Approach to transport theory using generalized Langevin equations*

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The use of generalized Langevin equations in the study of transport in simple classical liquids is extended by the derivation of the second such equation in the hierarchy of coupled phase-space transport equations. This set of generalized Langevin equations is applied to the description of self-diffusion. An approximation is made to simplify the second generalized Langevin equation, and a perturbation solution is presented for the velocity autocorrelation function. The method introduced is related to the Mori continued-fraction representation, but poses a different point of view for analysis.

I. INTRODUCTION

A satisfactory theoretical description of transport in realistic simple classical liquids remains almost as elusive as when the analysis was first attempted. Early formulations concentrated on calculations of the transport coefficients.[1] Much more detailed information is now available from computer dynamics and neutron-scattering experiments and these new results must be explained by the theory. For this purpose the older theories are not adequate.

The existence of the new experimental information has already stimulated some theoretical progress. For example, the computer-generated velocity autocorrelation function due to Rahman[2,3] and Levesque and Verlet[4] has led to the introduction of formalisms not based on solution of a kinetic equation for the distribution function, and various approximations to these formalisms.[5-16] Now the velocity autocorrelation function provides an excellent test of a transport theory. It is a rather simple quantity to define, its power spectrum possesses an uncomplicated structure,[2,3] and the self-diffusion constant may be obtained from it in the hydrodynamic limit. Analysis of the velocity autocorrelation function is one aspect of the description of self-diffusion. It is also necessary to describe the nature of the incoherent neutron scattering, for which we need to calculate the incoherent scattering law $S_s(k, \omega)$.

We shall analyze self-diffusion along previously established lines. In particular, we shall follow the theory of Akcasu, Corngold, and Duderstadt.[15] Using the projection operator methods of Zwanzig[17] and Mori,[18] these authors have obtained a classical generalized Langevin equation (GLE) for the autocorrelation function of the microscopic specific single-particle phase-space density,

$$g_\alpha(\vec{x}, \vec{p}; t) = \delta[\vec{x} - \vec{x}_\alpha(t)]\delta[\vec{p} - \vec{p}_\alpha(t)]. \tag{1.1}$$

This single-particle operator gives the μ-space probability density for the specific particle numbered α, where $[\vec{x}_\alpha(t), \vec{p}_\alpha(t)]$ is the trajectory of particle α. Since the trajectory of the particle may be obtained from g_α, it is clear that it contains all of the information about the particle α. Consequently, the autocorrelation function of g_α is the most informative of all specific single-particle time-correlation functions; in fact, all other such specific single-particle time-correlation functions may be obtained from $\langle g_\alpha(t) g_\alpha(0)\rangle$.

Formulation of the self-diffusion problem in terms of calculation of $\langle g_\alpha(t) g_\alpha(0)\rangle$ offers great advantages over past calculations of specific "lower-order" autocorrelation functions, because such reduced time-correlation functions satisfy correspondingly reduced equations of motion from which some details of the general dynamics are omitted; these details are left explicit in the equations of motion for the single-particle phase-space density g_α.

The GLE obtained by Akcasu *et al.* [Eq. (2.14)] introduces a damping matrix $\varphi_1(\vec{k}, \vec{p}, \vec{p}'; t)$; unfortunately only the initial value of φ_1 is known exactly. Low-density and weak-coupling perturbation expansions of φ_1 have been published, but these are not useful for the case of dense gases and liquids, e.g., argon near its triple point, to which we address ourselves. In particular, the time dependence of the damping matrix for a dense fluid is not known. With the cautions previously raised on this matter in mind,[9] we do not believe that the present status of the theory warrants assumptions about this time dependence. To rectify this situation we have derived a GLE for the damping matrix itself, effecting in the process a phase-space generalization of Mori's continued-fraction hierarchy.

We review briefly the work of Akcasu, Corngold, and Duderstadt in the next section. Following that we present our work on the second GLE in Secs. III–IX. Finally, we suggest a solution for the velocity autocorrelation function based on the simplest useful approximation to the second GLE.

II. THE FIRST GENERALIZED LANGEVIN EQUATION

Suppose we are interested in a classical dynamical variable $a(\vec{p},t;\Gamma)$ which is indexed by the continuous vector variable $\vec{p}$ (as would be the case for a microscopic phase-space density operator) and which depends on the dynamics of a dense many-body system. Akcasu and Duderstadt[19] have pointed out that the GLE's of Mori may be extended to this case to obtain the following exact equation of motion for the variable $a(\vec{p},t;\Gamma)$:

$$\frac{\partial}{\partial t}a(\vec{p},t)-i\int d\vec{p}\,'\,\Omega_1(\vec{p},\vec{p}\,')a(\vec{p}\,',t)+\int_0^t d\tau\int d\vec{p}\,'\,\varphi_1(\vec{p},\vec{p}\,';\tau)a(\vec{p}\,',t-\tau)=F_1(\vec{p},t). \tag{2.1}$$

In Eq. (2.1) we have suppressed the Γ-space dependence of the dynamical variable, as we shall continue to do consistently below. Equation (2.1) is derived through the use of a projection operator $\hat{P}_1$, which is defined to project out the initial value of the chosen variable, $a(\vec{p})=a(\vec{p},t=0)$. It is also necessary to define the inner product of two variables $b(\vec{p},t)$ and $c(\vec{p},t)$ by

$$\langle b(\vec{p},t),c(\vec{p},t)\rangle=\int d\Gamma\, b(\vec{p},t)c^*(\vec{p},t)w(\Gamma), \tag{2.2}$$

where $w(\Gamma)$ is the canonical distribution and we have allowed for complex dynamical variables. Finally, we define an inverse $\langle a(\vec{p}),a(\vec{p}\,')\rangle^{-1}$ for the static correlation matrix $\langle a(\vec{p}),a(\vec{p}\,')\rangle$ as follows:

$$\int d\vec{p}\,''\langle a(\vec{p}),a(\vec{p}\,'')\rangle\langle a(\vec{p}\,''),a(\vec{p}\,')\rangle^{-1}=\delta(\vec{p}-\vec{p}\,'). \tag{2.3}$$

With these definitions we are able to obtain explicit representations for the remaining undefined quantities in the GLE above: The first frequency matrix Ω_1 is given by

$$i\Omega_1(\vec{p},\vec{p}\,')=\int d\vec{p}\,''\langle iLa(\vec{p}),a(\vec{p}\,'')\rangle\langle a(\vec{p}\,''),a(\vec{p}\,')\rangle^{-1}, \tag{2.4}$$

the first generalized force F_1 by

$$F_1(\vec{p},t)=e^{it(1-\hat{P}_1)L}[(1-\hat{P}_1)iLa(\vec{p})], \tag{2.5}$$

and the first damping matrix φ_1 by

$$\varphi_1(\vec{p},\vec{p}\,';t)=\int d\vec{p}\,''\langle F_1(\vec{p},t),F_1(\vec{p}\,'')\rangle\langle a(\vec{p}\,''),a(\vec{p}\,')\rangle^{-1}, \tag{2.6}$$

where L is the classical Liouville operator and

$$F_1(\vec{p})=F_1(\vec{p},t=0).$$

We also obtain an explicit formula for the action of the first-projection operator $\hat{P}_1$ on an arbitrary phase-space function $G(\vec{p})$, namely,

$$\hat{P}_1G(\vec{p})=\int dp''\,dp'''\langle G(\vec{p}),a(\vec{p}\,'')\rangle\langle a(\vec{p}\,''),a(\vec{p}\,''')\rangle^{-1}a(\vec{p}\,'''). \tag{2.7}$$

Nordholm[20] has pointed out that the static correlation matrix $\langle a(\vec{p}),a(\vec{p}\,')\rangle$ may be singular for some choices of dynamical variable, thereby preventing one from solving equation (2.3) for the inverse $\langle a(\vec{p}),a(\vec{p}\,')\rangle^{-1}$. This does not occur for Akcasu's choice of variable, but we shall encounter the problem below.

