

Theory of Self-Diffusion in Classical Fluids: The Van Hove Self-Correlation Function $G_s(\mathbf{r}, t)$

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Projection operator techniques have been applied to study the diffusion of a test particle in a classical many-particle system such as a liquid or a plasma. Particular attention has been directed towards the calculation of the Van Hove self-correlation function $G_s(\mathbf{r}, t)$. This calculation proceeds through the development of exact descriptions of $G_s(\mathbf{r}, t)$, both in configuration space (analogous to generalized hydrodynamic equations) and phase space (kinetic equations) which are then suitably approximated and solved using either perturbation or modeling methods. These results compare quite favorably with molecular dynamics computer experiments.

I. INTRODUCTION

Perhaps one of the most intensively studied phenomena in nonequilibrium statistical mechanics has been the motion of a test particle through a many-body system. When the mass of the test particle is much larger than the masses of the surrounding particles, then this problem can be identified as just that of Brownian motion. Of comparable interest, however, is the case in which the test particle is identical to the particles in the surrounding system. This latter problem is of particular concern to the theory of dense fluidlike systems such as liquids and plasmas.

Of principal concern in both of these problems is the calculation of time correlation functions involving the dynamical variables characterizing the test particle, since these quantities can frequently be related to direct experimental investigations. Two such correlation functions are particularly significant in this regard. The momentum auto-correlation function $\langle \mathbf{p}_1(0) \cdot \mathbf{p}_1(t) \rangle$ plays the fundamental role in the development of the transport equation¹ characterizing the test particle motion (e.g., the Langevin or diffusion equations) and can be directly related to the corresponding transport parameters (e.g., the friction constant or the coefficient of self-diffusion). Of comparable significance is the Van Hove self-correlation function $G_s(\mathbf{r}, t)$ which characterizes correlations between fluctuations in the test particle density and is directly related to the incoherent scattering cross section for thermal neutrons from the system.²

The calculation of both of these quantities has

received considerable attention in the past.^{3,4} In recent years an effort has been made to calculate such correlation functions directly by utilizing nonequilibrium statistical mechanics. By and large, all such approaches can be classified into one of two general schemes: either a perturbation solution of the Liouville equation, or a semiphenomenological modeling approach. In the former approach, one utilizes the powerful techniques of modern perturbation theory⁵ to directly attack the many-body problem involved in self-diffusion.⁶⁻⁸ The latter approach generally utilizes one of the recent formalisms of nonequilibrium statistical mechanics, e.g., the Kubo⁹-Kadanoff-Martin¹⁰ formalism or the Zwanzig¹¹-Mori¹² projection operator formalism, to recast the Liouville equation into a form which depends on a quantity which can then be "guessed" or modeled. These approaches¹³⁻¹⁶ have been successful in describing self-motions in liquids, particularly, when compared with molecular dynamics computer experiments.¹⁷

This work will attempt to develop some new ideas concerning the topic of self-diffusion in liquids by employing the projection operator methods of Zwanzig and Mori. While it is readily admitted that the application of these methods to the problem of test particle motions in many-body systems is not new, it is felt that the full potential of these methods has yet to be exploited. In particular, the connection between a hydrodynamic-like description of the test particle motion (involving only dynamic variables defined in configuration space) and a kinetic equation approach will be developed and

applied to the calculation of $G_s(\mathbf{r}, t)$ [or, more particularly, its Fourier transform $S_s(\mathbf{k}, \omega)$].

First, however, let us review the projection operator formalism developed by Zwanzig and Mori for the study of irreversible processes. As one of several specific illustrations of projection methods, Zwanzig¹¹ derived an exact integrodifferential equation for the autocorrelation function of a dynamical variable. This approach was subsequently generalized and extended by Mori,¹² who utilized projection operators similar to those of Zwanzig to derive an exact "generalized Langevin equation" describing the time evolution of an arbitrary vector $\mathbf{a}(t)$ whose components $a_i(t)$ are dynamical variables of the phase $(\mathbf{x}^1, \dots, \mathbf{x}^N, \mathbf{p}^1, \dots, \mathbf{p}^N)$ of a many-body system:

$$\dot{\mathbf{a}} - i\boldsymbol{\Omega} \cdot \mathbf{a}(t) + \int_0^t d\tau \boldsymbol{\varphi}(\tau) \cdot \mathbf{a}(t - \tau) = \mathbf{f}(t). \quad (1)$$

Here, the state vector, $\mathbf{a}(t)$, is defined such that it has no time invariant part, i.e.,

$$\mathbf{a}(t) \equiv \mathbf{A}(t) - \langle \mathbf{A}(t) \rangle, \quad (2)$$

where $\langle \dots \rangle$ denotes an average over the equilibrium canonical ensemble, $\rho_0 = \exp(-\beta H)/Z$. Notice that Eq. (1) can be regarded as a generalized form of the Langevin equation familiar from the stochastic theory of Brownian motion.³ However, unlike the Langevin equation, Eq. (1) is an exact equation for $\mathbf{a}(t)$, and hence is equivalent to the equations of motion for the many-body system.

In the generalized Langevin equation (1), the "frequency matrix" $\boldsymbol{\Omega}$ is defined by

$$i\boldsymbol{\Omega} \equiv \langle \dot{\mathbf{a}}\mathbf{a}^* \rangle \cdot \langle \mathbf{a}\mathbf{a}^* \rangle^{-1}, \quad (3)$$

where \mathbf{a} denotes $\mathbf{a}(0)$; the "damping matrix" $\boldsymbol{\varphi}$ is given by

$$\boldsymbol{\varphi}(\tau) \equiv \langle \mathbf{f}(\tau)\mathbf{f}^*(0) \rangle \cdot \langle \mathbf{a}\mathbf{a}^* \rangle^{-1}; \quad (4)$$

and the "random force" $\mathbf{f}(\tau)$ is given by

$$\mathbf{f}(\tau) \equiv \exp[i\tau(1 - P)L]i(1 - P)L\mathbf{a}. \quad (5)$$

Here, \mathbf{a}^* is the row vector adjoint to \mathbf{a} , P is a projection operator defined by its action on an arbitrary dynamical variable vector \mathbf{G} as

$$P\mathbf{G} \equiv \langle \mathbf{G}\mathbf{a}^* \rangle \cdot \langle \mathbf{a}\mathbf{a}^* \rangle^{-1} \cdot \mathbf{a}, \quad (6)$$

and L is the Liouville operator, $L = i\{H, \cdot\}$. The matrix $\langle \mathbf{a}\mathbf{a}^* \rangle^{-1}$ is the inverse of the static correlation matrix, $\langle \mathbf{a}\mathbf{a}^* \rangle \equiv [\langle a_i a_j^* \rangle]$.

