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On the Calculation of Autocorrelation Functions of Dynamical Variables*

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In this paper we develop a formalism for calculating the autocorrelation function of a dynamical variable in terms of a well-defined memory function. Guided by simple physical arguments, an ansatz is adopted for the functional form of the memory function. This ansatz asserts that the memory of dynamical coherence decays exponentially. It is found that:

(a) Despite the monotonic exponential decay of the memory function, the autocorrelation function deduced can display negative regions in some circumstances and decay monotonically in other circumstances.

(b) The form of the autocorrelation function deduced is identical with that obtained from two other very different analyses, suggesting that the major properties of the function are of general validity.

(c) The computed linear momentum autocorrelation function and power spectrum for liquid Ar are in good agreement with the computer experiments of Rahman.

(d) The computed dipolar autocorrelation function reproduces all the features of the experimentally determined autocorrelation function, though at present insufficient data are available to provide a quantitative test of the theory.

(e) The ansatz used, although obviously not exact, is consistent with the theory of linear regression (Appendix B).

I. INTRODUCTION

DESPITE recent advances in the theory of linear transport phenomena in dense fluids,[1,2] relatively little is known about the autocorrelation function of the linear or angular momentum. In addition, aside from qualitative arguments, little can be said of the structure of the few autocorrelation functions which have been determined.[3,4] One of the major difficulties encountered in developing a theory of the autocorrelation function arises from the fact that there seems to be, at least at present, no simple way of bypassing the complex many-body dynamics in a realistic fashion. Now, Gray[5,2] has shown how a simple statistical model, in which the divergence of the center-of-mass flux in the equation of continuity for the pair density is replaced by a relaxation time term, can lead to both oscillatory and exponentially decaying time dependence of the (linear) momentum autocorrelation function. While it is difficult to determine the full set of implications of Gray's hypothesis, it is apparent that simple statistical models may lead to valuable insight into the behavior of molecules in a liquid. In this paper we examine a very different and more general statistical model than that considered by Gray. Starting from a general formulation of linear non-Markoffian response functions, we show that a simple ansatz relevant to the decay of the coherence of molecular motions leads to a form for the momentum autocorrelation function which is easily interpreted. It is found that:

(a) The assumption that the memory of coherence decays exponentially leads to an autocorrelation function which can display negative regions in some circumstances and decay monotonically in other circumstances.

(b) The computed linear-momentum autocorrelation function and power spectrum for liquid Ar are in good agreement with the computer experiments of Rahman.[3]

(c) The computed dipolar autocorrelation function reproduces all the features of the experimentally determined autocorrelation function,[4] though at present insufficient data are available to provide a quantitative test of the theory.

(d) The ansatz used, although obviously not exact, is consistent with the requirements of the thermodynamics of irreversible processes[6] and with simple notions about the time dependence of interactions in dense fluid.

II. REVIEW OF THE COHERENCE TIME CONCEPT[7]

The role of the dynamical coherence time in determining the rate of approach to equilibrium is clearly displayed in the autocorrelation function representation of the linear transport coefficients.[8–10] If it is assumed

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[1] I. Prigogine, *Non-Equilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962).

[2] S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (John Wiley & Sons, Inc., New York, 1965).

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[5] P. Gray, Mol. Phys. **7**, 235 (1964).

[6] S. R. De Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland Publ. Co., Amsterdam, 1962).

[7] U. Fano, in *Lectures on the Many-Body Problem*, E. R. Caianello, Ed. (Academic Press Inc., New York, 1964), Vol. 2, pp. 217–239.

[8] M. S. Green, J. Chem. Phys. **20**, 1281 (1952); **22**, 398 (1954).

[9] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[10] H. Mori, Phys. Rev. **112**, 1829 (1958).

that, for example, the momentum autocorrelation function decays as $\exp(-t/\tau_c)$, then the correlation time τ_c (relaxation time) determines the diffusion coefficient. What is not explicitly clear, and is indeed only the subtle end result of the interactions in, and time evolution of, the N coupled molecules, is how the coherence time is related to the details of molecular dynamics. While we certainly cannot offer any analysis remotely approaching completeness, a few remarks pertinent to the relationship sought may be made.[11]

It is, of course, just a restatement of what is well known, to note that a subsystem, in interaction with a large reservoir, quickly dissipates the effects of a disturbance if the interactions between the subsystem and reservoir and within the reservoir are such that the disturbance propagates away as fast or faster than the disturbance is built up in the subsystem. What is less obvious is how important the history of the evolution of the disturbance is to the instantaneous rate of dissipation, i.e., whether the rate of dissipation should be Markoffian or non-Markoffian. In general, a Markoffian description will be valid only if it is possible to neglect effects created within the lifetime of the dynamical correlations. More explicitly, the Liouville equation

$$(\partial/\partial t)f^{(N)}=i\mathfrak{L}^{(N)}f^{(N)} \tag{1}$$

$$\mathfrak{L}^{(N)}=i\sum_j[(\mathbf{p}_j/m)\cdot\nabla_j+\mathbf{F}_j\cdot\nabla_{p_j}] \tag{2}$$

has the solution

$$\begin{aligned}f^{(N)}(t)&=\exp[i(t-t')\mathfrak{L}^{(N)}]f^{(N)}(t')\\&=G^{(N)}(t,t')f^{(N)}(t'),\end{aligned} \tag{3}$$

and it is clear that $G^{(N)}(t,t')$ has the group property

$$G^{(N)}(t,t'')=G^{(N)}(t,t')G^{(N)}(t',t''), \tag{4}$$

which defines a Markov process. In the case of the full N-body system, the Markov process is trivial in the sense that the transition probability for the motion of the phase point is a delta function with argument determined by the N-body dynamics. However, the transition probability describing the motion of a phase point in a subspace, for example, the point Γ_N in the phase space of a pair of molecules, is not determined solely by the two-body dynamics and is not a Markov process. If, however, the quantity

$$G^{(n)}=\int d\Gamma_{N-n}G^{(N)} \tag{5}$$

(which is obtained by expanding the exponential operator $G^{(N)}$ in its defining power series and integrating term by term with a suitable test function) can be written in the form

$$G^{(n)}(t-t'')\simeq[G^{(n)}(\tau)]^m, \tag{6}$$

then the projection $G^{(n)}$ defines an *approximately* Markoffian process. Now, Eq. (6) will only be valid, if at all, provided that τ_c, the lifetime of the dynamical correlations build up in the time interval $t-t''$, satisfies the inequality $\tau\gg\tau_c$, where $t-t''=m\tau$. It is just because τ_c is finite that Eq. (6) can represent only an approximately Markoffian process. It is clear that the correlations neglected when Eq. (6) is adopted are those built up in the interval τ_c just prior to t''. Whether or not their neglect introduces negligible error depends on the phenomenon under discussion.

The reader should note that a Markoffian kinetic equation leads to the same transport coefficients as obtained from the autocorrelation-function representation, because of the implicit long time integration involved in the use of asymptotic cross sections in the kinetic equation. Thus, for the computation of linear-transport coefficients from a kinetic equation, it is not necessary to examine the dynamical behavior of the system at short times. On the other hand, consideration of the structure of the autocorrelation function of a dynamical variable requires just such an examination of the dynamics. We see that in our formulation of the problem the calculation of the time dependence of the autocorrelation function for short times cannot be carried out using only asymptotic (and Markoffian) considerations.