Actually, we are interested only in time-dependent autocorrelation functions and we define, with Akcasu *et al.*,

$$\Gamma(\vec{p},\vec{p}\,';t)=\langle a(\vec{p},t),a(\vec{p}\,')\rangle. \tag{2.8}$$

Taking the inner product of Eq. (2.1) with $a(\vec{p}\,'')$, we obtain the first GLE:

$$\frac{\partial}{\partial t}\Gamma(\vec{p},\vec{p}\,'';t)-i\int d\vec{p}\,'\,\Omega_1(\vec{p},\vec{p}\,')\Gamma(\vec{p}\,',\vec{p}\,'';t)+\int_0^t d\tau\int d\vec{p}\,'\,\varphi_1(\vec{p},\vec{p}\,';\tau)\Gamma(\vec{p}\,',\vec{p}\,'';t-\tau)=0, \tag{2.9}$$

since by definition of $\hat{P}_1$

$$\langle F_1(\vec{p},t),a(\vec{p}\,'')\rangle=0. \tag{2.10}$$

We now follow the development of Akcasu, Corngold, and Duderstadt[15] who have chosen the dynamical variable to be

$$a(\vec{p},t)=g_\alpha(\vec{k},\vec{p},t)-\langle g_\alpha(\vec{k},\vec{p},t)\rangle, \tag{2.11}$$

where $g_\alpha(\vec{k},\vec{p},t)$ is the Fourier transform

$$g_\alpha(\vec{k},\vec{p},t)=\int d\vec{x}\,e^{i\vec{k}\cdot\vec{x}}g_\alpha(\vec{x},\vec{p},t) \tag{2.12}$$

of the specific single-particle phase-space density defined in equation (1.1). We omit, occasionally, the α and $\vec{k}$ dependence of the dynamical variable for the sake of brevity.

Akcasu *et al.* demonstrate that the first frequency matrix (2.4) for the above choice of variable is

$$i\Omega_1(\vec{p},\vec{p}\,')=(i\vec{k}\cdot\vec{p}/m)\delta(\vec{p}-\vec{p}\,'). \tag{2.13}$$

Thus the first GLE (2.9) becomes

$$\left(\frac{\partial}{\partial t}-\frac{i\vec{k}\cdot\vec{p}}{m}\right)\Gamma(\vec{k},\vec{p},\vec{p}\,'';t)+\int_0^t d\tau\int d\vec{p}\,'\,\varphi_1(\vec{k},\vec{p},\vec{p}\,';\tau)\Gamma(\vec{k},\vec{p}\,',\vec{p}\,'';t-\tau)=0, \tag{2.14}$$

so that the frequency matrix contributes the free-streaming term. The initial value of the first generalized force which results is given by

$$F_1(\vec{p}) = (1-\hat{P}_1)iLa(\vec{p}) = \vec{F}_\alpha \cdot \frac{\partial}{\partial \vec{p}_\alpha}\delta(\vec{p}-\vec{p}_\alpha)e^{i\vec{k}\cdot\vec{x}_\alpha}, \tag{2.15}$$

while the static correlation matrix of this quantity is

$$\langle F_1(\vec{p}), F_1(\vec{p}')\rangle = -D(0)\frac{\partial}{\partial \vec{p}}\cdot\left(\frac{\partial}{\partial \vec{p}}+\frac{\beta\vec{p}}{m}\right)M(\vec{p})\delta(\vec{p}-\vec{p}'), \tag{2.16}$$

where

$$\langle \vec{F}_\alpha \vec{F}_\alpha\rangle = D(0)\vec{1} \tag{2.17}$$

and

$$M(\vec{p}) = (\beta/2\pi m)^{3/2}e^{-\beta p^2/2m}. \tag{2.18}$$

The result (2.16) is of fundamental significance to the analysis presented in Sec. III. The occurrence of the Fokker-Planck operator in (2.16) is reminiscent of the older kinetic theories of classical liquids[1] and defines the dominant structure of the present theory. The initial value of the first damping matrix may be obtained by the use of (2.16) and is given by

$$\varphi_1(\vec{k},\vec{p},\vec{p}';t=0) = -D(0)\frac{\partial}{\partial \vec{p}}\cdot\left(\frac{\partial}{\partial \vec{p}}+\frac{\beta\vec{p}}{m}\right)\delta(\vec{p}-\vec{p}'). \tag{2.19}$$

Akcasu *et al.* close their article by discussing the weak-coupling expansion and the low-density expansion of the first damping matrix. They demonstrate that the weak-coupling expansion results in a linear Fokker-Planck equation and they suggest that the low-density expansion yields a linear Boltzmann equation. The latter expectation has been confirmed by the recent work of Mazenko.[21] Neither of these results is helpful in the study of a dense gas or liquid. Akcasu *et al.* conclude that the most useful technique in that case is to model the damping matrix as a product of its initial value and some decaying function of time, $g(t)$:

$$\varphi_1(\vec{k},\vec{p},\vec{p}';t) \approx g(t)\varphi_1(\vec{k},\vec{p},\vec{p}';t=0). \tag{2.20}$$

Several workers[16] have pursued this idea, usually with exponential or Gaussian damping factors $g(t)$. It should be noted that a completely equivalent development was given earlier by Lebowitz, Percus, and Sykes,[12] who also presented a solution for the model given above (2.20) for an arbitrary function $g(t)$. Our use of the results derived by Akcasu, Corngold, and Duderstadt merely reflects a preference for the Mori-Zwanzig projection operator methods, which we believe afford a distinct computational advantage over other methods.

III. SECOND GENERALIZED LANGEVIN EQUATION

Having adopted the Mori-Zwanzig projection operator approach, we now proceed to exploit the formalism to obtain a GLE for the first damping matrix (2.6). We see from the definition of the first damping matrix that its time development arises wholly from the presence of the first generalized force, $F_1(\vec{p},t)$. Thus we proceed by deriving a GLE for the first generalized force; this takes the form

$$\frac{\partial}{\partial t}F_1(\vec{p},t) - i\int d\vec{p}'\,\Omega_2(\vec{p},\vec{p}')F_1(\vec{p}',t) + \int_0^t d\tau \int d\vec{p}'\,\varphi_2(\vec{p},\vec{p}';\tau)F_1(\vec{p}',t-\tau) = F_2(\vec{p},t). \tag{3.1}$$

Equation (3.1) is derived by the use of a projection operator $\hat{P}_2$, which projects out the initial value of the first generalized force $F_1(\vec{p})$.