The generalized Langevin equation (1) can be used either to study correlations among the variables in the set \mathbf{a} , or to obtain equations of motion

for the ensemble averaged components of \mathbf{a} . In the first instance, one proceeds by noting that¹²

$$\langle \mathbf{f}(t)\mathbf{a}^* \rangle = 0, \quad t \geq 0. \quad (7)$$

Hence by multiplying (1) by $\mathbf{a}^* \cdot \langle \mathbf{a}\mathbf{a}^* \rangle^{-1}$ from the right, and averaging, one can derive an equation for the correlation matrix

$$\mathbf{R}(t) \equiv \langle \mathbf{a}(t)\mathbf{a}^* \rangle \cdot \langle \mathbf{a}\mathbf{a}^* \rangle^{-1} \quad (8)$$

which takes the form

$$\dot{\mathbf{R}} - i\boldsymbol{\Omega} \cdot \mathbf{R}(t) + \int_0^t d\tau \boldsymbol{\varphi}(\tau) \cdot \mathbf{R}(t - \tau) = 0. \quad (9)$$

If one wishes, instead, to obtain an equation of motion for the ensemble average of \mathbf{a} , then Eq. (1) can be averaged over a constrained equilibrium ensemble¹²

$$\rho(0) \equiv \exp(-\beta H - \mathbf{a}^* \cdot \mathbf{b})/Z_0 \quad (10)$$

to find an equation for $\overline{\mathbf{a}(t)} \equiv \langle \mathbf{a}(t) \rangle_{\rho(0)}$:

$$\dot{\overline{\mathbf{a}}} - i\boldsymbol{\Omega} \cdot \overline{\mathbf{a}(t)} + \int_0^t d\tau \boldsymbol{\varphi}(\tau) \cdot \overline{\mathbf{a}(t - \tau)} = \overline{\mathbf{f}(t)}. \quad (11)$$

In the linear approximation of small departures from equilibrium, $\overline{\mathbf{f}(t)} = 0$; but in the more general case, $\overline{\mathbf{f}(t)}$ will introduce nonlinear terms in \mathbf{a} into the equation.

Since Eq. (9) and (11) are still exact, and hence only formal identities with the equations of motion, one must eventually resort to approximation in order to obtain useful results. The frequency matrix $\boldsymbol{\Omega}$ can usually be calculated explicitly in terms of static quantities. However, the damping matrix $\boldsymbol{\varphi}$ requires the study of the modified propagator $\exp[i\tau(1 - P)L]$ which, in turn, would involve solving the many-body problem directly. The attractive feature of equations such as (9) which are generated by projection operator techniques is that the "damping" or "memory" terms are quite susceptible to approximation or modeling. That is, the generalized Langevin equation is of value primarily because it re-expresses the quantities of interest (e.g., time correlation functions) in forms involving damping terms which can then be easily approximated.

In Mori's formalism¹² the choice of the set of dynamical variables \mathbf{a} was essentially arbitrary. Different choices of \mathbf{a} will lead to different, but exact, descriptions of the system under consideration. However, a given approximation of the damping term will yield results which may vary considerably, depending upon the choice one makes for \mathbf{a} . Usually by increasing the number of components

in the set \mathbf{a} , one can improve the description of the system within the framework of a given approximation.

In the past the generalized Langevin equation has been applied to study the momentum auto-correlation function^{7,8,13} by choosing $\mathbf{a} = \mathbf{p}_1$, and obtaining the equation

$$\begin{aligned} & \frac{d}{dt} \langle \mathbf{p}_1(0) \cdot \mathbf{p}_1(t) \rangle \\ & - \int_0^t d\tau \frac{\langle \mathbf{F}_1(0) \cdot \exp [i\tau(1-P)L] \mathbf{F}_1(0) \rangle}{\langle \mathbf{p}_1(0) \cdot \mathbf{p}_1(0) \rangle} \\ & \cdot \langle \mathbf{p}_1(0) \cdot \mathbf{p}_1(t-\tau) \rangle = 0 \end{aligned} \quad (12)$$

and then either modeling the "damping kernel" $\varphi(\tau)$ or investigating its properties using perturbation methods.

We shall turn our attention instead to the calculation of the Van Hove self-correlation function

$$G_s(\mathbf{r}, t) \equiv \frac{1}{N} \sum_{\alpha=1}^N \int d^3r' \langle \delta[\mathbf{r} + \mathbf{x}^\alpha(0) - \mathbf{r}'] \cdot \delta[\mathbf{r}' - \mathbf{x}^\alpha(t)] \rangle, \quad (13)$$

or, if we Fourier transform in configuration space,

$$G_s(k, t) = \frac{1}{N} \sum_{\alpha=1}^N \langle \exp(-i\mathbf{k} \cdot \mathbf{x}^\alpha) \exp[i\mathbf{k} \cdot \mathbf{x}^\alpha(t)] \rangle. \quad (14)$$

In analogy with Eq. (12), we might choose $\mathbf{a} = \exp(i\mathbf{k} \cdot \mathbf{x}^\alpha)$. Such a "one-component" description turns out to be inadequate within the context of the particular approximations we will utilize in computing the damping term $\varphi(\tau)$. Hence, an alternative choice of \mathbf{a} is necessitated.