It is worthwhile to probe a little more deeply into the way that the property expressed in Eq. (6) is used to obtain both a kinetic equation and an autocorrelation-function representation. Consider the derivation of the singlet kinetic equation for a dilute gas. A purely formal representation of the time dependence of the singlet distribution function can be given in terms of the propagator $\exp(it\mathfrak{L}^{(N)})$ acting on the N-body distribution function at $t=0$, and an integration over the phase space of $N-1$ molecules. The system of N molecules may be thought of as a subsystem of one molecule and a reservoir of $N-1$ molecules, to which corresponds a decomposition of $\mathfrak{L}^{(N)}$ into operators for the subsystem, the reservoir, and their complete interaction. If the interaction operator is regarded as a perturbation, and the formal representation of the singlet function expanded in a perturbation series with use of the initial condition that the full distribution function can be written as the product $f^{(1)}(0)f^{(N-1)}(0)$, then the resulting expansion may be converted to a kinetic equation as follows. The structure of the perturbation series involves multiple time integrations over products of the interaction representation of the perturbation operator. Consider some small time interval τ, with τ chosen so that $\tau\gg\tau_c$, but also small enough that the terms in the perturbation series involving more than two time integrations are small and may be neglected. Provided that $\tau\gg\tau_c$ as assumed, the time dependence of the singlet distribution function at long times may be generated from the truncated perturbation expansion by replacing the actual N-body distri-

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[11] The following introductory remarks are based on a discussion by Fano (see Ref. 7).

bution function generated from the initial state with the product function $f^{(1)}(\tau)f^{(N-1)}(0)$. When this condition is entered into the integrand of the perturbation expansion and the procedure repeated chainwise, the resultant $f^{(1)}(t)$ is the same as the function that would be obtained from the integration of a differential equation on a time mesh of size τ. Thus, the variations of $f(t)$ obtained satisfy a kinetic equation where the interval τ is treated formally as a differential. The reader should note that the repeated use of the product function at intervals of length τ is very close to the philosophy of time smoothing, where a dynamical event occurring in an interval τ is taken to be independent of prior dynamical events.[2]

How do short time correlations appear in the representation of dissipative processes? When $\tau \gg \tau_c$, it is to be expected that the coherence imposed by the molecular dynamics is lost because of propagation of the disturbance away from the source (the dynamical event studied) by the coupling with the surrounding molecules. Then, the average of the products of operators in the perturbation expansion described in the last paragraph is expected to approach a product of the averages of the operators. By introduction of cumulants representing the difference between an average of several operators and the product of the averages taken all possible ways, it may be shown that the perturbation expansion may be expressed in terms of the autocorrelation function of the cumulants. But, by definition, if $t \gg \tau_c$ the cumulants vanish, and therefore in this representation the effects of short-time correlations in the molecular dynamics are displayed.

Since both representations discussed can be obtained from perturbation theory, their connection is easily established in the same formalism. The key point is that the cumulants vanish rapidly as t increases, so that integrals over the cumulants rapidly approach their asymptotic values and are not sensitive to the precise value of the upper limit of integration. Under these circumstances, the neglect of third- and higher-order cumulant terms leads to a kinetic equation in which the entire effect of the dissipative interaction enters through integrals over the pair cumulant function. Thus, even though the dissipation appears through the structure of the pair cumulant, an asymptotic limit must be used to obtain a kinetic equation. A much more general and incisive analysis of the relationship between kinetic equations and the autocorrelation-function representation has been given by Resibois.[12] The preceding simple arguments suffice to introduce the points of interest to us.

It is indeed a remarkable result in many ways, that a Markoffian kinetic equation leads to the same linear transport coefficients as does the autocorrelation-function representation of the transport coefficients. Because of the role played by the coherence time in defining both the autocorrelation function of a dynamical variable and the corresponding kinetic equation, we are encouraged to pose the following question: Given a formal, but usable, definition of dynamical memory, what do simple physical arguments about the nature of the dynamical memory imply about the autocorrelation function? In the following sections we seek to answer this question.

III. EQUATION FOR THE AUTOCORRELATION FUNCTION[13]

In this section an equation is derived which describes the time evolution of the normalized autocorrelation-function $\psi(t)$ of the phase function $U(\Gamma_N)$. $\psi(t)$ is defined by

$$\psi(t)=Z_N^{-1}\int d\Gamma_N U(\Gamma_N)\exp(it\mathcal{L}^{(N)})U(\Gamma_N)\exp\left(\frac{-H^{(N)}}{kT}\right), \tag{7}$$

where Z_N is the canonical partition function for the N-molecule system, and $\mathcal{L}^{(N)}$, $H^{(N)}$, are the corresponding Liouville operator, and Hamiltonian function, respectively. The phase function $U(\Gamma_N)$ is assumed to have the following properties:

$$\langle U\rangle=0, \qquad \langle U^2\rangle=1, \tag{8}$$

where the bracket defines an average in the canonical ensemble,

$$\langle\alpha\rangle=Z_N^{-1}\int d\Gamma_N\ \alpha\exp\left(\frac{-H^{(N)}}{kT}\right). \tag{9}$$

If $\psi(t)$ is differentiated twice with respect to t,

$$\frac{d^2\psi(t)}{dt^2}=Z_N^{-1}\int d\Gamma_N U(\Gamma_N)i\mathcal{L}^{(N)}\exp(it\mathcal{L}^{(N)})[i\mathcal{L}^{(N)}U(\Gamma_N)]\exp\left(\frac{-H^{(N)}}{kT}\right), \tag{10}$$

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[12] P. Resibois, in *N-Particle Physics*, E. Meeron, Ed. (Gordon and Breach, New York, 1966).

[13] R. Zwanzig, *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1961), Vol. 3, pp. 106–141.

and the right-hand side of this equation integrated by parts, it is found that

$$\frac{d^2\psi(t)}{dt^2}=-Z_N^{-1}\int d\Gamma_N[i\mathcal{L}^{(N)}U(\Gamma_N)]\exp(it\mathcal{L}^{(N)})[i\mathcal{L}^{(N)}U(\Gamma_N)]\exp\left(\frac{-H^{(N)}}{kT}\right)$$

$$=-\langle\Phi(\Gamma_N)\exp(it\mathcal{L}^{(N)})\Phi(\Gamma_N)\rangle, \tag{11}$$

where

$$\Phi(\Gamma_N)=i\mathcal{L}^{(N)}U(\Gamma_N)=\dot{U}(\Gamma_N), \tag{12}$$

since the time evolution of the phase function $U(\Gamma_N)$ is described by the relation

$$(d/dt)U(\Gamma_N)=i\mathcal{L}^{(N)}U(\Gamma_N). \tag{13}$$

Now, the operator $\exp(it\mathcal{L}^{(N)})$ is the unitary time-displacement operator which, when applied to an arbitrary phase function, displaces it in time according to the canonical equations of motion. Thus, Eq. (11) can be rewritten, using the previous notation, in the form

$$d^2\psi(t)/dt^2=-\langle\dot{U}(0)\dot{U}(t)\rangle. \tag{14}$$

Equation (14) is to be solved subject to the initial conditions

$$\psi(0)=1$$

and

$$\dot{\psi}(0)=\langle U(0)\dot{U}(0)\rangle=0. \tag{15}$$

The first of Eqs. (15) is merely the second condition in Eq. (8), whereas the second of Eqs. (15) follows from considerations of parity.

Denoting the Laplace transform with respect to t of the functions $\psi(t)$ and $\phi(t)=\langle\dot{U}(0)\dot{U}(t)\rangle$, respectively, by $\tilde{\psi}(s)$ and $\tilde{\phi}(s)$, with s the Laplace variable, Eq. (14) is Laplace transformed as

$$s^2\tilde{\psi}(s)-s=-\tilde{\phi}(s). \tag{16}$$

From the following identity, for $s\neq0$,

$$(s^2\tilde{\psi}(s)-s)\tilde{\psi}(s)=[1+(1/s)(s^2\tilde{\psi}(s)-s)](s\tilde{\psi}(s)-1), \tag{17}$$

and substitution of (16) into (17) yields

$$-\tilde{\phi}(s)\tilde{\psi}(s)=[1-(1/s)\tilde{\phi}(s)](s\tilde{\psi}(s)-1). \tag{18}$$

For values of s such that $1-(1/s)\tilde{\phi}(s)\neq0$, Eq. (18) can be written in the form

$$s\tilde{\psi}(s)-1=-[1-(1/s)\tilde{\phi}(s)]^{-1}\tilde{\phi}(s)\tilde{\psi}(s), \tag{19}$$

and by inversion,

$$\frac{d\psi(t)}{dt}=-\int_0^t d\tau K(\tau)\psi(t-\tau), \tag{20}$$

where

$$\tilde{K}(s)=[1-(1/s)\tilde{\phi}(s)]^{-1}\tilde{\phi}(s). \tag{21}$$

Consider, now, the function $\tilde{\phi}(s)$. This function may be written in terms of the resolvent operator $(s-i\mathcal{L}^{(N)})^{-1}$, i.e.,

$$\tilde{\phi}(s)=\langle\dot{U}(s-i\mathcal{L}^{(N)})^{-1}\dot{U}\rangle. \tag{22}$$