We must also define an inverse for the second static correlation matrix $\langle F_1(\vec{p}), F_1(\vec{p}')\rangle$. At this point we must deal with the singularity alluded to above. Consider Eq. (2.16) for $\langle F_1(\vec{p}), F_1(\vec{p}')\rangle$. Now $M(\vec{p}')\delta(\vec{p}-\vec{p}')$ contains a component which is an eigenfunction of the Fokker-Planck operator with vanishing eigenvalue. In a diagonal representation in terms, say, of the eigenfunctions of the Fokker-Planck operator, $\langle F_1(\vec{p}), F_1(\vec{p}')\rangle$ has a vanishing component. Hence it is a singular matrix and its inverse may not be defined as simply as Eq. (2.3). This difficulty may be eliminated by simply removing the component with vanishing eigenvalue. The definition of the inverse which results from this procedure is

$$\int d\vec{p}''\langle F_1(\vec{p}), F_1(\vec{p}'')\rangle\langle F_1(\vec{p}''), F_1(\vec{p}')\rangle^{-1} = \delta(\vec{p}-\vec{p}') - M(\vec{p}) \tag{3.2}$$

and we obtain an explicit formula for the second projection operator,

$$\hat{P}_2 G(\vec{p}) = \int d\vec{p}'\,d\vec{p}''\langle G(\vec{p}), F_1(\vec{p}')\rangle \times \langle F_1(\vec{p}'), F_1(\vec{p}'')\rangle^{-1}F_1(\vec{p}''). \tag{3.3}$$

The remaining undefined quantities in the GLE (3.1) are the following: the second frequency matrix Ω_2 given by

$$i\Omega_2(\vec{p},\vec{p}') = \int d\vec{p}''\langle iLF_1(\vec{p}), F_1(\vec{p}'')\rangle \times \langle F_1(\vec{p}''), F_1(\vec{p}')\rangle^{-1}; \tag{3.4}$$

the second generalized force F_2 by

$$F_2(\vec{p},t) = e^{it(1-\hat{P}_2)(1-\hat{P}_1)L}[(1-\hat{P}_2)(1-\hat{P}_1)iLF_1(\vec{p})]; \tag{3.5}$$

and the second damping matrix by

$$\varphi_2(\vec{p},\vec{p}';t) = \int d\vec{p}''\langle F_2(\vec{p},t), F_2(\vec{p}'')\rangle \times \langle F_1(\vec{p}''), F_1(\vec{p}')\rangle^{-1}. \tag{3.6}$$

We are able to omit the troublesome component of $M(\vec{p}')\delta(\vec{p}-\vec{p}')$ for the following reason: The appearance of the inverse matrix $\langle F_1(\vec{p}), F_1(\vec{p}')\rangle^{-1}$ in the theory results from an implicit use of the second projection operator $\hat{P}_2$ given by Eq. (3.3). The component omitted, in fact, makes no contribution to the integral since

$$\int d\vec{p}'\, M(\vec{p})F_1(\vec{p}') = 0. \tag{3.7}$$

Now by taking the inner product of the GLE (3.1) with $F_1(\vec{p}'')$ and weighting the resulting equation with $\langle a(\vec{p}''), a(\vec{p}''')\rangle^{-1}$, we obtain a GLE for the first damping matrix:

$$\frac{\partial}{\partial t}\varphi_1(\vec{k},\vec{p},\vec{p}'';t) - i\int d\vec{p}'\,\Omega_2(\vec{p},\vec{p}')\varphi_1(\vec{k},\vec{p}',\vec{p}'';t) + \int_0^t d\tau \int d\vec{p}'\,\varphi_2(\vec{k},\vec{p},\vec{p}';\tau)\varphi_1(\vec{k},\vec{p}',\vec{p}'';t-\tau) = 0, \tag{3.8}$$

where the inhomogeneous term vanishes because

$$\langle F_2(\vec{p},t), F_1(\vec{p}'')\rangle = 0. \tag{3.9}$$

We shall refer to Eq. (3.8) as the second GLE and to Eqs. (2.9) and (2.14) as the first GLE.

It should be noted that although the two GLE's could have been formulated by analogy with the discrete-indexed continued-fraction hierarchy of Mori,[22] we have actually derived these equations to confirm the definitions involved. Our derivation proceeds somewhat along the lines taken by Zwanzig,[17] but more specifically we have worked by analogy with a discrete index derivation detailed by Nordholm.[23] The detailed proof is straightforward, but lengthy, and we defer it to a separate article.

We now proceed with the explicit development of the second GLE for the given choice of dynamical variable. We seek to calculate the second frequency matrix and the initial value of the second damping matrix. But first we must obtain the inverse static correlation matrix $\langle F_1(\vec{p}), F_1(\vec{p}')\rangle^{-1}$. Substitution of Eq. (2.16) for $\langle F_1(\vec{p}), F_1(\vec{p}')\rangle$ into the definition of its inverse (3.2) results in the following partial differential equation for the inverse:

$$-D(0)\frac{\partial}{\partial\vec{p}}\cdot\left(\frac{\partial}{\partial\vec{p}}+\frac{\beta\vec{p}}{m}\right)M(\vec{p})\langle F_1(\vec{p}), F_1(\vec{p}')\rangle^{-1} = \delta(\vec{p}-\vec{p}') - M(\vec{p}). \tag{3.10}$$

Equation (3.10) implies that the inverse is virtually a Green's function for the Fokker-Planck operator. One of the most convenient ways of expressing the solution to such an equation is an eigenfunction expansion. To progress further we must digress to discuss the eigenfunctions of the Fokker-Planck operator.

IV. EIGENFUNCTIONS OF THE FOKKER-PLANCK OPERATOR

We identify the Fokker-Planck operator:

$$L_{\mathrm{FP}} = \frac{\partial}{\partial\vec{p}}\cdot\left(\frac{\partial}{\partial\vec{p}}+\frac{\beta\vec{p}}{m}\right), \tag{4.1}$$

and its adjoint operator

$$L_{\mathrm{FP}}^{\dagger} = \left(\frac{\partial}{\partial\vec{p}}+\frac{\beta\vec{p}}{m}\right)\cdot\frac{\partial}{\partial\vec{p}}, \tag{4.2}$$

and we define the dimensionless momentum variable

$$\vec{\xi} = (\beta/2m)^{1/2}\vec{p} \tag{4.3}$$

and

$$b_{nlj}(\vec{p}) = H_n(\xi_x)H_l(\xi_y)H_z(\xi_z), \tag{4.4}$$

where $H_n(\xi)$ are Hermite polynomials. We adopt the convention that any sum over these indices below will cover the entire range of nonnegative integers. Now $b_{nlj}(\vec{p})$ is an eigenfunction of the adjoint operator (4.2),

$$L_{\mathrm{FP}}^{\dagger}b_{nlj}(\vec{p}) = -(\beta/m)(n+l+j)b_{nlj}(\vec{p}), \tag{4.5}$$

just as

$$a_{nlj}(\vec{p}) = M(\vec{p})b_{nlj}(\vec{p}) \tag{4.6}$$

is an eigenfunction of the Fokker-Planck operator (4.1),

$$L_{\mathrm{FP}}a_{nlj}(\vec{p}) = -(\beta/m)(n+l+j)a_{nlj}(\vec{p}). \tag{4.7}$$

Now define two renormalized sets of eigenfunctions by

$$\tilde{b}_{nlj}(\vec{p}) = (n!l!j!2^{n+l+j})^{-1}b_{nlj}(\vec{p}), \qquad \tilde{a}_{nlj}(\vec{p}) = (n!l!j!2^{n+l+j})^{-1}a_{nlj}(\vec{p}). \tag{4.8}$$

Equations (4.8) provide two biorthonormal sets of eigenfunctions which have the following orthogonal-

ity relations:

$$\int d\vec{p}\,\tilde{a}_{nlj}(\vec{p})b_{n'l'j'}(\vec{p}) = \delta_{nn'}\delta_{ll'}\delta_{jj'},$$
$$\int d\vec{p}\,a_{nlj}(\vec{p})\tilde{b}_{n'l'j'}(\vec{p}) = \delta_{nn'}\delta_{ll'}\delta_{jj'}. \tag{4.9}$$

We may now obtain useful representations of various quantities of interest. We find that

$$M(\vec{p})\delta(\vec{p}-\vec{p}') = \sum_{nlj}\tilde{a}_{nlj}(\vec{p}')a_{nlj}(\vec{p}). \tag{4.10}$$

The second static correlation matrix becomes

$$\langle F_1(\vec{p}), F_1(\vec{p}')\rangle = \frac{\beta D(0)}{m}\sum_{nlj}(n+l+j)\tilde{a}_{nlj}(\vec{p}')a_{nlj}(\vec{p}). \tag{4.11}$$

Note that the matrix is singular since the first term vanishes. Equation (3.10) for the inverse avoids this difficulty, and we obtain the following solution for the inverse:

$$\langle F_1(\vec{p}), F_1(\vec{p}')\rangle^{-1} = \frac{m}{\beta D(0)}\sum_{nlj}\frac{(1-\delta_{n0}\delta_{l0}\delta_{j0})}{n+l+j} \times \tilde{b}_{nlj}(\vec{p}')b_{nlj}(\vec{p}), \tag{4.12}$$

while for the initial value of the first damping matrix we find

$$\varphi_1(\vec{k},\vec{p},\vec{p}';t=0) = \frac{\beta D(0)}{m}\sum_{nlj}(n+l+j) \times \tilde{b}_{nlj}(\vec{p}')a_{nlj}(\vec{p}). \tag{4.13}$$

We will now use eigenfunction expansions to convert the complicated GLE's to matrix equations and to facilitate the solution of these equations.