II. THE CONFIGURATION SPACE OR "HYDRODYNAMIC" DESCRIPTION

Using symmetry, we can rewrite (14) as

$$G_s(k, t) = \langle \exp[i\mathbf{k} \cdot \mathbf{x}^\alpha(t)] \exp(-i\mathbf{k} \cdot \mathbf{x}^\alpha) \rangle. \quad (15)$$

Hence, it is obvious that one of our set of dynamical variables \mathbf{a} will be

$$\rho \equiv \exp(i\mathbf{k} \cdot \mathbf{x}^\alpha). \quad (16)$$

Additional candidates would be

$$J \equiv \dot{\rho} = (i\mathbf{k} \cdot \mathbf{p}^\alpha/m) \exp(i\mathbf{k} \cdot \mathbf{x}^\alpha), \quad (17)$$

$$\begin{aligned} \pi \equiv \dot{J} = & [(i\mathbf{k} \cdot \mathbf{F}^\alpha/m) \\ & + (i\mathbf{k} \cdot \mathbf{p}^\alpha/m)^2] \exp(i\mathbf{k} \cdot \mathbf{x}^\alpha). \end{aligned} \quad (18)$$

However, rather than choosing (ρ, J, π) as the appropriate set of dynamical variables, we shall instead define a linear combination of ρ and π as

$$\sigma \equiv \pi - (\langle \pi \rho^* \rangle / \langle \rho \rho^* \rangle) \rho. \quad (19)$$

The vector \mathbf{a} in Mori's formalism will then be taken to be

$$\mathbf{a} \equiv \text{col} [\rho_k, J_k, \sigma_k]. \quad (20)$$

[We will accept it as understood that the invariant parts of these variables have been subtracted out. That is, $\rho_k, J_k,$ and π_k represent fluctuations, e.g., $\rho_k = \rho - \langle \rho \rangle$. For $k \neq 0$, $\rho_k = \rho$, etc.] Notice that the components of this vector are "orthogonal" in the sense that

$$\langle \rho_k J_k^* \rangle = \langle \rho_k \sigma_k^* \rangle = \langle J_k \sigma_k^* \rangle = 0. \quad (21)$$

Using these relations and the symmetry properties of the set \mathbf{a} , we can easily calculate the frequency matrix

$$\begin{aligned} i\Omega &= \langle \dot{\mathbf{a}} \mathbf{a}^* \rangle \cdot \langle \mathbf{a} \mathbf{a}^* \rangle^{-1} \\ &= \begin{bmatrix} 0 & 1 & 0 \\ -\frac{\langle J_k J_k^* \rangle}{\langle \rho_k \rho_k^* \rangle} & 0 & 1 \\ 0 & -\frac{\langle \sigma_k \sigma_k^* \rangle}{\langle J_k J_k^* \rangle} & 0 \end{bmatrix}, \end{aligned} \quad (22)$$

where the static correlations can be calculated as

$$\begin{aligned} \langle \rho_k \rho_k^* \rangle &= 1, \\ \langle J_k J_k^* \rangle &= k^2/m\beta, \\ \langle \sigma_k \sigma_k^* \rangle &= \frac{k^2}{m\beta} \left[\frac{\langle \nabla^2 V \rangle}{3m} + 2 \frac{k^2}{m\beta} \right], \end{aligned} \quad (23)$$

where

$$\frac{1}{3} \langle \nabla^2 V \rangle \equiv n \int d^3R \frac{\partial^2 V}{\partial x_i^2} g(R). \quad (24)$$

In a similar fashion, one can calculate the damping matrix $\varphi(\tau)$ to be

$$\varphi(\tau) = \langle \mathbf{f}(\tau) \mathbf{f}^* \rangle \cdot \langle \mathbf{a} \mathbf{a}^* \rangle^{-1} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \varphi_k(\tau) \end{bmatrix}, \quad (25)$$

where

$$\begin{aligned} \varphi_k(\tau) &= \langle (1-P) \dot{\sigma}_k^* \exp [i\tau(1-P)L] \\ & \cdot (1-P) \dot{\sigma}_k \rangle / \langle \sigma_k \sigma_k^* \rangle. \end{aligned} \quad (26)$$

Hence, the generalized Langevin equation (1) becomes the set of equations

$$\begin{aligned} \dot{\rho}_k(t) &= J_k(t), \\ \dot{J}_k(t) + (k^2/m\beta) \rho_k(t) &= \sigma_k(t), \end{aligned} \quad (27)$$

$$\begin{aligned} \dot{\sigma}_k(t) + \left[\frac{\langle \nabla^2 V \rangle}{3m} + 2 \frac{k^2}{m\beta} \right] J_k(t) \\ + \int_0^t d\tau \varphi_k(\tau) \sigma_k(t-\tau) = f(t). \end{aligned}$$

We can now take the correlation of this set with ρ_k^* to obtain an expression for

$$G_s(k, t) = \langle \rho_k(t) \rho_k^* \rangle. \quad (28)$$

Actually, we are more directly interested in the Fourier transform of $G_s(k, t)$ in time, $S_s(k, \omega)$, defined in terms of the Laplace transform of $G_s(k, t)$ by

$$S_s(k, \omega) \equiv \frac{1}{\pi} \operatorname{Re} \left[\lim_{\epsilon \rightarrow 0^+} \int_0^\infty dt \exp(-i\omega t) \exp(-\epsilon t) G_s(k, t) \right]. \quad (29)$$

Hence, if we multiply the set (27) by ρ_k^* , then ensemble average, and take the Laplace transform of the resultant set in time, we can solve in a straightforward manner for

$$S_s(k, \omega) = \frac{1}{\pi} \frac{k^2}{m\beta\omega^2} \operatorname{Re} \left\{ \left[i \left(\omega - \frac{k^2}{m\beta\omega} \right) + \frac{\langle \nabla^2 V \rangle / 3m}{i\omega + \bar{\varphi}_k(i\omega)} + \frac{2k^2/m\beta}{i\omega + \bar{\varphi}_k(i\omega)} \right]^{-1} \right\}, \quad (30)$$

where $\bar{\varphi}_k(s)$ is the Laplace transform of the damping term $\varphi_k(\tau)$.

It should be noted that (30) is still an *exact* expression for $S_s(k, \omega)$. All of the complexity of the many-body problem is merely buried in the calculation of $\bar{\varphi}_k(s)$. Hence, we must provide some prescription by which we can approximately calculate $\bar{\varphi}_k(s)$. Of course, one could attempt a direct perturbation calculation of the damping term. This approach will be deferred until the next section, however. We will instead introduce a "Markovian" description¹¹ of the system by replacing $\bar{\varphi}_k(i\omega)$ by its zero frequency limit

$$\alpha_H(k) \equiv \lim_{\omega \rightarrow 0} \bar{\varphi}_k(i\omega). \quad (31)$$

But even the direct calculation of this zero frequency form is a formidable problem. We will bypass this problem by attempting to guess the relevant behavior of $\alpha_H(k)$ as a function of k .

