decided by mathematics alone.

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[1]For a review, see J. R. Dorfman, in *Fundamental Problems in Statistical Mechanics III*, edited by E. G. D. Cohen (North-Holland, Amsterdam, 1975).
[2]R. Kubo, J. Math. Phys. **4**, 174 (1963).
[3]T. Keyes and I. Oppenheim, Physica (Utrecht) **70**, 100 (1973).
[4]Y. Pomeau and J. Weber, J. Chem. Phys. **65**, 3616 (1976).
[5]N. G. van Kampen, Physica (Utrecht) **74**, 215 (1974).
[6]I. A. Michaels and I. Oppenheim, Physica (Utrecht) A **81**, 522 (1975).
[7]H. H.-H. Yuan and I. Oppenheim, Physica (Utrecht) A **90**, 1 (1978).
[8]T. J. Messenger, thesis, Harvard University, 1973.
[9]B. J. Berne, J. Chem. Phys. **56**, 2164 (1972).