V. REDUCTION OF THE FIRST GENERALIZED LANGEVIN EQUATION TO A MATRIX EQUATION

In this section we reduce the first GLE (2.14) to a matrix equation relating the various eigenfunction expansion coefficients. We assume that the autocorrelation function possesses an eigenfunction expansion of the following type:

$$\Gamma(\vec{k},\vec{p},\vec{p}'';t) = \sum_{nljihm} G^{ihm}_{nlj}(\vec{k},t)\tilde{a}_{ihm}(\vec{p}'')a_{nlj}(\vec{p}), \tag{5.1}$$

where the expansion coefficients may be obtained from the orthogonality relation (4.9):

$$G^{ihm}_{nlj}(\vec{k},t) = \int d\vec{p}\,d\vec{p}''\,\tilde{b}_{nlj}(\vec{p})b_{ihm}(\vec{p}'')\Gamma(\vec{k},\vec{p},\vec{p}'';t). \tag{5.2}$$

We may also think of these coefficients as momentum moments of the autocorrelation function and the first GLE to follow as a recurrence relation between these moments.

Similarly, we assume an eigenfunction expansion for the first damping matrix of the form

$$\varphi_1(\vec{k},\vec{p},\vec{p}'';t) = \sum_{nljihm}\mathfrak{M}^{ihm}_{nlj}(\vec{k},t)\tilde{b}_{ihm}(\vec{p}'')a_{nlj}(\vec{p}), \tag{5.3}$$

where

$$\mathfrak{M}^{n'l'j'}_{nlj}(\vec{k},t) = \int d\vec{p}\,d\vec{p}''\,\tilde{b}_{nlj}(\vec{p})a_{n'l'j'}(\vec{p}'')\varphi_1(\vec{k},\vec{p},\vec{p}'';t). \tag{5.4}$$

From our previous calculation of the initial value of the first damping matrix (4.13) we obtain the initial value of the coefficient matrix above:

$$\mathfrak{M}^{n'l'j'}_{nlj}(\vec{k},t=0) = [\beta D(0)/m](n+l+j)\delta_{nn'}\delta_{ll'}\delta_{jj'}. \tag{5.5}$$

Now we choose the orientation of the Cartesian coordinate system in which we have expressed the eigenfunctions so that the wave number k lies along the x axis. We also take note of the recurrence formula

$$p_x a_{nlj}(\vec{p}) = (2m/\beta)^{1/2}[\tfrac{1}{2}a_{n+1,lj}(\vec{p}) + n a_{n-1,lj}(\vec{p})]. \tag{5.6}$$

Using (5.6), it is a straightforward task to take matrix elements of the first GLE (2.14) to obtain the matrix form

$$\frac{\partial}{\partial t}G^{n'l'j'}_{nlj}(\vec{k},t) - ik\left(\frac{2}{m\beta}\right)^{1/2}\left(\frac{1-\delta_{n0}}{2}G^{n'l'j'}_{n-1,lj}(\vec{k},t) + (n+1)G^{n'l'j'}_{n+1,lj}(\vec{k},t)\right) + \sum_{ihm}\int_0^t d\tau\,\mathfrak{M}^{ihm}_{nlj}(\vec{k},\tau)G^{n'l'j'}_{ihm}(\vec{k},t-\tau) = 0. \tag{5.7}$$

We observe that the momentum moment of the autocorrelation function is coupled to one higher and one lower moment through the first frequency matrix and possibly to all other moments through the first damping matrix. Since the initial value (5.5) is diagonal the coupling occurs only through the frequency matrix at short times, but progresses to higher-order couplings with increasing time. This view is confirmed by our solution for the first damping matrix below.

VI. SECOND FREQUENCY MATRIX AND THE REDUCTION OF SECOND GENERALIZED LANGEVIN EQUATION TO MATRIX FORM

First we turn our attention to the calculation of the second frequency matrix. We obtain, quite readily, the result

$$\langle iLF_1(\vec{p}), F_1(\vec{p}'')\rangle\rangle = -D(0)\frac{\partial}{\partial\vec{p}}\cdot\left(\frac{i\vec{k}\cdot\vec{p}}{m}M(\vec{p})\frac{\partial}{\partial\vec{p}}\delta(\vec{p}-\vec{p}'')\right). \tag{6.1}$$

Use of (6.1) reveals that the frequency matrix may be expressed as

$$i\Omega_2(\vec{p},\vec{p}') = -D(0)\frac{\partial}{\partial\vec{p}}\cdot\left(\frac{i\vec{k}\cdot\vec{p}}{m}M(\vec{p})\frac{\partial}{\partial\vec{p}}\right) \times\langle F_1(\vec{p}), F_1(\vec{p}')\rangle\rangle^{-1}, \tag{6.2}$$

which, with the aid of the recurrence relation

$$\frac{\partial}{\partial p_x}b_{nlj}(\vec{p}) = n(2\beta/m)^{1/2}b_{n-1,lj}(\vec{p}), \tag{6.3}$$

Eqs. (5.6) and (4.12), may be expressed as the eigenfunction expansion

$$i\Omega_2(\vec{p},\vec{p}') = ik\left(\frac{2}{m\beta}\right)^{1/2}\sum_{nlj}(1-\delta_{n0}\delta_{l0}\delta_{j0})\tilde{b}_{nlj}(\vec{p}') \times\left(\tfrac{1}{2}a_{n+1,lj}(\vec{p}) + \frac{n(n+l+j-1)}{n+l+j}a_{n-1,lj}(\vec{p})\right). \tag{6.4}$$

We now employ (6.4) to realize a matrix formulation of the second GLE. First we assume an eigenfunction expansion for the second damping matrix of the form

$$\varphi_2(\vec{k},\vec{p},\vec{p}';t) = \sum_{nljihm}\mathcal{J}_{nlj}^{ihm}(\vec{k},t)\tilde{b}_{ihm}(\vec{p}')a_{nlj}(\vec{p}), \tag{6.5}$$

where

$$\mathcal{J}_{nlj}^{n'l'j}(\vec{k},t) = \int d\vec{p}\,d\vec{p}''\,\tilde{b}_{nlj}(\vec{p})a_{n'l'j'}(\vec{p}'')\varphi_2(\vec{k},\vec{p},\vec{p}'';t). \tag{6.6}$$

Taking the appropriate matrix elements of the second GLE (3.8) with Eq. (6.4) for the second frequency matrix, we obtain a matrix version of the second GLE:

$$\frac{\partial}{\partial t}\mathfrak{M}_{nlj}^{n'l'j'}(\vec{k},t) - ik\left(\frac{2}{m\beta}\right)^{1/2}\left[\frac{1-\delta_{n0}}{2}(1-\delta_{n1}\delta_{l0}\delta_{j0})\mathfrak{M}_{n-1,lj}^{n'l'j'}(\vec{k},t) + \frac{(n+1)(n+l+j)}{n+l+j+1}\mathfrak{M}_{n+1,lj}^{n'l'j'}(\vec{k},t)\right] + \sum_{ihm}\int_0^t d\tau\,\mathcal{J}_{nlj}^{ihm}(\vec{k},\tau)\mathfrak{M}_{ihm}^{n'l'j'}(\vec{k},t-\tau) = 0. \tag{6.7}$$

Now the matrix elements of the second damping matrix contain all of the difficulties of the many-body problem. Formally, the second damping matrix is more complicated than the first damping matrix, because while the first damping matrix evolves in time with the orthogonal Liouville operator $(1-\hat{P}_1)L$, the second damping matrix evolves with the doubly orthogonal operator $(1-\hat{P}_2)(1-\hat{P}_1)L$. Additionally, as we shall see, the initial values of the two damping matrices have about the same ratio of complexity; the initial value of the second damping matrix presents us with a great deal of structure. Our hope is that, in fact, the resulting time dependence is simplified by the additional formalism and by the removal of significant structure in the two calculated frequency matrices and initial values of the two damping matrices.