To this end, return to the exact expression for $S_s(k, \omega)$ and evaluate it for $\omega = 0$:

$$S_s(k, 0) = \frac{m\beta}{\pi k^2 \alpha_H(k)} \left[\frac{\langle \nabla^2 V \rangle}{3m} + 2 \frac{k^2}{m\beta} \right]. \quad (32)$$

[Again, it must be stressed that this is an exact relation. Our principal approximation is made only when we neglect the frequency dependence of $\bar{\varphi}_k(i\omega)$ in the calculation of $S_s(k, \omega)$.] We will now utilize our knowledge of $S_s(k, 0)$ to infer the form of $\alpha_H(k)$. In particular, we know that as $k \rightarrow 0$, $S_s(k, 0)$ reduces to the usual diffusion result

$$\lim_{k \rightarrow 0} [\pi k^2 S_s(k, 0)] = D_s^{-1}, \quad (33)$$

where D_s is the coefficient of self-diffusion. Hence, $\alpha_H(k)$ must behave for small k in such a manner that

$$\alpha_H(k) \sim \frac{1}{3} \beta \langle \nabla^2 V \rangle D_s \quad \text{as } k \rightarrow 0. \quad (34)$$

For large k , $S_s(k, 0)$ must approach the ideal gas behavior

$$S_s(k, 0) \sim (m\beta/2\pi k^2)^{1/2} \quad (35)$$

which, in turn, implies

$$\alpha_H(k) \sim (8/\pi m\beta)^{1/2} k \quad \text{as } k \rightarrow \infty. \quad (36)$$

Furthermore, $\alpha_H(k)$ must be an even function of k (since we have a homogeneous system in which quantities can only depend upon $|\mathbf{k}|$). We shall adopt the simplest functional form of $\alpha_H(k)$ consistent with these requirements:

$$\alpha_H(k) = [(D_s \beta \langle \nabla^2 V \rangle / 3)^2 + (8k^2 / \pi m\beta)]^{1/2}. \quad (37)$$

Recall the approximations we have introduced into the calculation of $S_s(k, \omega)$:

(i) A Markovian approximation of the damping term $\varphi(\tau)$ in the three-component $\mathbf{a} = (\rho_k, \mathbf{J}_k, \sigma_k)$ description.

(ii) A modeled description of the intermediate k behavior of $\alpha_H(k)$. Note further that there are no "free" or adjustable parameters in this model.

We have employed this description [i.e., Eqs. (30), (31), and (37)] to calculate $S_s(k, \omega)$ for liquid argon at $T = 85.5^\circ\text{K}$, $mn = 1.407 \text{ g/cm}^3$, $D_s = 1.88 \times 10^{-5} \text{ cm}^2/\text{sec}$, and $\langle \nabla^2 V \rangle / 3m = 45 \times 10^{24} \text{ sec}^{-2}$, and compared the results of this calculation with the molecular dynamics calculation of Nijboer and Rahman¹⁷ in Figs. 1, 2, and 3. It is evident that the

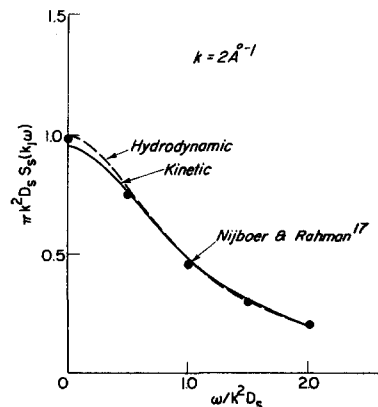


FIG. 1. $\pi D_s k^2 S_s(k, \omega)$ vs $\omega/k^2 D_s$ for $k = 2.0 \text{ \AA}^{-1}$. The dashed curve represents the three-component hydrodynamic description, the solid curve being the modeled kinetic equation results, while the dots represent the molecular dynamics calculations of Nijboer and Rahman.¹⁷

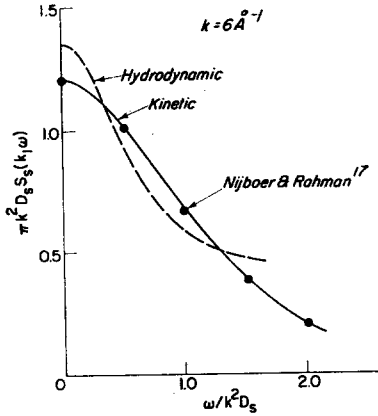


FIG. 2. $\pi D_s k^2 S_s(k, \omega)$ vs $\omega/k^2 D_s$ for $k = 6.0 \text{ \AA}^{-1}$.

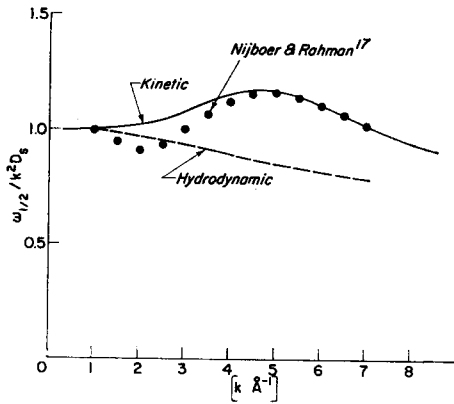


FIG. 3. The half-width at half-maximum, $\omega_{1/2}/k^2 D_s$ vs k . Again the dashed curve represents the hydrodynamic description; the solid curve, the kinetic description; and the dots, the molecular dynamics results.

three-component description (ρ_k, J_k, σ_k) is certainly adequate to yield agreement with the molecular dynamics calculations, and hence will probably suffice for the calculation of incoherent neutron scattering cross sections. More refined configuration space descriptions can be easily achieved by extending the set α .

III. THE PHASE SPACE OR "KINETIC EQUATION" DESCRIPTION

An alternative approach to the calculation of $G_s(\mathbf{r}, t)$ is to develop a kinetic equation for the correlation function

$$\mathcal{G}_s(k, \mathbf{p}, \mathbf{p}', t) \equiv \frac{1}{N} \sum_{\alpha=1}^N \langle \exp[i\mathbf{k} \cdot \mathbf{x}^\alpha(t)] \delta[\mathbf{p} - \mathbf{p}^\alpha(t)] \cdot \exp(-i\mathbf{k} \cdot \mathbf{x}^\alpha) \delta[\mathbf{p}' - \mathbf{p}^\alpha] \rangle \quad (38)$$

and then to note

$$G_s(k, t) = \int d^3 p \int d^3 p' \mathcal{G}_s(k, \mathbf{p}, \mathbf{p}', t). \quad (39)$$

Such a kinetic approach has been pioneered in the work of Nelkin *et al.*^{18,19} in which an approximate kinetic equation for $\mathcal{G}_s(k, \mathbf{p}, \mathbf{p}', t)$ was proposed and solved to provide information about $G_s(\mathbf{r}, t)$. More recently, several workers²⁰⁻²² have developed exact (but formal) kinetic equations for phase space correlation functions such as (38) which could then be used to generate approximate descriptions more amenable to investigation. In this section, we will employ projection operators to achieve such a phase space description.