We now define a projection operator $\mathcal{P}$ on a well-behaved function of the phase Γ_N, $G(\Gamma_N)$, as follows:

$$\mathcal{P}G(\Gamma_N)=U(\Gamma_N)f_{\text{eq}}^{(N)}\int d\Gamma'_N U(\Gamma'_N)G(\Gamma'_N), \tag{23}$$

where

$$f_{\text{eq}}^{(N)}=Z_N^{-1}\exp(-H^{(N)}/kT). \tag{24}$$

Noting that, for the operators $\mathcal{A}$ and $\mathcal{B}$, there exists the identity

$$\mathcal{A}^{-1}=\mathcal{B}^{-1}+\mathcal{A}^{-1}(\mathcal{B}-\mathcal{A})\mathcal{B}^{-1}, \tag{25}$$

we find that

$$\tilde{\phi}(s)=\langle\dot{U}[s-i(1-\mathcal{P})\mathcal{L}^{(N)}]^{-1}\dot{U}\rangle$$
$$+\langle\dot{U}[s-i\mathcal{L}^{(N)}]^{-1}i\mathcal{P}\mathcal{L}^{(N)}[s-i(1-\mathcal{P})\mathcal{L}^{(N)}]^{-1}\dot{U}\rangle. \tag{26}$$

Now, exploiting the definition of $\mathcal{P}$ in Eq. (23) and integrating by parts,

$$i\mathcal{P}\mathcal{L}^{(N)}[s-i(1-\mathcal{P})\mathcal{L}^{(N)}]^{-1}\dot{U}f_{\text{eq}}^{(N)}$$
$$=-Uf_{\text{eq}}^{(N)}\langle\dot{U}[s-i(1-\mathcal{P})\mathcal{L}^{(N)}]^{-1}\dot{U}\rangle. \tag{27}$$

Thus, from Eqs. (26) and (27), we find

$$\tilde{\phi}(s)=\langle\dot{U}[1-i(-\mathcal{P})\mathcal{L}^{(N)}]^{-1}\dot{U}\rangle$$
$$-\langle\dot{U}(s-i\mathcal{L}^{(N)})^{-1}U\rangle\langle\dot{U}[s-i(1-\mathcal{P})\mathcal{L}^{(N)}]^{-1}\dot{U}\rangle. \tag{28}$$

Furthermore, it is easily recognized that

$$\langle\dot{U}(s-i\mathcal{L}^{(N)})^{-1}U\rangle=(1/s)\langle\dot{U}(s-i\mathcal{L}^{(N)})^{-1}\dot{U}\rangle. \tag{29}$$

The substitution of (29) into (28), and of the latter result into Eq. (21) yields

$$\tilde{K}(s)=\langle\dot{U}[s-i(1-\mathcal{P})\mathcal{L}^{(N)}]^{-1}\dot{U}\rangle, \tag{30}$$

which, by inverse transformation, becomes

$$K(t)=\langle\dot{U}\exp[it(1-\mathcal{P})\mathcal{L}^{(N)}]\dot{U}\rangle. \tag{31}$$

From the structure of Eq. (31) it is clear that the kernel $K(t)$ is related to the memory, or dynamical coherence time, of the system, an interpretation which is exploited later in this paper.

In a subsequent paper we shall show how Eq. (30) may be used to generalize the linear trajectory hypotheses first used by Helfand,[14] thereby permitting

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[14] E. Helfand, Phys. Fluids 4, 681 (1961).

calculation of the coefficients of shear viscosity and thermal conductance.

In this paper we are interested in autocorrelation functions of vector quantities such as $\psi_\alpha(t)$ defined by

$$\psi_\alpha(t)=\langle\boldsymbol{\alpha}(0)\cdot\boldsymbol{\alpha}(t)\rangle. \tag{32}$$

The analysis necessary can be carried through with only one minor change: the projection operator in this case must be defined by its action on an arbitrary well-behaved vector point function of the phase Γ_N, say $\mathbf{G}(\Gamma_N)$,

$$\mathcal{P}\mathbf{G}(\Gamma_N)=\boldsymbol{\alpha}f_{\text{eq}}^{(N)}\int d\Gamma'_N\,\boldsymbol{\alpha}(\Gamma'_N)\cdot\mathbf{G}(\Gamma'_N). \tag{33}$$

These modifications are easily introduced into the preceding analysis.

Using a projection operator formalism, Zwanzig[13] has derived an equation describing the time evolution of autocorrelation functions. The equation obtained from this very elegant formalism is identical with Eq. (20), with $K(\tau)$ defined by Eq. (31). By a different procedure we have obtained Eq. (20) with $\tilde{K}(s)$ defined by Eq. (21). By exploitation of Zwanzig's projection operator, Eq. (23), it was possible to demonstrate the identity of our equations with his. We feel that the form of $\tilde{K}(s)$ presented in Eq. (21) is useful in generating new approximations, such as the linear trajectory approximation discussed above. This form of $\tilde{K}(s)$ has not been presented before.[15]

IV. APPROXIMATE REPRESENTATION OF THE MEMORY FUNCTION

In this section we seek a representation of $K(\tau)$ since, once this function is known, the autocorrelation function is determined by solution of Eq. (20) with the boundary conditions $\psi(0)=1$ and $\dot{\psi}(0)=0$. It is useful to begin by specializing the discussion to the case of the normalized velocity autocorrelation function

$$\psi_v(t)=\langle\mathbf{v}_1\cdot\exp(it\mathcal{L}^{(N)})\mathbf{v}_1\rangle/\langle v_1^2\rangle, \tag{34}$$

which is connected to Eq. (7) by setting $\mathbf{U}=\mathbf{v}_1(\langle v_1^2\rangle)^{-\frac{1}{2}}$ and with the requisite projection operator

$$\mathcal{P}\mathbf{G}(\Gamma_N)=(\langle v_i^2\rangle)^{-1}\,\mathbf{v}_1f_{\text{eq}}^{(N)}\int d\Gamma'_N\mathbf{v}_1\cdot\mathbf{G}(\Gamma'_N). \tag{35}$$

Then, since

$$i\mathcal{L}^{(N)}\mathbf{v}_1=\mathbf{F}_1/m, \tag{36}$$

the kernel function becomes

$$\tilde{K}(s)=\left(1-s^{-1}\frac{\langle\mathbf{F}_1\cdot\tilde{\mathbf{F}}_1(s)\rangle}{m^2\langle v_1^2\rangle}\right)^{-1}\frac{\langle\mathbf{F}_1\cdot\tilde{\mathbf{F}}_1(s)\rangle}{m^2\langle v_1^2\rangle}, \tag{37}$$

where $\mathbf{F}_1$ is the force on Molecule 1. The value of $\tilde{K}(0)$ is easily determined from the Einstein relation for the diffusion coefficient. For

$$\begin{aligned}D&=\frac{kT}{m}\int_0^\infty dt\psi(t)\\&=\frac{kT}{m}\lim_{s\to0}\int_0^\infty\exp(-st)\psi(t)dt\\&=(kT/m)\tilde{\psi}(0),\end{aligned} \tag{38}$$

whereupon, using the Laplace transform of Eq. (20),

$$s\tilde{\psi}(s)=1-\tilde{K}(s)\tilde{\psi}(s), \tag{39}$$

it is seen that

$$D=(kT/m)[\tilde{K}(0)]^{-1}=kT/m\beta. \tag{40}$$

Thus $\tilde{K}(0)$ is just the translational friction coefficient. Note that the friction coefficient $\beta=\zeta/m$, where ζ is the friction coefficient often used in other papers.[2] A relationship involving $K(0)$ and $(\partial^2\psi/\partial t^2)_{t=0}$ is easily obtained when it is noticed that

$$K(0)=\langle(i\mathcal{L}^{(N)}\mathbf{U})^2\rangle=\langle F_1^2\rangle/m^2\langle v_1^2\rangle, \tag{41}$$

and

$$\partial^2\psi(t)/\partial t^2=-\langle\mathbf{F}_1\cdot\mathbf{F}_1(t)\rangle/m^2\langle v_1^2\rangle. \tag{42}$$

Finally, it can be shown that the memory function must be even in the time and have zero derivative at $t=0$ (see Appendix A).