VII. MATRIX FORM OF THE PHYSICAL VARIABLES

Now that we have obtained a matrix representation of the two GLE's it is desirable to find matrix expressions for the quantities of physical interest.

It was demonstrated by Van Hove[24] that the incoherent inelastic neutron scattering could be interpreted in terms of the incoherent scattering law which is defined by

$$S_s(\vec{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\langle e^{i\vec{k}\cdot\vec{R}(t)}, e^{i\vec{k}\cdot\vec{R}(0)}\rangle. \tag{7.1}$$

Equation (7.1) can be expressed in terms of Γ in the following manner:

$$S_s(\vec{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\int d\vec{p}\,d\vec{p}''\,\Gamma(\vec{k},\vec{p},\vec{p}'';t). \tag{7.2}$$

However, use of Eq. (5.2) simplifies this result to the form

$$S_s(\vec{k},\omega) = (1/2\pi)G_{000}^{000}(\vec{k},\omega), \tag{7.3}$$

where

$$G_{nlj}^{\overline{nlj}}(\vec{k},\omega) = \int_{-\infty}^{\infty}dt\,e^{-i\omega t}\,G_{nlj}^{\overline{nlj}}(\vec{k},t). \tag{7.4}$$

Now we focus attention on the momentum autocorrelation function. We obtain the following result:

$$\langle \vec{p}_1(t)\cdot\vec{p}_1\rangle = \lim_{k\to 0}\int d\vec{p}\,d\vec{p}''\,\vec{p}\cdot\vec{p}''\,\Gamma(\vec{k},\vec{p},\vec{p}'';t) \quad (7.5)$$

[where $\vec{p}_1 \equiv \vec{p}_1(0)$], which reduces to the matrix form

$$\langle \vec{p}_1(t)\cdot\vec{p}_1\rangle = \lim_{k\to 0}\frac{m}{\beta}[G^{100}_{100}(\vec{k},t)+G^{010}_{010}(\vec{k},t)+G^{001}_{001}(\vec{k},t)]. \quad (7.6)$$

Finally, we may derive an expression for the self-diffusion constant by the use of the Green-Kubo[25,26] formula,

$$D=\frac{1}{6m^2}\int_{-\infty}^{\infty}dt\,\langle \vec{p}_1(t)\cdot\vec{p}_1\rangle . \quad (7.7)$$

Substitution of the matrix representation (7.6) into this last expression (7.7) yields the following result for the self-diffusion constant:

$$D=\frac{1}{6m\beta}\int_{-\infty}^{\infty}dt\Big(\lim_{k\to 0}\{G^{100}_{100}(\vec{k},t)+G^{010}_{010}(\vec{k},t)+G^{001}_{001}(\vec{k},t)\}\Big), \quad (7.8)$$

which becomes, by use of the Fourier transform (7.4),

$$D=\lim_{\omega\to 0}\lim_{k\to 0}\frac{1}{6m\beta}[G^{100}_{100}(\vec{k},\omega)+G^{010}_{010}(\vec{k},\omega)+G^{001}_{001}(\vec{k},\omega)]. \quad (7.9)$$

Thus we have obtained three relations [(7.3), (7.6), and (7.9)] which connect our matrix versions of the self-correlation function Γ with measurable physical quantities. Note that physically interesting quantities are determined by the first two momentum moments, relating to the density and velocity current, a fact which is known from hydrodynamics. The present formulation differs from hydrodynamics in that instead of closing off the hierarchy with the energy density term, the third momentum moment, we shall attempt an approximate solution of the GLE which relates all of the moments, thus taking into account all higher moments at least approximately.

VIII. INITIAL VALUE OF THE SECOND DAMPING MATRIX

As was pointed out, the initial value of the first damping matrix has played a central role in previous models of the first GLE. In the same manner, we expect that the initial value of the second damping matrix will play an essential role in any reasonable model of the second GLE. The calculation of this initial value proves to be of excessive length and unenlightening detail; hence only a survey of the derivation will be given here.

From the definition of the second damping matrix (3.6) we obtain for the initial value

$$\varphi_2(\vec{k},\vec{p},\vec{p}';t=0)=\int d\vec{p}''\,\langle\langle F_2(\vec{p}),F_2(\vec{p}'')\rangle\rangle\times\langle\langle F_1(\vec{p}''),F_1(\vec{p}')\rangle\rangle^{-1}. \quad (8.1)$$

Now, the k-dependent terms may be calculated most easily, and we find that

$$\varphi_2(\vec{k},\vec{p},\vec{p}';t=0)-\varphi_2(\vec{k}=0,\vec{p},\vec{p}';t=0)=\frac{k^2}{m\beta}\sum_{nlj}(1-\delta_{n0}\delta_{l0}\delta_{j0})\tilde{b}_{nlj}(\vec{p}')a_{nlj}(\vec{p})\left(1+\frac{n(n+l+j-1)}{n+l+j}-\frac{(n+1)(n+l+j)}{n+l+j+1}\right). \quad (8.2)$$

It is the k-independent terms which are the most difficult to calculate, since these all involve complicated configurational averages of the fourth order in the force. After a lengthy calculation, one obtains the following result for the initial value:

$$\begin{aligned}\varphi_2(\vec{k},\vec{p},\vec{p}'';t=0)=&\sum_{nlj}(1-\delta_{n,0}\delta_{l0}\delta_{j0})\tilde{b}_{nlj}(\vec{p}'')\\ &\times\Big\{a_{nlj}(\vec{p})\Big[\Gamma_0+\frac{k^2}{m\beta}+\Gamma_1(n+l+j)+\Gamma_2\frac{n(n-1)+l(l-1)+j(j-1)}{n+l+j}\\ &\quad+\frac{k^2}{m\beta}\left(\frac{n(n+l+j-1)}{n+l+j}-\frac{(n+1)(n+l+j)}{n+l+j+1}\right)\Big]\\ &\quad+\Sigma_1\left(\frac{[12-6(n+l+j)]}{n+l+j}[n(n-1)a_{n-2,lj}(\vec{p})+l(l-1)a_{n,l-2,j}(\vec{p})+j(j-1)a_{nl,j-2}(\vec{p})]\right.\\ &\quad\left.-\tfrac{3}{2}[a_{n+2,lj}(\vec{p})+a_{n,l+2,j}(\vec{p})+a_{nl,j+2}(\vec{p})]\right)\\ &\quad+\frac{\Gamma_2}{n+l+j}\Big(n(n-1)[a_{n-2,l+2,j}(\vec{p})+a_{n-2,l,j+2}(\vec{p})]+l(l-1)[a_{n+2,l-2,j}(\vec{p})+a_{n,l-2,j+2}(\vec{p})]\\ &\quad+j(j-1)[a_{n+2,l,j-2}(\vec{p})+a_{n,l+2,j-2}(\vec{p})]\Big)\Big\}, \end{aligned} \quad (8.3)$$