It is straightforward to apply the Mori formalism to the development of kinetic equations²⁰ by choosing \mathbf{a} to be the "vector" whose "components" $a_i \rightarrow a(\mathbf{p})$ are indexed by a continuous parameter \mathbf{p} and defined by

$$a(\mathbf{p}) \equiv \exp(i\mathbf{k} \cdot \mathbf{x}^\alpha) \delta(\mathbf{p} - \mathbf{p}^\alpha) - M(\mathbf{p}) \delta(\mathbf{k}). \quad (40)$$

If we note that

$$\mathcal{G}_s(k, \mathbf{p}, \mathbf{p}', t) = \langle a(\mathbf{p}, t) a^*(\mathbf{p}') \rangle + M(\mathbf{p}) M(\mathbf{p}') \delta(\mathbf{k}), \quad (41)$$

then it is apparent that our objective is to develop a kinetic equation for the correlation function

$$\Gamma(k, \mathbf{p}, \mathbf{p}', t) = \langle a(\mathbf{p}, t) a^*(\mathbf{p}') \rangle. \quad (42)$$

The extension of Mori's generalized Langevin equation (1) to vectors with continuous parameter dependence is

$$\begin{aligned} \frac{\partial a}{\partial t} - i \int d^3 p' \Omega(\mathbf{p}', \mathbf{p}) a(\mathbf{p}', t) \\ + \int_0^t d\tau \int d^3 p' \varphi(\mathbf{p}, \mathbf{p}', \tau) a(\mathbf{p}', t - \tau) = f(\mathbf{p}, t). \end{aligned} \quad (43)$$

The appropriate projection operator becomes

$$PG(\mathbf{p}) \equiv \int d^3 p' \int d^3 p'' \langle G(\mathbf{p}) a^*(\mathbf{p}') \rangle \phi^{-1}(\mathbf{p}', \mathbf{p}'') a(\mathbf{p}''), \quad (44)$$

where $\phi^{-1}(\mathbf{p}', \mathbf{p}'')$ is the inverse of the static correlation function defined by

$$\begin{aligned} \phi(\mathbf{p}, \mathbf{p}') \equiv \langle a(\mathbf{p}) a^*(\mathbf{p}') \rangle = M(\mathbf{p}) \delta(\mathbf{p} - \mathbf{p}') \\ - M(\mathbf{p}) M(\mathbf{p}') \delta(\mathbf{k}). \end{aligned} \quad (45)$$

By its definition, $\phi^{-1}(\mathbf{p}', \mathbf{p}'')$ satisfies

$$\int d^3 p' \phi(\mathbf{p}, \mathbf{p}') \phi^{-1}(\mathbf{p}', \mathbf{p}'') = \delta(\mathbf{p} - \mathbf{p}''). \quad (46)$$

But substituting the explicit form (46) into (45), we arrive at an inhomogeneous integral equation for $\phi^{-1}(\mathbf{p}, \mathbf{p}')$

$$M(\mathbf{p})\phi^{-1}(\mathbf{p}, \mathbf{p}'') - \delta(\mathbf{k})M(\mathbf{p}) \cdot \int d^3p' M(\mathbf{p}')\phi^{-1}(\mathbf{p}', \mathbf{p}'') = \delta(\mathbf{p} - \mathbf{p}'') \quad (47)$$

which yields, as its solution,

$$\phi^{-1}(\mathbf{p}, \mathbf{p}'') = [M(\mathbf{p})]^{-1} \delta(\mathbf{p} - \mathbf{p}'') + \delta(\mathbf{k}). \quad (48)$$

To evaluate the frequency kernel

$$i\Omega(\mathbf{p}, \mathbf{p}') = \int d^3p'' \langle \dot{a}(\mathbf{p})a^*(\mathbf{p}'') \rangle \phi^{-1}(\mathbf{p}'', \mathbf{p}'), \quad (49)$$

we note

$$\dot{a}(\mathbf{p}) = (i\mathbf{k} \cdot \mathbf{p}/m)a(\mathbf{p}) + \sigma(\mathbf{p}), \quad (50)$$

where we define

$$\sigma(\mathbf{p}) \equiv \exp(i\mathbf{k} \cdot \mathbf{x}^\alpha) \mathbf{F}^\alpha \cdot \frac{\partial}{\partial \mathbf{p}^\alpha} \delta(\mathbf{p} - \mathbf{p}^\alpha). \quad (51)$$

Hence,

$$\begin{aligned} \langle \dot{a}(\mathbf{p})a^*(\mathbf{p}'') \rangle &= (i\mathbf{k} \cdot \mathbf{p}/m)\langle a(\mathbf{p})a^*(\mathbf{p}'') \rangle \\ &+ \langle \mathbf{F}^\alpha \cdot \left[\left\langle \frac{\partial}{\partial \mathbf{p}^\alpha} \delta(\mathbf{p} - \mathbf{p}^\alpha) \delta(\mathbf{p}'' - \mathbf{p}^\alpha) \right\rangle \right. \\ &\left. - M(\mathbf{p}'') \delta(\mathbf{k}) \left\langle \frac{\partial}{\partial \mathbf{p}^\alpha} \delta(\mathbf{p} - \mathbf{p}^\alpha) \right\rangle \right]. \quad (52) \end{aligned}$$

But the average force on the test particle, $\langle \mathbf{F}^\alpha \rangle$, vanishes for an equilibrium system. Hence,

$$\begin{aligned} i\Omega(\mathbf{p}, \mathbf{p}') &= \frac{i\mathbf{k} \cdot \mathbf{p}}{m} \int d^3p'' \langle a(\mathbf{p})a^*(\mathbf{p}'') \rangle \phi^{-1}(\mathbf{p}'', \mathbf{p}') \\ &= \frac{i\mathbf{k} \cdot \mathbf{p}}{m} \delta(\mathbf{p} - \mathbf{p}'). \quad (53) \end{aligned}$$