The exact relations given above are insufficient to uniquely determine the form of the kernel function, and we propose to proceed by introducing a two-parameter trial function, $K(\alpha,\gamma)$, with the parameters determined by use of Eqs. (40) and (42). It is now necessary to consider the functional form for the trial kernel.

Consider the case of the dilute gas. The probability that a molecule will travel a distance R without undergoing collision is proportional to $\exp(-R/\lambda_f)$, where λ_f is the mean free path. This form indicates that the sequence of collisions experienced by a molecule forms a Poisson process, and, since each collision causes partial loss of the persistence of momentum, the memory of the initial momentum decays as $\exp(-t/\tau_c)$, where τ_c is the mean time between collisions.

Consider now the case of a dense fluid. Each molecule may be imagined to be surrounded by a cage of other atoms. The cage is, of course, not stationary, and in response to fluctuations in the surrounding medium undergoes quasirandom alterations as a function of time. A molecule moving away from the center of its cage interacts with the moving wall molecules. Although a strongly repulsive encounter with the wall molecules is likely to almost reverse the central particle momentum, the fact that the cage is fluctuating suggests that the sequence of interactions leading to loss of memory of the initial momentum of the particle can be approximated as a Poisson process. In the Rice–Allnatt theory,[2] successive strongly repulsive binary

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[15] After this paper was submitted for publication, R. Zwanzig drew to our attention that he was aware of the form of $K(s)$ given in Eq. (21), but that he had never reported it in a publication. (See Appendix C.)

encounters are taken to be independent, and the present argument suggests that the soft interactions leading to dissipation of momentum are sufficiently close to forming a Poisson process that a reasonable first approximation to the memory function is the exponential decay $\exp(-\alpha t)$. Clearly, this form has the proper regression property, but is inexact since it has finite slope at $t=0$. The reader should note that a simple exponential memory function is consistent with the velocity autocorrelation function having negative regions, as is shown shortly. We emphasize this point in advance of demonstration so as to clearly differentiate the time dependence of the memory function from the time dependence of the corresponding autocorrelation function. One last point: If the time sequence of interactions is a Gaussian Markov process, then the correlation function is, rigorously, exponentially decaying.[16] In addition, as shown in Appendix B, the exponential memory function is derivable from linear regression theory.[6]

With the preceding arguments as motivation, we adopt the two-parameter trial kernel

$$K(\alpha,\gamma;t)=\gamma\exp(-\alpha\,|\,t\,|), \tag{43}$$

where $|\,t\,|$ is required by the parity of $K(t)$. However, in all that follows we consider only the positive time axis, and the modulus bars on t are therefore dropped. The degree to which (43) is an adequate approximation to the true memory function can be tested only *a posteriori.*

To obtain the autocorrelation function, $K(\alpha,\gamma;t)$ as defined in Eq. (43) is Laplace transformed, and the result is substituted into Eq. (39) to give

$$\bar{\psi}(s)=(\alpha+s)/(s-s_+)(s-s_-), \tag{44}$$

$$s_\pm=-\tfrac{1}{2}\alpha\{1\mp[1-(4\gamma/\alpha^2)]^{\frac{1}{2}}\}. \tag{45}$$

Equation (44) is inverted to yield

$$\psi(t)=[1/(s_+-s_-)][s_+\exp(s_-t)-s_-\exp(s_+t)]. \tag{46}$$

This result may be tested against the "experimental" data of Rahman[3] after numerical evaluation of α and γ. These parameters are determined, as indicated above: substitution of the Laplace transform of Eq. (43) into (40) yields

$$\beta=\lim_{s\to 0}\frac{\gamma}{s+\alpha}=\frac{\gamma}{\alpha}, \tag{47}$$

and from Eqs. (42), (45), and (46) it is found that

$$\gamma=\frac{\langle F_1^2\rangle}{m^2\langle v_1^2\rangle}=\frac{\langle F_1^2\rangle}{3mkT}=\frac{\langle\nabla_1^2V\rangle}{3m}. \tag{48}$$

V. APPLICATION TO THE AUTOCORRELATION FUNCTION OF THE LINEAR MOMENTUM

Rahman, using a large digital computer, has solved the equations of motion for 864 atoms in a cubical box with periodic boundary conditions. The state of the system was chosen to correspond to liquid Ar at $T=94.4$°K and $\rho_m=1.374$ g cm^{-3}. The interaction between the atoms was described by the known Ar–Ar Lennard-Jones potential.[17] From the solutions obtained, Rahman has calculated the velocity autocorrelation function, the power spectrum, the pair correlation function, the mean-square displacement of an atom as a function of time, and the diffusion coefficient. All of these are of use in our considerations.

Using Rahman's data, it is found that $\langle\nabla_1^2V\rangle=11.0\times10^3$ erg cm^{-2}. To check the integration over the radial distribution function, we note that for very short times the time derivative of the autocorrelation function is, from Eq. (46),

$$d\psi/dt=-s_+s_-t=-\alpha\beta t;\qquad s_+t\ll1,\quad s_-t\ll1. \tag{49}$$

Thus, the value of $d\psi/dt$ for t small also provides a measure of $\langle\nabla_1^2V\rangle$ [see Eqs. (47) and (48)]. From the data presented by Rahman we find that $\langle\nabla_1^2V\rangle=11.0\times10^3$ erg cm^{-2}, in perfect agreement with the determination by direct integration. Using $D=2.43\times10^{-5}$ cm^2 sec^{-1}, as computed, and the value of $\langle\nabla_1^2V\rangle$ quoted, it is found that $\alpha=8.06\times10^{12}$ sec^{-1} and $\alpha\beta=6.5\times10^{25}$ sec^{-2}. With these values of α and β, the roots $s_\pm$ are complex, and

$$\begin{aligned}\psi(t)&=\exp(-4.03t/\tau_0)\\&\quad\times\{\cos[4.03\surd3\,(t/\tau_0)]+3^{-\frac{1}{2}}\sin[4.03\surd3\,(t/\tau_0)]\},\\\tau_0&=10^{-12}\text{ sec.}\end{aligned} \tag{50}$$

In Fig. 1 the theoretical autocorrelation function, Eq. (50), is plotted along with the Markoffian approximation, $\psi^M(t)=\exp(-\beta t)$, and the "experimental" data of Rahman. As can be seen, the qualitative features of the autocorrelation function are reproduced, but the theoretical function oscillates with somewhat larger amplitude than does the observed autocorrelation function. Indeed, the agreement between the two functions is quite good up to $(t/\tau_0)\simeq0.3-0.4$, and it is very important to note that the theoretical function correctly predicts a negative region for $\psi(t)$, despite the very simple form of the trial memory function.

A somewhat different test of the theory proposed here can be made by comparing the theoretical and observed normalized power spectra, defined by

$$G(\omega)=\beta\int_0^\infty dt\psi(t)\cos(\omega t). \tag{51}$$

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[16] M. S. Bartlett, *Stochastic Processes* (Cambridge University Press, London, 1955).

[17] Note, however, that the Lennard-Jones potential is not an adequate representation of the Ar–Ar interaction. For example, under the conditions descriptive of Rahman's calculation, the computed pressure and energy of vaporization are 51.2 atm and 1335 cal mole^{-1}, respectively. The observed values are 160 atm and 1550 cal mole^{-1}.

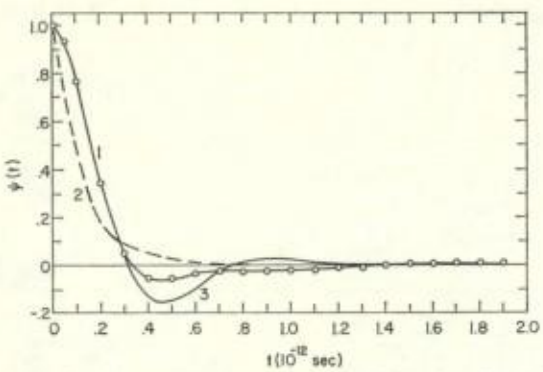

FIG. 1. The linear momentum autocorrelation function, $\psi(t)$, from Rahman's "experiment" (1), the Markoffian approximation (2), and Eq. (50), (3).