where

$$\Gamma_0 = (c_0 - 2c_3 + c_4 - 2c_1)/m\beta D(0), \tag{8.4}$$

$$\Gamma_1 = (3c_3 + 3c_4 + 2c_1)/m\beta D(0) - \beta D(0)/m, \tag{8.5}$$

$$\Gamma_2 = (3c_4 + c_1)/m\beta D(0), \tag{8.6}$$

$$\Sigma_1 = c_1/m\beta D(0), \tag{8.7}$$

and the c's are defined by the following configurational averages:

$$\langle(\partial_1^l \partial_1^j F_1^k) F_1^n\rangle = c_1(\delta_{jk}\delta_{ln} + \delta_{lj}\delta_{kn} + \delta_{lk}\delta_{jn}), \tag{8.8}$$

$$\langle(\partial_1^j F_1^k)(\partial_1^l F_1^n)\rangle = c_4(\delta_{nj}\delta_{lk} + \delta_{nk}\delta_{lj}) + c_3\delta_{jk}\delta_{ln}, \tag{8.9}$$

where the indices refer to the Cartesian axes. This simplification is a direct result of the use of spherically symmetric interparticle potentials which we have assumed. It is convenient to define those parts of c_3 and c_4 above which result from pair correlations alone. Neglecting the triplet correlations in the last result (8.9), we define

$$(N-1)\langle(\partial_1^j F_{12}^k)(\partial_1^l F_{12}^n)\rangle = \bar{c}_4(\delta_{nj}\delta_{lk} + \delta_{nk}\delta_{lj}) + \bar{c}_3\delta_{jk}\delta_{ln} \tag{8.10}$$

and

$$c_0 = \bar{c}_3 + 4\bar{c}_4. \tag{8.11}$$

Comparing the result (8.3) for the initial value of the second damping matrix with the expansion for the initial value of the first damping matrix (4.13), we see that there is a great deal more information contained in Eq. (8.3). It may be demonstrated that our knowledge of the two frequency matrices $i\Omega_1$, and $i\Omega_2$, and the initial values of the two damping matrices $\varphi_1(t=0)$ and $\varphi_2(t=0)$ is equivalent to the first four sum rules on the original autocorrelation function $\Gamma(\vec{k}, \vec{p}, \vec{p}'; t)$.

IX. EQUILIBRIUM CORRELATIONS

At this point we shall give the explicit results for the equilibrium correlations defined above. First we introduce the radial derivatives

$$J(R) = \frac{1}{R}\frac{dV}{dR}, \quad K(R) = \frac{1}{R}\frac{dJ}{dR}, \quad L(R) = \frac{1}{R}\frac{dK}{dR}, \quad M(R) = \frac{1}{R}\frac{dL}{dR}, \tag{9.1}$$

where $V(R)$ is the assumed pair potential. In our application to liquid argon we shall take $V(R)$ to be the Lennard-Jones (6-12) potential,

$$V(R) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6], \tag{9.2}$$

with $\sigma = 3.40$ Å and $\epsilon/k = 120°$. In the remainder of this section we shall express the results first for a general potential $V(R)$ using the definitions (9.1). Second, we give explicit results for the Lennard-Jones potential. In the latter case we make the integrals dimensionless by the change of variable

$$R = r\sigma. \tag{9.3}$$

Then

$$D(0) = (4\pi n/\beta)\int_0^\infty dR\, g(R)[R^2 J(R) + \tfrac{1}{3}R^4 K(R)] \tag{9.4}$$

$$= (32\pi n\epsilon\sigma/\beta)\int_0^\infty dr\, g(r\sigma)(22/r^{12} - 5/r^6), \tag{9.5}$$

where $g(R)$ is the pair-correlation function, and

$$c_1 = \frac{4\pi n}{\beta}\int_0^\infty dR\, g(R)[R^2 K(R) + \tfrac{2}{3}R^4 L(R) + \tfrac{1}{15}R^6 M(R)] \tag{9.6}$$

$$= \frac{128\pi n\epsilon}{5\beta\sigma}\int_0^\infty dr\, g(r\sigma)\left(\frac{1001}{r^{14}} - \frac{70}{r^8}\right). \tag{9.7}$$

The calculation of the triplet-correlations contribution to c_3 and c_4 is a difficult problem. For the numerical calculations we have neglected these triplet correlations hoping that the pair correlations dominate (this implies that the results of the calculation are best applied to dense gases):

$$c_3 \approx \bar{c}_3; \quad c_4 \approx \bar{c}_4, \tag{9.8}$$

$$\bar{c}_3 = 4\pi n\int_0^\infty dR\, g(R) \times [R^2 J(R) + \tfrac{2}{3}R^4 J(R)K(R) + \tfrac{1}{15}R^6 K(R)] \tag{9.9}$$

$$= \frac{768\pi n\epsilon^2}{5\sigma}\int_0^\infty dr\, g(r\sigma)\left(\frac{284}{r^{26}} - \frac{68}{r^{20}} - \frac{1}{r^{14}}\right) \tag{9.10}$$

and

$$\bar{c}_4 = \frac{4\pi n}{15}\int_0^\infty dR\, R^6 g(R)K^2(R) \tag{9.11}$$

$$= \frac{12\,228\pi n\epsilon^2}{5\sigma}\int_0^\infty dr\, g(r\sigma)\left(\frac{49}{r^{26}} - \frac{28}{r^{20}} + \frac{4}{r^{14}}\right), \tag{9.12}$$

and c_0 is given in Sec. VIII. The fact that the configurational correlations may be reduced by partial integration to terms dependent only on the triplet- and pair-correlation function results from the fortuitous fact that we are generally calculating correlations of the total force on a single particle. The reduction occurs because of a property of the

canonical distribution function,

$$\vec{\nabla}_1 e^{-\beta V} = \beta \vec{F}_1 e^{-\beta V}. \tag{9.13}$$

The correlations above still contain information about the simultaneous interaction of five particles just as the mean-square force $D(0)$ pertains to the interaction of three particles.

X. FIRST APPROXIMATION TO THE SECOND GENERALIZED LANGEVIN EQUATION

The only information which we have relating to the second damping matrix is its initial value. In order to avoid making further assumptions about the time dependence of the second damping matrix we shall approximate the entire convolution term in the second GLE as

$$\int_0^t d\tau\, \mathcal{G}^{ihm}_{n'l'j'}(\vec{k},\tau)\mathfrak{M}^{n'l'j'}_{ihm}(\vec{k},t-\tau) \sim t\mathcal{G}^{ihm}_{n'l'j'}(\vec{k},0)\mathfrak{M}^{n'l'j'}_{ihm}(\vec{k},t). \tag{10.1}$$