Finally, we can simplify the damping kernel

$$\begin{aligned} \varphi_k(\mathbf{p}, \mathbf{p}', \tau) &= \int d^3p'' \langle f(\mathbf{p}, \tau)f^*(\mathbf{p}'') \rangle \phi^{-1}(\mathbf{p}'', \mathbf{p}') \\ &= [M(\mathbf{p}')]^{-1} \langle f(\mathbf{p}, \tau)f^*(\mathbf{p}') \rangle \\ &+ \delta(\mathbf{k}) \left\langle f(\mathbf{p}, \tau) \int d^3p'' f^*(\mathbf{p}'') \right\rangle. \quad (54) \end{aligned}$$

But if we note

$$f(\mathbf{p}) = (1 - P)\dot{a}(\mathbf{p}) = (1 - P)\sigma(\mathbf{p}) = \sigma(\mathbf{p}) \quad (55)$$

and

$$\int d^3p'' \sigma(\mathbf{p}'') = 0, \quad (56)$$

then

$$\varphi_k(\mathbf{p}, \mathbf{p}', t) = [M(\mathbf{p}')]^{-1} \langle \sigma^*(\mathbf{p}') \exp[it(1 - P)L]\sigma(\mathbf{p}) \rangle. \quad (57)$$

Summarizing, then, the generalized Langevin equation for $a(\mathbf{p}, t)$ can be written as

$$\begin{aligned} \frac{\partial a}{\partial t} - \frac{i\mathbf{k} \cdot \mathbf{p}}{m} a(\mathbf{p}, t) \\ + \int_0^t d\tau \int d^3p' \varphi_k(\mathbf{p}, \mathbf{p}', \tau) a(\mathbf{p}', t - \tau) \\ = \exp[it(1 - P)L]\sigma(\mathbf{p}). \quad (58) \end{aligned}$$

Hence, by multiplying by $a^*(\mathbf{p}'')$ and performing the ensemble average, noting $\langle f(\mathbf{p}, t)a^*(\mathbf{p}'') \rangle = 0$ we find an exact kinetic equation for the correlation function $\Gamma(k, \mathbf{p}, \mathbf{p}'', t)$

$$\begin{aligned} \frac{\partial \Gamma}{\partial t} - \frac{i\mathbf{k} \cdot \mathbf{p}}{m} \Gamma(k, \mathbf{p}, \mathbf{p}'', t) \\ + \int_0^t d\tau \int d^3p' \varphi_k(\mathbf{p}, \mathbf{p}', \tau) \\ \cdot \Gamma(k, \mathbf{p}', \mathbf{p}'', t - \tau) = 0. \quad (59) \end{aligned}$$

It should be noted that a similar, exact kinetic equation for $\Gamma(k, \mathbf{p}, \mathbf{p}'', t)$ has been obtained using a somewhat different approach by Lebowitz, Percus, and Sykes.²² However, the projection operator formalism we have utilized appears to yield a somewhat more explicit form (57) for the "damping" or memory kernel $\varphi_k(\mathbf{p}, \mathbf{p}', \tau)$.

Again, we have merely succeeded in disguising the complexities of the many-body problem by deferring them to the calculation of the damping kernel $\varphi_k(\mathbf{p}, \mathbf{p}', \tau)$. Just as before, there are essentially two approaches one can take at this point: either a direct perturbative calculation of $\varphi_k(\mathbf{p}, \mathbf{p}', \tau)$, or as in the hydrodynamic description, an educated guess at the form of $\varphi_k(\mathbf{p}, \mathbf{p}', \tau)$.

To demonstrate the perturbation approach, we will calculate the form of the kinetic equation in the weak coupling limit; that is, we will calculate $\varphi_k(\mathbf{p}, \mathbf{p}', \tau)$ only to lowest order in the interaction strength $\lambda = O(V) = O(F)$. We first note that

$$\begin{aligned} \langle \sigma^*(\mathbf{p}') \exp[i\tau(1 - P)L]\sigma(\mathbf{p}) \rangle \\ = \langle \sigma^*(\mathbf{p}') \exp(i\tau L_0)\sigma(\mathbf{p}) \rangle + O(\lambda^3), \quad (60) \end{aligned}$$

where

$$L_0 \equiv -i \sum_{\beta=1}^N \frac{\mathbf{p}^\beta}{m} \cdot \frac{\partial}{\partial \mathbf{x}^\beta}. \quad (61)$$

Hence, we can calculate

$$\begin{aligned}
 & \int d^3p' \varphi_k(\mathbf{p}, \mathbf{p}', \tau) a(\mathbf{p}', t - \tau) \\
 &= \int d^3p' \frac{a(\mathbf{p}', t - \tau)}{M(\mathbf{p}')} \frac{\partial}{\partial \mathbf{p}'} M(\mathbf{p}') \cdot \langle \mathbf{F}^\alpha \exp(i\tau L_0) \mathbf{F}^\alpha \rangle \\
 & \quad \cdot \exp_k \left(-\frac{i\mathbf{k} \cdot \mathbf{p}\tau}{m} \right) \cdot \frac{\partial}{\partial \mathbf{p}} \delta(\mathbf{p} - \mathbf{p}') \\
 &= -\frac{1}{\beta} \frac{\partial}{\partial \mathbf{p}} \cdot \Xi_k(\mathbf{p}, \tau) \cdot \left(\frac{\partial}{\partial \mathbf{p}} + \frac{\beta}{m} \mathbf{p} \right) a(\mathbf{p}, t - \tau) + O(\lambda^3),
 \end{aligned} \tag{62}$$

where

$$\begin{aligned}
 \Xi_k(\mathbf{p}, \tau) \equiv & \beta \left\langle \mathbf{F}^\alpha \mathbf{F}^{\alpha\beta} \left(\mathbf{x}^\alpha - \mathbf{x}^\beta + \frac{\mathbf{p}\tau}{m} - \frac{\mathbf{p}^\beta\tau}{m} \right) \right\rangle \\
 & \cdot \exp \left(-\frac{i\mathbf{k} \cdot \mathbf{p}\tau}{m} \right).
 \end{aligned} \tag{63}$$