It is easily seen that

$$G(0)=1,$$

and for our memory ansatz

$$G(\omega)=\beta\,\mathrm{Re}\int_0^\infty dt\exp(-i\omega t)\psi(t)$$

$$=\frac{\alpha^2\beta^2}{\alpha^2\beta^2+\alpha^2[1-(2\beta/\alpha)]\omega^2+\omega^4}. \qquad (52)$$

With the values of the parameters already cited, we find

$$G(\omega)=0.420/(0.420-6.5\times10^{-27}\omega^2+10^{-52}\omega^4). \qquad (53)$$

In Fig. 2 is plotted the theoretical power spectrum, Eq. (53), along with the Markoffian approximation $[G^M(\omega)=\beta^2/(\omega^2+\beta^2)]$ and the "experimental" data of Rahman. Again, the agreement between theory and experiment is quite good, especially in the matching of the peak in $G(\omega)$, which reaches a value of about 1.4.

Before discussing the implications of these results any further, we examine another application of the formalism and the exponential memory ansatz.

VI. APPLICATION TO THE STUDY OF NUCLEAR SPIN–LATTICE RELAXATION

The relaxation of nuclear spins is determined by the coupling of the spins to the rotational and translational motions of the molecules in the system. For systems with nuclei of spin $\frac{1}{2}$, the spin–rotation interaction for a linear molecule leads to an interaction Hamiltonian of the form

$$H=-c\mathbf{I}\cdot\mathbf{J}, \qquad (54)$$

where **I** and **J** are the angular momenta of the nuclear spin and molecular rotation, respectively, and c is the spin–rotation coupling constant. When the interaction described by Eq. (54) is the only dissipative perturbation, the relaxation to equilibrium is determined by the time constant T_1^{SR},

$$\frac{1}{T_1^{SR}}=\frac{2c^2}{3\hbar^2}\int\langle\mathbf{J}(0)\cdot\mathbf{J}(t)\rangle dt, \qquad (55)$$

a form similar to Eq. (38).

An analysis similar to that presented in Sec. IV is obviously pertinent. Consider the case of a diatomic molecule (or more generally a symmetric-top molecule). We assume the existence of a Langevin equation describing the rotational motion. In writing such an equation it is important to take advantage of the symmetry of the molecule, for in general the relationship between, say, the time derivative of the angular momentum and the angular momentum itself involves a tensor friction coefficient. For a diatomic molecule (or symmetric-top molecule) it is possible to choose the symmetry axis so as to diagonalize the friction coefficient tensor. We seek to evaluate

$$\psi_R(t)=\langle\mathbf{J}(0)\cdot\mathbf{J}(t)\rangle/\langle J^2\rangle=\langle\mathbf{J}(0)\cdot\mathbf{J}(t)\rangle/3IkT, \qquad (56)$$

where I is the moment of inertia of the molecule. The calculation of $\psi_R(t)$ leads to consideration of exactly the same set of equations as already discussed in Sec. IV. In the case of rotational motion, the equation equivalent to Eq. (42) involves the autocorrelation of the torque on Molecule 1, $\mathbf{N}_1(t)$,

$$\partial^2\psi_R(t)/\partial t^2=-\langle\mathbf{N}_1(0)\cdot\mathbf{N}_1(t)\rangle/3IkT. \qquad (57)$$

Using the definition of the mean torque acting on Particle 1,

$$\mathbf{N}_1(t)=-\zeta_R\boldsymbol{\omega}_{12}(t), \qquad (58)$$

with ζ_R the rotational friction coefficient and $\boldsymbol{\omega}_{12}$ the relative angular diffusion velocity, it is found from (57) that

$$[\partial^2\psi_R(t)/\partial t^2]_{t=0}=-2\zeta_R^2/I^2. \qquad (59)$$

For the case of the exponential memory,

$$K_R(t)=\gamma_R\exp(-\alpha_Rt), \qquad (60)$$

Eq. (59) leads to the condition

$$\gamma_R=2(\zeta_R^2/I^2). \qquad (61)$$

A second relation between the coefficients α_R and γ_R is needed; this relation is obtained as follows: $\psi_R(t-\tau)$ is expanded about τ in a Taylor series and the result is substituted in the rhs of the original equation (20). The exponential ansatz is then introduced, and the equation is integrated. In what immediately follows we are interested in long times; then, since $t\gg\alpha_R^{-1}$, the limits on the integral can be extended to infinity and

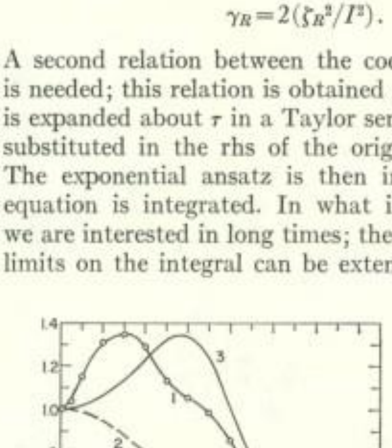

FIG. 2. The power spectrum $G(\omega)$ from Rahman's "experiment" (1), the Markoffian approximation (2), and Eq. (53), (3).

one obtains

$$\frac{d\psi_R(t)}{dt} = -\frac{\gamma_R}{\alpha_R}\psi_R(t) + \frac{\gamma_R}{\alpha_R^2}\frac{d\psi_R(t)}{dt} - \cdots. \tag{62}$$

Discarding terms of order γ_R/α_R^n for $n \geq 3$ (γ_R is of the order of α_R^2 and α_R is very large), this equation (after rearranging the terms) is identified with

$$\dot{\psi}_R(t) = -2(\zeta_R/I)\psi_R(t) \tag{63}$$

to yield the second condition

$$\zeta_R/I = \tfrac{1}{2}\alpha_R\gamma_R/(\alpha_R^2 - \gamma_R). \tag{64}$$

Equation (63) is easily derived from the assumed Langevin equation for the rotational motion, once it is noted that in an equilibrium ensemble the average torque on a molecule vanishes.

The rotational friction coefficient was evaluated following the procedure introduced in the Rice–Kirkwood small-step diffusion theory[18]; its estimated value was found to represent about 25% to 30% of the central part of the coefficient (when the noncentral part of the intermolecular potential contributes for 10%–15% to the total potential). It is now easy to obtain numerical values for the roots s_+^R and s_-^R, and thereby for $\psi_R(t)$ [see Eq. (46)]. In Fig. 3 is displayed a typical autocorrelation as obtained from Eqs. (46), (61), and (64); the shape of the curve (for short times) as well as the order of magnitude of the relaxation time is comparable with those from the autocorrelation calculated by Steele,[19] though no actual comparison can be made between both approaches, since Steele's is for free rotation (or nearly free rotators).

VII. APPLICATION TO THE STUDY OF DIPOLAR RELAXATION

The line shape of rotational transitions in the infrared spectrum of a molecule is determined by the rate of randomization of the molecular dipole moment. Indeed, the line shape can be expressed directly in terms of the dipolar autocorrelation function,[4] so that Fourier transformation of experimental spectra provides a direct and easily applicable method of determining this function. One of the remarkable results of such an analysis is the discovery that, in the gas phase at low pressures, the autocorrelation function has a negative portion, whereas at high pressures the decay of the autocorrelation function is monotonic. It is the purpose of this section to account for the major features of the density dependence of the dipole correlation function.