This is correct at small times and it decays to zero at long times because of the Gaussian-like behavior it induces on the first damping matrix. Use of equation (10.1) yields an approximate second GLE of the form

$$\begin{aligned}
&\frac{\partial}{\partial t}\mathfrak{M}^{n'l'j'}_{nlj}(\vec{k},t) - ik\left(\frac{2}{m\beta}\right)^{1/2}\left[\tfrac{1}{2}\mathfrak{M}^{n'l'j'}_{n-1,lj}(\vec{k},t) + \frac{(n+1)(n+l+j)}{n+l+j+1}\mathfrak{M}^{n'l'j'}_{n+1,lj}(\vec{k},t)\right] \\
&\quad + t\mathfrak{M}^{n'l'j'}_{nlj}(\vec{k},t)\left[\Gamma_0 + \frac{k^2}{m\beta} + \Gamma_1(n+l+j) + \Gamma_2\frac{n(n-1)+l(l-1)+j(j-1)}{n+l+j} + \frac{k^2}{m\beta}\left(\frac{n(n+l+j-1)}{n+l+j} - \frac{(n+1)(n+l+j)}{n+l+j+1}\right)\right] \\
&\quad - t\Sigma_1\left(\frac{6(n+l+j)}{n+l+j+2}\left[(n+1)(n+2)\mathfrak{M}^{n'l'j'}_{n+2,lj}(\vec{k},t) + (l+1)(l+2)\mathfrak{M}^{n'l'j'}_{n,l+2,j}(\vec{k},t) + (j+1)(j+2)\mathfrak{M}^{n'l'j'}_{nl,j+2}(\vec{k},t)\right]\right. \\
&\qquad \left. + \tfrac{3}{2}\left[\mathfrak{M}^{n'l'j'}_{n-2,lj}(\vec{k},t) + \mathfrak{M}^{n'l'j'}_{n,l-2,j}(\vec{k},t) + \mathfrak{M}^{n'l'j'}_{n,l,j-2}(\vec{k},t)\right]\right) \\
&\quad + t\Gamma_2\left(\frac{(n+1)(n+2)}{n+l+j}\left[\mathfrak{M}^{n'l'j'}_{n+2,l-2,j}(\vec{k},t) + \mathfrak{M}^{n'l'j'}_{n+2,l,j-2}(\vec{k},t)\right] + \frac{(l+1)(l+2)}{n+l+j}\left[\mathfrak{M}^{n'l'j'}_{n-2,l+2,j}(\vec{k},t) + \mathfrak{M}^{n'l'j'}_{n,l+2,j-2}(\vec{k},t)\right]\right. \\
&\qquad \left. + \frac{(j+1)(j+2)}{n+l+j}\left[\mathfrak{M}^{n'l'j'}_{n-2,l,j+2}(\vec{k},t) + \mathfrak{M}^{n'l'j'}_{n,l-2,j+2}(\vec{k},t)\right]\right) = 0,
\end{aligned} \tag{10.2}$$

where we have made the convention that

$$\mathfrak{M}^{n'l'j'}_{nlj}(\vec{k},t) = 0 \quad \text{if } n=l=j=0, \text{ or any } n,l,j \text{ is negative.} \tag{10.3}$$

Equation (10.3) is a trivial result of the assumption (10.1). Its use as a convention allows many cumbersome Kronecker deltas to be omitted and the "simplified" equation (10.2) results. The first condition, that $\mathfrak{M}^{n'l'j'}_{000}(\vec{k},t) = 0$, is important because it ensures particle-number conservation at all times.

We then obtain a solution of the following form:

$$\begin{aligned}
\mathfrak{M}^{n'l'j'}_{nlj}(\vec{k},t) &= \exp\left[-\frac{t^2}{2}\left(\Gamma_0 + \frac{k^2}{m\beta}\right)\right] \\
&\quad \times \sum_{\mu=0}^{\infty} t^{\mu} N^{n'l'j'}_{nlj}[k,\mu].
\end{aligned} \tag{10.4}$$

The first coefficient in this expansion is the initial value obtained previously, namely (5.5). The second coefficient is

$$\begin{aligned}
N^{n'l'j'}_{nlj}[k,1] &= ik\left(\frac{2}{m\beta}\right)^{1/2}\frac{\beta D(0)}{m} \\
&\quad \times\left[\tfrac{1}{2}(n+l+j-1)\delta_{n-1,n'}\delta_{ll'}\delta_{jj'}\right. \\
&\quad \left. + (n+1)(n+l+j)\delta_{n+1,n'}\delta_{ll'}\delta_{jj'}\right].
\end{aligned} \tag{10.5}$$

Higher-order coefficients become exceedingly complicated and we shall not present expressions for them although several have been used in the calculations below. All of the odd order terms $N[k, 2n+1]$ are proportional to a power of k. Thus, the $k=0$ limit makes the theory much more tractible and we work in that limit below. This restricts us to a discussion of the velocity autocorrelation function. The $k=0$ limit of the first GLE (5.7) is clearly given by

$$\frac{\partial}{\partial t}G^{n'l'j'}_{nlj}(0,t) + \sum_{ihm}\int_0^t d\tau\, \mathfrak{M}^{ihm}_{nlj}(0,\tau)G^{n'l'j'}_{ihm}(0,t-\tau) = 0. \tag{10.6}$$

Now we have a solution for Eq. (10.4) of which we have calculated the $k=0$ limit through $N[0,4]$, the third nonvanishing term. The analytical results for $N[0,2]$ and $N[0,4]$ are quite complicated and we have had to resort to a perturbation solution of the first GLE (10.6), treating $N[0,2]$ and $N[0,4]$ as perturbations on $N[0,0]$ [the initial value (5.5)].

We shall be solving for the momentum autocor-

relation function which can be written

$$\langle \vec{p}_1(t)\cdot\vec{p}_1\rangle = (m/\beta)G(0,t), \tag{10.7}$$

where

$$G(0,t) = G^{100}_{100}(0,t) + G^{010}_{010}(0,t) + G^{001}_{001}(0,t). \tag{10.8}$$

In fact, we actually present a perturbation series for the Fourier transform:

$$G(0,\omega) = \int_{-\infty}^{\infty} dt\, e^{-i\omega t} G(0,t), \tag{10.9}$$

$$G(0,\omega) = G[0,\omega;0] + G[0,\omega;2] + G[0,\omega;4] + \cdots . \tag{10.10}$$

The zeroth-order solution is

$$G[0,\omega;0] = \frac{6mA_0(\omega)}{\beta D(0)\{A_0^2(\omega) + [B_0(\omega) - m\omega/\beta D(0)]^2\}}, \tag{10.11}$$

where

$$A_0(\omega) = \int_0^{\infty} dt\, e^{-t^2\Gamma_0/2}\cos\omega t, \qquad B_0(\omega) = \int_0^{\infty} dt\, e^{-t^2\Gamma_0/2}\sin\omega t, \tag{10.12}$$

and the second-order solution is

$$G[0,\omega;2] = \frac{3m\Gamma_1}{\beta D(0)}\,\frac{A_2(\omega)\{A_0^2(\omega) - [B_0(\omega) - m\omega/\beta D(0)]^2\}}{\{A_0^2(\omega) + [B_0(\omega) - m\omega/\beta D(0)]^2\}^2} + \frac{6m\Gamma_1}{\beta D(0)}\,\frac{B_2(\omega)A_0(\omega)[B_0(\omega) - m\omega/\beta D(0)]}{\{A_0^2(\omega) + [B_0(\omega) - m\omega/\beta D(0)]^2\}^2}, \tag{10.13}$$

where

$$A_2(\omega) = \int_0^{\infty} dt\, t^2 e^{-t^2\Gamma_0/2}\cos\omega t, \qquad B_2(\omega) = \int_0^{\infty} dt\, t^2 e^{-t^2\Gamma_0/2}\sin\omega t. \tag{10.14}$$

Because of its length we shall not detail the fourth-order term $G[0,\omega;4]$, but we have used it in the calculations and given its hydrodynamic limit below.

We observe that the self-diffusion constant D is given by

$$D = \lim_{\omega\to 0}\frac{G(0,\omega)}{6m\beta}, \tag{10.15}$$

which leads, after application of the perturbation series above (10.10), to the form

$$D = \frac{1}{\beta^2 D(0)}\left[\left(\frac{2\Gamma_0}{\pi}\right)^{1/2} + \frac{\Gamma_1}{(2\pi\Gamma_0)^{1/2}} - \frac{(\Gamma_1^2 + 30\Sigma_1^2)}{(32\pi\Gamma_0^3)^{1/2}} + \cdots\right]. \tag{10.16}$$

XI. RESULTS AND CONCLUSIONS

The numerical results that we have obtained from the approximate solution presented in Sec. X depend quite heavily on our ability to calculate the equilibrium-correlation constants introduced in Sec. VIII. Our calculations have been carried out with the numerical-pair-correlation functions of Verlet[27] for nine sets of data (three distinct densities $n = 1.65, 1.91, 2.16\times10^{22}$ cm^{-3}, and three different temperatures) although we present graphical results at only the highest density and, usually, at $T = 86.3$°K. The latter condition is of particular interest since it corresponds most closely to the conditions of recent neutron-scattering experiments and to conditions leading to a negative region in the velocity autocorrelation function of several molecular dynamics (MD) calculations. The results of the present theory are to be compared to the MD results.