Hence to $O(\lambda^2)$, the kinetic equation (59) takes the form

$$\begin{aligned}
 \frac{\partial \Gamma}{\partial t} - \frac{i\mathbf{k} \cdot \mathbf{p}}{m} \Gamma(k, \mathbf{p}, \mathbf{p}'', t) \\
 - \frac{1}{\beta} \int_0^t d\tau \frac{\partial}{\partial \mathbf{p}} \cdot \Xi_k(\mathbf{p}, \tau) \cdot \left(\frac{\partial}{\partial \mathbf{p}} + \frac{\beta}{m} \mathbf{p} \right) \\
 \cdot \Gamma(k, \mathbf{p}, \mathbf{p}'', t - \tau) = 0.
 \end{aligned} \tag{64}$$

Notice that if we take the Markovian limit¹¹ $\lambda \rightarrow 0$, $t \rightarrow \infty$, $\mathbf{x} \rightarrow \infty$ such that $\lambda^2 t$ and $\lambda^2 \mathbf{x}$ remain finite, then we find

$$\begin{aligned}
 \frac{\partial \Gamma}{\partial t} - \frac{i\mathbf{k} \cdot \mathbf{p}}{m} \Gamma(k, \mathbf{p}, \mathbf{p}'', t) \\
 - \frac{1}{\beta} \frac{\partial}{\partial \mathbf{p}} \cdot \xi(\mathbf{p}) \cdot \left(\frac{\partial}{\partial \mathbf{p}} + \frac{\beta}{m} \mathbf{p} \right) \Gamma(k, \mathbf{p}, \mathbf{p}'', t) = 0,
 \end{aligned} \tag{65}$$

where

$$\xi(\mathbf{p}) \equiv \beta \int_0^\infty d\tau \left\langle \mathbf{F}^\alpha \mathbf{F}^{\alpha\beta} \left(\mathbf{x}^\alpha - \mathbf{x}^\beta + \frac{\mathbf{p}\tau}{m} - \frac{\mathbf{p}^\beta\tau}{m} \right) \right\rangle. \tag{66}$$

But Eq. (65) is just the usual linear Fokker-Planck equation for a test particle,^{1,7} with $\xi(\mathbf{p})$ appearing as a momentum-dependent friction tensor. This weak-coupling result, while perhaps not too surprising, does serve as a verification of the more general equation (59).

A similar perturbative calculation of $\varphi_k(\mathbf{p}, \mathbf{p}', \tau)$ can be performed using density n as the expansion parameter. Similar calculations performed by Bixon and Zwanzig²¹ and Van Leeuwen and Yip²³ suggest that one might expect such a scheme to yield the linear test-particle Boltzmann equation as the analog of Eq. (65).

The above perturbative procedures for approximating $\varphi_k(\mathbf{p}, \mathbf{p}', \tau)$ yield kinetic equations which, while being very suggestive in appearance, are in fact rather difficult to solve. To avoid these complexities, we will now turn to a modeled calculation of the damping kernel. In particular, we will assume that the time behavior of $\varphi_k(\mathbf{p}, \mathbf{p}', \tau)$ is exponential such that

$$\varphi_k(\mathbf{p}, \mathbf{p}', \tau) = \varphi_k(\mathbf{p}, \mathbf{p}', 0) \exp[-\alpha_K(k)\tau], \tag{67}$$

where $\alpha_K(k)$ is a k -dependent relaxation constant which will be specified momentarily. Such a "single-relaxation time" approximation has yielded a remarkably good agreement with molecular dynamics calculations, both for the momentum autocorrelation function^{13,14} and for current-current correlations.²⁴ Of course, a more general time dependence could have been taken in the modeling (67) of $\varphi_k(\mathbf{p}, \mathbf{p}', \tau)$. Lebowitz, Percus, and Sykes²² have developed and solved the kinetic equation (59) for a slightly more general model $\varphi_k(\mathbf{p}, \mathbf{p}', \tau) = \varphi_k(\mathbf{p}, \mathbf{p}', 0)g(\tau)$. However by choosing the particular time dependence (67), we will be able to evaluate $\alpha_K(k)$ and hence obtain explicit results for $G_*(\mathbf{r}, t)$.

The calculation of $\varphi_k(\mathbf{p}, \mathbf{p}', 0)$ is straightforward

$$\begin{aligned}
 \varphi_k(\mathbf{p}, \mathbf{p}', 0) &= \langle \sigma(\mathbf{p}) \sigma^*(\mathbf{p}') \rangle \\
 &= \langle \mathbf{F}^\alpha \mathbf{F}^\alpha \rangle : \frac{\partial}{\partial \mathbf{p}'} M(\mathbf{p}') \frac{\partial}{\partial \mathbf{p}} \delta(\mathbf{p} - \mathbf{p}')
 \end{aligned} \tag{68}$$

which yields

$$\begin{aligned}
 & \int d^3p' \varphi(\mathbf{p}, \mathbf{p}', 0) \Gamma(k, \mathbf{p}', \mathbf{p}'', t - \tau) \\
 &= -\frac{\langle \nabla^2 V \rangle}{3\beta} \left[\frac{\partial}{\partial \mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{p}} + \frac{\beta}{m} \frac{\partial}{\partial \mathbf{p}} \cdot \mathbf{p} \right] \Gamma(k, \mathbf{p}, \mathbf{p}'', t - \tau).
 \end{aligned} \tag{69}$$

Hence our modeled kinetic equation becomes (in Laplace transformed form)

$$\begin{aligned}
 & \left(s - i \frac{\mathbf{k} \cdot \mathbf{p}}{m} \right) \tilde{\Gamma}(k, \mathbf{p}, \mathbf{p}'', s) \\
 & - \frac{\langle \nabla^2 V \rangle / 3\beta}{s + \alpha_K(k)} \left\{ \frac{\partial}{\partial \mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{p}} + \frac{\beta}{m} \frac{\partial}{\partial \mathbf{p}} \cdot \mathbf{p} \right\} \tilde{\Gamma}(k, \mathbf{p}, \mathbf{p}'', s) \\
 &= \tilde{\Gamma}(k, \mathbf{p}, \mathbf{p}'', 0).
 \end{aligned} \tag{70}$$