Let **u** be a unit vector along the internuclear axis of a dipolar diatomic molecule. The normalized dipolar autocorrelation function is

$$\psi_D(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle, \tag{65}$$

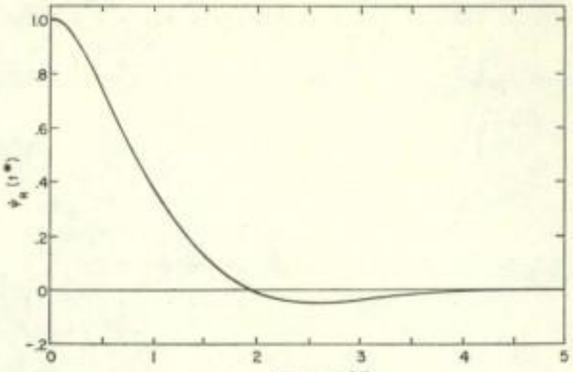

FIG. 3. The spin-relaxation autocorrelation function, $\psi_R(t^*)$, from Eqs. (46), (58), and (59).

which has the following properties in the limit as $t \to 0$:

$$(d\psi_D/dt)_{t=0} = 0, \tag{66}$$

$$(d^2\psi_D/dt^2)_{t=0} = -2kT/I. \tag{67}$$

Using the exponential memory function,[20]

$$K_D(t) = \gamma_D \exp(-\alpha_D t), \tag{68}$$

and Eq. (20), Eqs. (67) and (68) lead to

$$\gamma_D = 2kT/I. \tag{69}$$

To obtain the roots in the transform we also require

$$A_D = \int_0^\infty \psi_D(t)\,dt = \tilde{\psi}_D(0), \tag{70}$$

where, as before,

$$\tilde{\psi}_D(0) = [\tilde{K}_D(0)]^{-1}. \tag{71}$$

With some simple algebra we are now led to

$$\begin{aligned} \tilde{K}_D(0) &= \gamma_D/\alpha_D = 1/A_D, \\ \alpha_D &= \gamma_D A_D = 2A_D kT/I, \end{aligned} \tag{72}$$

and $\psi_D(t)$ assumes the form

$$\psi_D(t) = [1/(s_+^D - s_-^D)][s_+^D \exp(s_-^D t) - s_-^D \exp(s_+^D t)], \tag{73}$$

$$s_\pm^D = -(A_D kT/I)\{1 \mp [1 - (2I/A_D^2 kT)]\}. \tag{74}$$

The available experimental data for CO are displayed in Fig. 4. At present, they are insufficient to permit the exact determination of A_D. Nevertheless, it

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[18] S. A. Rice and J. G. Kirkwood, J. Chem. Phys. **31**, 901 (1959).

[19] W. A. Steele, J. Chem. Phys. **38**, 2411 (1963).

[20] The choice of memory function should be such that in the limit as $\alpha \to 0$, the dynamical behavior of the system becomes that of the free particle. In the case of translational motion, the simple exponential form for K has this property. However, in the case of the dipolar correlation function, in the zero interaction limit the autocorrelation function oscillates. Thus, a better choice for K would be the free-rotation dipolar correlation function multiplied by an exponential decay term. Since the analysis cannot be carried through exactly for this choice of K, we have considered the simpler case that K is an exponential. The reader should note, however, that because of this choice of K our treatment of dipolar correlation is less satisfactory than our treatment of translational motion, and we do not recover simply the free-rotation behavior as $\alpha \to 0$.

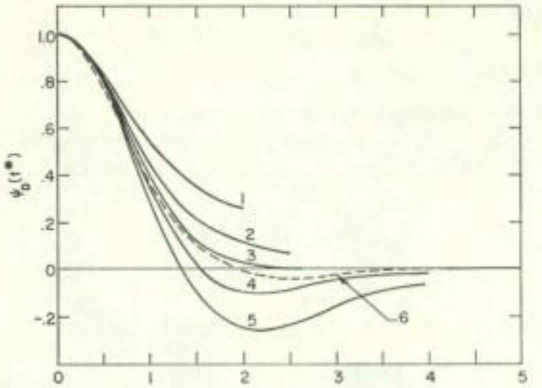

FIG. 4. The dipole correlation function, $\psi_D(t^*)$, from Gordon's calculation on carbon monoxide: pure liquid (1); pure gas just above the critical point at 1520 atm (2) and 270 atm (3), and with argon at room temperature at 850 atm (4) and 270 atm (5); (6) is a typical curve as obtained from Eq. (73).

is clear that Eqs. (73) and (74) reproduce the striking dependence of ψ_D on the pressure. For, when A_D is small, s_+^D and s_-^D are complex and $\psi_D(t)$ has positive and negative portions, whereas when A_D is large, s_+^D and s_-^D are real, and $\psi_D(t)$ decays monotonically.

A qualitative argument can be based on the relative insensitivity of the positions of the minima in $\psi_D(t)$ in Fig. 4. Provided that A_D^2 is small relative to $2I/kT$, Eqs. (73) and (74) reproduce this behavior. Physically, it can be argued that at sufficiently high pressures the dipole moment is randomized within one period of rotation; whereas, at low pressures the dipole moment is randomized after many rotational periods. Clearly, the autocorrelation function $\psi_D(t)$ will oscillate at low pressures, whereas, it remains positive at high pressure. A_D will therefore be larger at high pressure. This is in qualitative accord with observation.

We conclude that, although a quantitative test cannot presently be made, the exponential memory ansatz is consistent with the available dipolar autocorrelation functions.

VIII. DISCUSSION

In this paper we have demonstrated that it is possible to obtain autocorrelation functions for a variety of phenomena using a simple ansatz, the exponentially decaying memory function, within the framework of an exact non-Markoffian representation of the integrodifferential equation defining the autocorrelation function. Although the choice of an exponentially decaying memory function can be somewhat motivated by consideration of the effect of as a (nearly) Poisson process, or by consideration of the effect of interactions as a Gaussian Markov process for which the correlation function is an exponential decay, it must be recognized that the success of the simple two-parameter kernel $K(\alpha, \gamma; t)$ in reproducing the observed autocorrelation functions is possibly fortuitous. At present we can present no real justification for the choice of functional form of $K(\alpha, \gamma; t)$.

Putting aside the justification for the ansatz used, it is important to note that many subtle characteristics of the autocorrelation functions of dynamical variables are simultaneously consistent with one simple form for the memory function. This observation suggests that the form of the memory function is a more general characteristic of the dynamics of the system than are other representations of dynamical coherence. Indeed, it might be possible to reformulate the representation of linear transport coefficients to take advantage of this particular feature of the memory-function analysis. It is our opinion that such a reformulation would be fruitful in suggesting new approximation schemes which might be suitable for the description of dense, strongly interacting systems.

The general characteristics of the time dependence of the autocorrelation function can be elucidated by examining two limiting cases. Consider first the high-density limit. Since $\alpha\beta$ is proportional to the mean-square force acting on a molecule, which increases as the density increases, while β also increases as the density increases, $(4\beta/\alpha)$ increases as the density increases. Referring to Eq. (45), it is seen that the roots are complex when $(4\beta/\alpha)>1$, whereupon the autocorrelation function displays a negative region which is more pronounced the higher the density. In the low-density limit both β and α tend to zero in a fashion such that β/α tends to zero. Referring again to Eq. (45), it is seen that the time dependence of the autocorrelation function is now a simple exponential decay. Both of these limits are in agreement with the available data, as has been described in Secs. V, VI, and VII.

It is interesting to examine the momentum autocorrelation function in the high-density limit from still another point of view. If the negative region of the momentum autocorrelation function is interpreted as indicating that, on the average, a displacement of a molecule towards its near neighbors is followed by a displacement back towards the original position, the exponential memory ansatz can be tested for internal consistency with a simple model. Let the average distance a molecule with given initial velocity travels before its momentum is reversed by interaction with a near neighbor be $\langle\Delta\mathbf{R}_1\rangle^1$. Now, the average velocity of a molecule at time t, given that the initial velocity is $\mathbf{v}_1(0)$, is approximately $\mathbf{v}_1(0)\psi(t)$. The average displacement is then

$$\langle\Delta\mathbf{R}_1(t)\rangle^1=\int_0^t\langle\mathbf{v}_1(t')\rangle dt'=\int_0^t\mathbf{v}_1(0)\psi(t')dt'. \quad (75)$$

We seek the values of $\langle\Delta\mathbf{R}_1(t)\rangle^1$ corresponding to a turning point in the motion, i.e., when $\langle\mathbf{v}_1(t)\rangle=0$. Such a turning point occurs at the time t_0 defined by

$$\psi(t_0)=0, \quad (76)$$

or

$$\langle\Delta\mathbf{R}_1(t_0)\rangle^1=\int_0^{t_0}\mathbf{v}_1(0)\psi(t')dt'. \quad (77)$$

For the case that $\mathbf{v}_1(0)$ is equal to the root-mean-square velocity, corresponding to the most probable initial velocity, it is found that $\langle\Delta\mathbf{R}_1\rangle^{\frac{1}{2}}$ has the value 0.25 Å, corresponding to an average internuclear separation of 3.67 Å. Since the negative region of the autocorrelation function is interpreted as arising from the (near) reversal of momentum resulting from the first interaction experienced by a molecule on leaving the centrosymmetric position at the center of a shell of near neighbors, the average internuclear separation for interaction ought to be equal to the equilibrium average internuclear separation. From the computed radial distribution function of Rahman,[8] this latter distance is 3.67 Å, demonstrating both the internal consistency of this physical interpretation and the accuracy of the exponential memory ansatz with respect to reproduction of the first zero of $\psi(t)$.