Heretofore, the most successful model has been a simple Gaussian approximation for the first damping matrix. In fact, our first term in Eq. (10.10), $G[0,\omega;0]$, is equivalent to a Gaussian approximation. When the Gaussian approximation is compared with MD results, it is found (Fig. 1) that the minimum of the velocity autocorrelation function invariably sinks too low in the negative region; the velocity autocorrelation function is also predicted to possess a negative region for densities lower than the liquid density, whereas

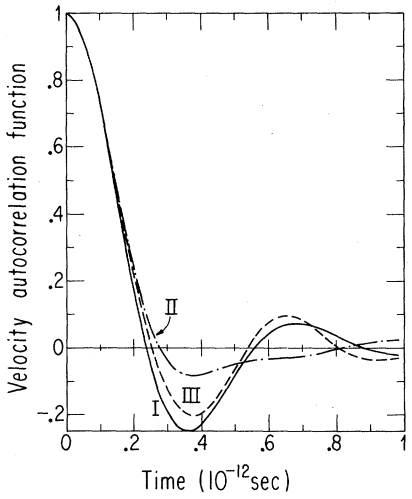

FIG. 1. Normalized-velocity autocorrelation function versus time at density $n = 2.16\times10^{22}$ cm^{-3} and temperature $T = 86.3$ °K. The curve labeled I is the Gaussian approximation while II and III represent the second and third approximations, respectively.

the MD curves no longer contain a negative region. Additionally, the Gaussian-model autocorrelation function oscillates between positive and negative values, unlike the MD results.

Our second approximation, which contains the first perturbation $\{G[0,\omega;2]$ in Eq. (10.10)$\}$ in addition to the Gaussian, is much more like the MD results except that the predicted curve seems to be even less oscillatory than the MD. The third approximation, resulting from the inclusion of the third nonvanishing term $G[0,\omega;4]$ invariably seems more like the Gaussian approximation than it does the second approximation. It does improve on the Gaussian approximation in that the minima do not go as far negative; however, there remain strong oscillations.

Disregarding their depth, the locations in time of the minima in all three approximations coincide quite closely with the MD. The results also have qualitatively the correct temperature and density dependence; the velocity autocorrelation functions for higher densities and higher temperatures decay faster than those for lower values and the minima move upward with increased temperature at constant density. These temperature effects may be observed in Fig. 2, which is based on our third approximation.

Now consider the Fourier transform of the velocity autocorrelation function, the power spectrum given in Fig. 3. Like past theories, the first approximation contains the "shoulder" of Rahman's spectrum at about 8×10^{12} sec^{-1}. In Rahman's results this "shoulder" occurs on the tail of the dominant peak at $(2.5-3)\times10^{12}$ sec^{-1}. Our results do not display this dominant peak, though the second approximation does suggest its presence. If this peak were present the perturbation solution we obtain would cause it to build up quite slowly as successive perturbation terms are added. It is clear that our spectrum [(10.11) and (10.13)] contains only the single-resonance denominator of the original approximation. Our results are inconclusive so far as this major peak is concerned, because of the slow convergence of the perturbation expansion.

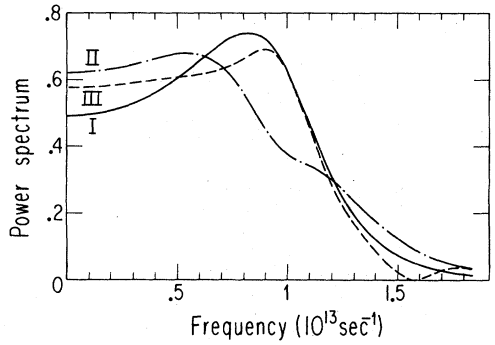

FIG. 3. Power spectrum of the normalized-velocity autocorrelation function versus frequency in all three approximations at density $n=2.16\times10^{22}$ cm^{-3} and temperature $T=86.3$ °K.

The results of the three approximations for the self-diffusion constant are shown in Fig. 4 for the highest density. The MD calculations of Levesque and Verlet[27] lie predominantly between our first and third approximation. Levesque and Verlet find empirically that at constant density the self-diffusion constant is essentially linear in the tem-

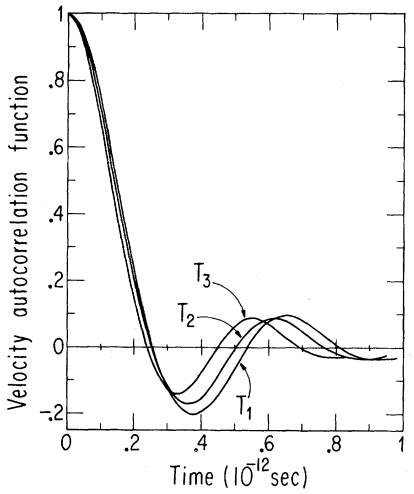

FIG. 2. Normalized-velocity autocorrelation function versus time at constant density, $n=2.16\times10^{22}$ cm^{-3}, for three different temperatures: $T_1=86.3$ °K, $T_2=105.6$ °K, $T_3=152.7$ °K. All three curves are calculated in the third approximation.

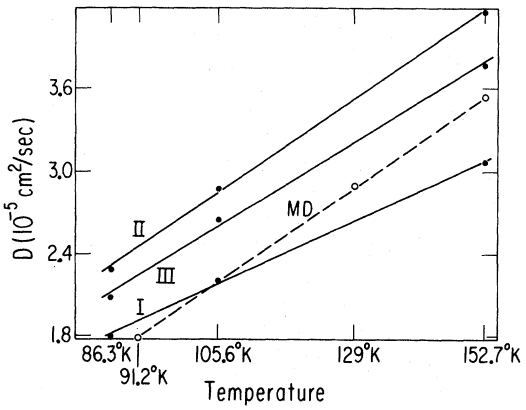

FIG. 4. Self-diffusion constant as a function of temperature at fixed density $n=2.16\times10^{22}$ cm^{-3}. The dots are our theoretical results while the crosses represent molecular dynamics results of Levesque and Verlet (Ref. 4).

perature. We have checked this result with our calculations at the three densities and to each order of perturbation theory separately. In each case the temperature dependence is quite linear, as is demonstrated in Fig. 4 for the highest density. This is remarkable considering the nonlinear combination of equilibrium constants (10.16) given for the self-diffusion constant and the long numerical calculation of these constants. Note that the slope of the second approximation is in good agreement with the MD while they differ by an additive temperature-independent constant.

There are several directions in which this theory could be improved. First, a reasonable model for the time decay of the second damping matrix is needed to replace the approximation (10.1). Second, great care must be taken in solving the GLE's resulting from such an approximation to the second damping matrix in order to allow the dominant structure of the power spectrum to be observed. The power-series solution used in this work is instructive, but converges far too slowly to make unambiguous numerical predictions. At this second stage of development we believe that models of the time dependence are warranted and we agree with Akcasu, Corngold, and Duderstadt that simple models of the time dependence offer the best hope of making progress on the general problem. The time dependence is generally known through the molecular dynamics results of Rahman, Levesque, and Verlet, and useful models should not be difficult to construct.

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