But this equation is essentially just the usual Fokker-Planck equation of Brownian motion, with a frequency and wavelength dependent friction coefficient. As such, it can readily be solved^{22,25} (e.g., by Fourier transforms in velocity), and the solution integrated to obtain (in the notation of Ref. 22)

$$\tilde{G}_s(k, s) = \frac{m\beta g(s)}{k^2 + sm\beta g(s)} \left\{ 1 + \exp(k^2)(k^2)^{-(z+\kappa^2)} \cdot \int_0^{\kappa^2} du \exp(-u)u^{(z+\kappa^2)} \right\}, \quad (71)$$

where

$$g(s) = \frac{\langle \nabla^2 V \rangle / 3m}{s + \alpha_K(k)} \equiv \frac{\Delta}{s + \alpha_K(k)}, \quad (72)$$

$$z = \frac{s}{g(s)}, \quad \kappa = \frac{k}{(m\beta)^{1/2}g(s)}. \quad (73)$$

We can then compute

$$S_s(k, \omega) = \frac{1}{\pi} \operatorname{Re} \left\{ \lim_{s \rightarrow i\omega} \tilde{G}_s(k, s) \right\}. \quad (74)$$

At this point we can determine the relaxation parameter $\alpha_K(k)$ by comparing the known behavior of $S_s(k, 0)$ at small and large k with the form obtained from (71)

$$S_s(k, 0) = \left(\frac{m\beta}{\pi k^2} \right) \left(\frac{\Delta}{\alpha_K} \right) \cdot \left[1 + \exp(\kappa_0^2)(\kappa_0^2)^{-\kappa_0^2} \int_0^{\kappa_0^2} du \exp(-u)u^{\kappa_0^2} \right], \quad (75)$$

where

$$\kappa_0^2 \equiv \left(\frac{k^2}{m\beta} \right) \left(\frac{\alpha_K}{\Delta} \right)^2. \quad (76)$$

The small k limit (33) demands

$$(\Delta m\beta / \alpha)[1 + O(\kappa_0^2)] \rightarrow D_s^{-1} \quad (77)$$

which implies

$$\alpha_K(k) \rightarrow (m\beta D_s)\Delta \text{ as } k \rightarrow 0. \quad (78)$$

To study the large k limit, first note that

$$I(\kappa^2, z) \equiv \exp(k^2)(k^2)^{-(z+\kappa^2)} \int_0^{\kappa^2} du \exp(-u)u^{(z+\kappa^2)} \\ \sim \left(\frac{\pi}{2} \right)^{1/2} \kappa - \left(z + \frac{2}{3} \right) \\ + \left(\frac{\pi}{32} \right)^{1/2} \frac{2z^2 + 2z - 3}{\kappa} + O\left(\frac{1}{\kappa^2} \right). \quad (79)$$

Hence it is apparent that if we choose $\alpha_K(k)$ such that

$$\alpha_K(k) \rightarrow O(k^2) \quad \text{as } k \rightarrow \infty, \quad (80)$$

then from (71) and (74)

$$S_s(k, \omega) \sim \left(\frac{m\beta}{2\pi k^2} \right)^{1/2} \left[1 - \left(\frac{\omega^2 m\beta}{k^2} \right) \frac{m\beta}{2} + \dots \right] \\ \text{as } k \rightarrow \infty, \quad (81)$$

which is the proper ideal gas behavior.

Consistent with requirements (78) and (80), we shall choose $\alpha_K(k)$ to increase quadratically in k as

$$\alpha_K(k) = (m\beta D_s)\Delta[1 + k^2/m\beta\Delta]. \quad (82)$$

When inserted into (75), such a choice yields rather remarkable agreement with molecular dynamics data (see Fig. 4) for $S_s(k, 0)$.

We have again computed $S_s(k, \omega)$ for argon at $T = 85.5^\circ\text{K}$, $mn = 1.407 \text{ g/cm}^3$ using the modeled kinetic description (71) with (82) and compared these results in Figs. 1, 2, and 3 with the molecular dynamics calculations as well as with the earlier hydrodynamic description (30). As one might expect, the kinetic description is far superior to the hydrodynamic results for large k [$k > 3\text{\AA}^{-1}$]. Neither description accounts for the dip in $\omega_{1/2}(k)$ vs k (Fig. 3) in the vicinity of 2\AA^{-1} , which suggests that this behavior is due to collective effects [i.e., dependent explicitly upon the peak in the static structure factor $S(k)$ at this value of k] which are unaccounted for in our theory.

IV. CONCLUDING REMARKS

This work has attempted to develop expressions for the space-time Fourier transform $S_s(k, \omega)$ of the Van Hove self-correlation function $G_s(\mathbf{r}, t)$. In particular, the projection operator formalism of Zwanzig and Mori has been used to develop exact descriptions for $S_s(k, \omega)$, based either upon a generalized hydrodynamic or kinetic equation description. Although standard perturbative methods can be used to study these descriptions, a more useful approach involves guessing or modeling the damping or memory terms in these equations. This latter scheme lends itself particularly well to the actual calculation of $S_s(k, \omega)$ and may prove of use in predicting and interpolating the results of incoherent neutron scattering experiments. When

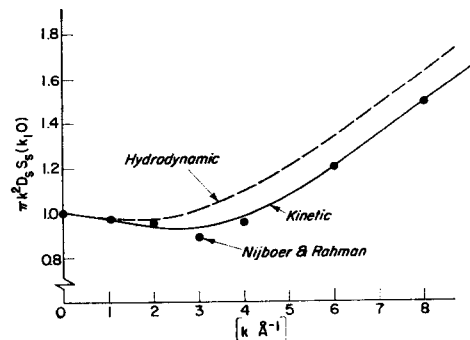


FIG. 4. $\pi D_s k^2 S_s(k, 0)$ vs k (notation convention similar to that of the first three figures).

combined with earlier work^{20,24} on the coherent scattering law $S(k, \omega)$, such schemes allow the calculation of the total differential scattering cross section for thermal neutrons from liquids (in this regard, refer to the very comprehensive work of Chung and Yip²⁶).

It is hoped that these results once again demonstrate the power and versatility of projection operator methods. The Zwanzig-Mori formalism allows one to develop rather sophisticated expressions for quantities characterizing the dynamics of many-body systems with a minimum of effort and approximation; and while the appropriateness of such expressions for facilitating perturbation schemes is open to question,⁷ their usefulness for obtaining modeled results has been amply demonstrated.

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