Finally, we note that Mori[21] has presented a continued fraction representation of time correlation functions. Mori's formalism differs from, but is closely related to, the general analysis of Sec. III of this paper. Indeed, Mori finds that, if the continued fraction is truncated by assuming that the Laplace transform of the autocorrelation function of the nth-order random force is independent of the Laplace variable (see Mori's paper for the definitions of these terms), then the momentum autocorrelation function is identical with that induced here [see Appendix B; Eqs. (B14), (B15), and (B16)]. Also, the differential equation for the linear-momentum autocorrelation function, deduced with the use of the exponential memory ansatz, is the same as the differential equation for the momentum autocorrelation function deduced by Gray from a model described in the introduction.[5] The analysis proposed here is considerably more general than that of Gray, since the general integrodifferential equation for the autocorrelation function is exact, and therefore consistent with many possible kinetic equations. Nevertheless, the deduction of the same autocorrelation function from three very different points of view suggests that the features displayed are rather general characteristics of the liquid phase and not anomalies of the approximations used.

ACKNOWLEDGMENTS

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APPENDIX A: SOME PROPERTIES OF THE MEMORY FUNCTION

In the main text we have stated that $K(t)$ must be an even function of t and have zero derivative at $t=0$. This is easily demonstrated using the expanded form of the propagator, which converts Eq. (31) to

$$K(t)=\sum_{n=0}^{\infty}\frac{t^n}{n!}\langle(i\mathcal{L}^{(N)}\mathbf{U})\cdot[i(1-\mathcal{P})\mathcal{L}^{(N)}]^n(i\mathcal{L}^{(N)}\mathbf{U})\rangle. \tag{A1}$$

Consider the term arising from $n=1$. This is

$$\begin{aligned}\langle(i\mathcal{L}^{(N)}\mathbf{U})\cdot[i(1-\mathcal{P})\mathcal{L}^{(N)}](i\mathcal{L}^{(N)}\mathbf{U})\rangle&\\ =\langle i\mathcal{L}^{(N)}\mathbf{U})\cdot[i\mathcal{L}^{(N)}(i\mathcal{L}^{(N)}\mathbf{U})]\rangle&\\ -\langle(i\mathcal{L}^{(N)}\mathbf{U})\cdot[i\mathcal{P}\mathcal{L}^{(N)}(i\mathcal{L}^{(N)}\mathbf{U})]\rangle.&\end{aligned} \tag{A2}$$

But, by reversal of coordinates and momenta it is seen that

$$\begin{aligned}\langle(i\mathcal{L}^{(N)}\mathbf{U})\cdot[i\mathcal{L}^{(N)}(i\mathcal{L}^{(N)}\mathbf{U})]\rangle&=0,\\ \langle(i\mathcal{L}^{(N)}\mathbf{U})\cdot[i\mathcal{P}\mathcal{L}^{(N)}(i\mathcal{L}^{(N)}\mathbf{U})]\rangle&\\ =\langle(i\mathcal{L}^{(N)}\mathbf{U})\cdot\mathbf{U}\rangle\langle\mathbf{U}\cdot[i\mathcal{L}^{(N)}(i\mathcal{L}^{(N)}\mathbf{U})]\rangle&\\ =-\langle\dot{\mathbf{U}}\cdot\mathbf{U}\rangle\langle(i\mathcal{L}^{(N)}\mathbf{U})\cdot(i\mathcal{L}^{(N)}\mathbf{U})\rangle&=0,\end{aligned} \tag{A3}$$

because $\langle\mathbf{U}\cdot\mathbf{U}\rangle=0$. By iteration of these arguments it can be shown that all terms arising from odd values of n in Eq. (A1) vanish, and therefore that $K(t)$ is an even function of t with zero slope at the origin.

APPENDIX B: AN ALTERNATIVE DERIVATION OF EQ. (20)

Equation (20) plays such a fundamental role in our analysis and is so deeply connected with the nature of the autocorrelation function that it is worthwhile to derive it from linear regression theory. In the process of making this derivation, some further insight is obtained into the nature of the exponential memory.

Consider a system described by two sets of variables. The sets are defined as follows: $\boldsymbol{\alpha}$ variables are defined by the condition $\boldsymbol{\alpha}(\mathbf{p})=\boldsymbol{\alpha}(-\mathbf{p})$ (even parity in the momentum), while $\boldsymbol{\beta}$ variables satisfy the condition $-\boldsymbol{\beta}(\mathbf{p})=\boldsymbol{\beta}(-\mathbf{p})$ (odd parity in the momentum). In terms of the arguments used in Sec. IV, the molecular velocity is a $\boldsymbol{\beta}$ variable, and the force acting on a molecule is an $\boldsymbol{\alpha}$ variable. Let $\langle\cdots\rangle^{\alpha_0\beta_0}$ refer to an ensemble average conditional on the initial values $\boldsymbol{\alpha}_0$ and $\boldsymbol{\beta}_0$. Linear regression theory[6] then defines the time rate of change of the average values of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ variables to be

$$\begin{aligned}(\partial/\partial t)\langle\boldsymbol{\alpha}\rangle^{\alpha_0\beta_0}&=\mathsf{L}_{\alpha\alpha}\cdot\langle\mathbf{X}\rangle^{\alpha_0\beta_0}+\mathsf{L}_{\alpha\beta}\cdot\langle\mathbf{Y}\rangle^{\alpha_0\beta_0},\\ (\partial/\partial t)\langle\boldsymbol{\beta}\rangle^{\alpha_0\beta_0}&=\mathsf{L}_{\beta\alpha}\cdot\langle\mathbf{X}\rangle^{\alpha_0\beta_0}+\mathsf{L}_{\beta\beta}\cdot\langle\mathbf{Y}\rangle^{\alpha_0\beta_0},\end{aligned} \tag{B1}$$

where the force terms $\mathbf{X}$ and $\mathbf{Y}$ are defined by

$$\begin{aligned}\mathbf{X}&=\partial\Delta S/\partial\boldsymbol{\alpha},\\ \mathbf{Y}&=\partial\Delta S/\partial\boldsymbol{\beta},\end{aligned} \tag{B2}$$

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[21] H. Mori, Progr. Theoret. Phys. **34**, 399 (1965).

where

$$\Delta S = -\tfrac{1}{2}\mathsf{g}:\boldsymbol{\alpha\alpha} - \tfrac{1}{2}\mathsf{m}:\boldsymbol{\alpha\beta} - \tfrac{1}{2}\mathsf{n}:\boldsymbol{\beta\alpha} - \tfrac{1}{2}\mathsf{h}:\boldsymbol{\beta\beta}, \quad \text{(B3)}$$

and g, h, m, n are the usual matrices (dyadics) constructed from the derivatives of the entropy with respect to the variables $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$. Noting that g and h are even on inversion of the sign of $\boldsymbol{\beta}$, while m and n are odd on inversion of the sign of $\boldsymbol{\beta}$, the Onsager reciprocal relations are obtained. The coefficients L_{ij} take the form

$$\mathsf{L}_{\mu\nu} = -\frac{1}{k}\lim_{t\to 0}\frac{1}{t}\iint \Delta\boldsymbol{\mu}\boldsymbol{\mu}_0 f(\mu_0, \nu_0) P(\mu_0, \nu_0 \mid \mu, \nu; t) \times d\boldsymbol{\mu}\, d\boldsymbol{\nu}\, d\boldsymbol{\mu}_0\, d\boldsymbol{\nu}_0; \qquad \boldsymbol{\mu}, \boldsymbol{\nu} = \boldsymbol{\alpha}, \boldsymbol{\beta}, \quad \text{(B4)}$$

with $P(\mu_0, \nu_0 \mid \mu, \nu; t)$ the probability of finding the system with variables $\boldsymbol{\mu}$, $\boldsymbol{\nu}$ at time t, given that the values of these variables were $\boldsymbol{\mu}_0$, $\boldsymbol{\nu}_0$ at time zero, while $f(\boldsymbol{\mu}_0, \boldsymbol{\nu}_0)$ is the probability density of finding the variables to have the values $\boldsymbol{\mu}_0$, $\boldsymbol{\nu}_0$ at time zero.

To obtain the form of the equation for the velocity autocorrelation function we take

$$\boldsymbol{\alpha} = \mathbf{F}_1/m,$$

$$\boldsymbol{\beta} = \mathbf{v}. \quad \text{(B5)}$$

In the limit as $t\to 0$, $\Delta\boldsymbol{\beta} = \boldsymbol{\alpha}_0 t$, so that

$$\lim_{t\to 0}\langle\Delta\boldsymbol{\beta}\rangle^{\alpha_0\beta_0} = \boldsymbol{\alpha}_0 t = \int \Delta\boldsymbol{\beta} P(\boldsymbol{\alpha}_0, \boldsymbol{\beta}_0 \mid \boldsymbol{\alpha}, \boldsymbol{\beta}; t)\, d\boldsymbol{\alpha}\, d\boldsymbol{\beta}, \quad \text{(B6)}$$

which leads to

$$\mathsf{L}_{\beta\beta} = -\frac{1}{k}\int \boldsymbol{\alpha}_0\boldsymbol{\beta}_0 f(\boldsymbol{\alpha}_0, \boldsymbol{\beta}_0)\, d\boldsymbol{\alpha}_0\, d\boldsymbol{\beta}_0 = 0,$$

$$\mathsf{L}_{\beta\alpha} = -\frac{1}{k}\int \boldsymbol{\alpha}_0\boldsymbol{\alpha}_0 f(\boldsymbol{\alpha}_0, \boldsymbol{\beta}_0)\, d\boldsymbol{\alpha}_0\, d\boldsymbol{\beta}_0$$

$$= -\frac{1}{k}\langle\boldsymbol{\alpha}_0\boldsymbol{\alpha}_0\rangle = -\mathsf{g}^{-1}, \quad \text{(B7)}$$

after application of parity arguments. The reciprocal relation $\mathsf{L}_{\alpha\beta} = -\mathsf{L}_{\beta\alpha}{}^{\mathrm{tr}}$ allows us to write

$$\mathsf{L}_{\alpha\beta} = (\mathsf{g}^{\mathrm{tr}})^{-1} = \mathsf{g}^{-1}, \quad \text{(B8)}$$

where the superscript tr indicates the transpose of the dyadic, and the second member of Eq. (B8) follows from the fact that g is a symmetric dyadic. Since $\mathsf{L}_{\alpha\alpha} \neq 0$, the use of $\langle\mathbf{X}\rangle^{\alpha_0\beta_0} = -\mathsf{g}\cdot\langle\boldsymbol{\alpha}\rangle^{\alpha_0\beta_0}$ and $\langle\mathbf{Y}\rangle^{\alpha_0\beta_0} = -\mathsf{h}\cdot\langle\boldsymbol{\beta}\rangle^{\alpha_0\beta_0}$ leads to

$$(\partial/\partial t)\langle\boldsymbol{\alpha}\rangle^{\alpha_0\beta_0} = -\mathsf{L}_{\alpha\alpha}\cdot\mathsf{g}\cdot\langle\boldsymbol{\alpha}\rangle^{\alpha_0\beta_0} - \mathsf{g}^{-1}\cdot\mathsf{h}\cdot\langle\boldsymbol{\beta}\rangle^{\alpha_0\beta_0},$$

$$(\partial/\partial t)\langle\boldsymbol{\beta}\rangle^{\alpha_0\beta_0} = \langle\boldsymbol{\alpha}\rangle^{\alpha_0\beta_0}, \quad \text{(B9)}$$

from which, by combination of the two equations (B9), it is found that

$$(\partial^2/\partial t^2)\langle\boldsymbol{\beta}\rangle^{\alpha_0\beta_0} = -\mathsf{L}_{\alpha\alpha}\cdot\mathsf{g}\cdot(\partial/\partial t)\langle\boldsymbol{\beta}\rangle^{\alpha_0\beta_0} - \mathsf{g}^{-1}\cdot\mathsf{h}\cdot\langle\boldsymbol{\beta}\rangle^{\alpha_0\beta_0}. \quad \text{(B10)}$$

Multiplication of Eq. (B10) by $\boldsymbol{\beta}_0$ and integration over the initial distribution of values of $\boldsymbol{\alpha}_0$ and $\boldsymbol{\beta}_0$ leads to an equation for the autocorrelation function $\psi_\beta(t) = \langle\boldsymbol{\beta}(0)\cdot\boldsymbol{\beta}(t)\rangle/\langle\beta(0)^2\rangle$. This equation is

$$(\partial^2/\partial t^2)\psi_\beta(t) = -\mathsf{L}_{\alpha\alpha}:\mathsf{g}[\partial\psi_\beta(t)/\partial t] - \mathsf{g}^{-1}:\mathsf{h}\psi_\beta(t). \quad \text{(B11)}$$

Equation (B11) is obtained from Eq. (20) when the memory function is chosen to be an exponential decay. To show this, let $\lambda = \mathsf{L}_{\alpha\alpha}:\mathsf{g}$, $\gamma = \mathsf{g}^{-1}:\mathsf{h}$. Then, using the normalization condition $\psi_\beta(0) = 1$, and taking the Laplace transform of (B11), it is found that

$$s^2\tilde{\psi}_\beta(s) - s + \lambda[s\tilde{\psi}_\beta(s) - 1] + \gamma\tilde{\psi}_\beta(s) = 0, \quad \text{(B12)}$$

the inverse transform of which, using the convolution theorem, is

$$\frac{\partial\psi_\beta(t)}{\partial t} = -\gamma\int_0^t d\tau \exp(-\lambda\tau)\psi_\beta(t-\tau). \quad \text{(B13)}$$

Thus, the linear-regression analysis implies Eq. (20) with the special kernel $K(\tau) = \gamma\exp(-\lambda\tau)$, and with γ and λ (before called α) just the parameters described in Sec. IV.

APPENDIX C: CONNECTION WITH THE KUBO, YOKOTO, NAKAJIMA (KYN) DERIVATION[22]

It is interesting to notice the close connection between the analysis presented in Sec. III and Appendix B and the rigorous version of the KYN derivation by Zwanzig.[23] The set of equations (41) and (44) of Ref. 23 is equivalent to the combination of Eqs. (16) and (39) of this work, once it is recognized that the transport coefficients can be expressed in the form

$$\mathsf{L}:\mathsf{h} = \int_0^\infty dt e^{-st}\langle\dot{\mathbf{U}}(0)\dot{\mathbf{U}}(t)\rangle, \quad \text{(C1)}$$

with

$$\mathbf{U} = \boldsymbol{\beta}(\langle\beta_0^2\rangle)^{-\frac{1}{2}},$$

$$\dot{\mathbf{U}} = \boldsymbol{\alpha}(\langle\beta_0^2\rangle)^{-\frac{1}{2}}, \quad \text{(C2)}$$

and

$$k\mathsf{h}^{-1} = \langle\boldsymbol{\beta}_0\boldsymbol{\beta}_0\rangle \quad \text{(C3)}$$

[with the variables, $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, as defined in Appendix B, (B5), the transport coefficient would be ζ/m, i.e., the diffusion coefficient in momentum space]. In our notation, Zwanzig's result [Eq. (45), Ref. 23] reads

$$\mathsf{L}:\mathsf{h} = \tilde{K}(s) - \{[\tilde{K}(s)]^2/[s+\tilde{K}(s)]\}, \quad \text{(C4)}$$

which is an exact equation, within the limits of the fluctuations regression assumption, as applied to the non-Markoffian transport equation. It is then a matter of simple algebra to show that Eq. (C4) is equivalent to Eq. (21) of Sec. III.

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