PHYSICAL REVIEW A VOLUME 13, NUMBER 3 MARCH 1976

Direct variational approach to the calculation of dynamic structure functions

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(Received 28 October 1975)

We consider the problem of calculating the dynamic structure function $S(k,\omega)$ via a properly posed initial-value problem for a linear kinetic equation. A variational principle is introduced and shown to give a direct bounded estimate of $S(k,\omega)$. The variational trial functions for the problem are the space-time transforms of the phase-space correlation function. The choice of such trial functions are discussed and general expressions for $S(k,\omega)$ are developed which are applicable to simple gases. Numerical results are presented for the specific case of hard spheres, these results being compared to previous first-principle calculations based upon kinetic equations with and without the inclusion of memory effects. Excellent agreement with previous results, at all ratios of fluctuation wavelength to mean free path, is obtained with considerably less computational complexity. This computational efficiency of the variational approach suggests that it should be a valuable technique, from the standpoint of feasibility, in attempts at first-principle calculations for more complex many-body systems. In this regard, further study and improvement of the variational techniques themselves appear to be warranted.

I. INTRODUCTION

It is widely known that contributions to observed spectral line shapes that relate to fluctuations in many-particle systems can be described in terms of time-correlation functions.[1] The time-correlation function description of the decay of fluctuations is valid in all regimes of fluctuation wavelengths and frequencies. Of current interest are the transition regimes in which the wavelengths and lifetimes of the fluctuations are comparable to the spatial and time intervals over which collisional equilibration occurs. The behavior of the time-correlation function in these transition regimes depends upon the details of the collision dynamics of the many-particle system. Such transition regimes for the density-density correlation functions of gases and liquids are presently accessible by light and neutron scattering experiments.[2] Correspondingly, the problem of calculating time-correlation functions for many-particle systems from microscopic theory has become an important theoretical problem. In particular, a calculation of fundamental importance is that for a moderately dilute gas. For such a system, detailed calculations may be performed without a totally forbidding amount of labor. Several such calculations of the density-density correlation function, or more specifically, $S(k,\omega)$, its Fourier transform in space and time, have been performed based upon the Boltzmann equation.[3-6] The Boltzmann equation, however, is intrinsically defective at high frequencies and short wavelengths because its asymptotic treatment of atomic collisions ignores those incomplete collisions which occur on spatial and time scales comparable to interatomic dimensions and the duration of collisions, respectively.

More recently, detailed calculations of the dynamic structure function $S(k,\omega)$ have been performed for moderately dilute gases based upon kinetic equations which incorporate memory effects into the collision operator.[7] These calculations quantitatively exhibit the deviation of the dynamic structure function from the predictions of the theories based upon the Boltzmann equation. Even in the case of moderately dilute gases, the calculation of $S(k,\omega)$ is quite complex. These calculations have primarily consisted of the kinetic modeling of either the Boltzmann collision operator or the memory function involving matrix representations of dimension 23 or greater.

In the present paper, we consider an alternative approach to the calculation of $S(k,\omega)$. A principal objective of the method is to simplify the computation without a loss of accuracy. In this regard, the approach is proposed as a feasible one for eventually performing detailed calculations on more complex many-particle systems. Here we shall consider specifically the case of moderately dilute gases for which existing detailed calculations may be used as a test of the accuracy of the calculation in the various ranges of fluctuation wavelengths and frequencies. The approach is based upon the use of a "direct" variational method for calculating the dynamic structure function.[8,9] In this variational method, the trial functions are the Fourier transforms of the phase-space correlations. The variational functional itself is physically equivalent to $S(k,\omega)$, with the variational approximation giving a bounded estimate of $S(k,\omega)$, accurate to second order in the errors in our trial phase-space correlation functions.

In Sec. II, a discussion of the variational formulation of the dynamic-structure-function calculation is given. The development given there is general in the sense of its applicability to arbitrary linear collision operators, including those with memory effects incorporated. The choice of trial functions is discussed in Sec. III. This choice is important for the obvious reason that the estimated $S(k,\omega)$ depends upon terms of second order in the errors made in the trial function. It is important in the sense that this choice actually distinguishes the variational method from other methods within the general class called moment methods.[8,10] The detailed calculation of $S(k,\omega)$ is given in Sec. IV. Results are first given in a form which may be readily applied to a given collision model. Numerical results are given in Sec. V for the case of hard spheres. Section VI gives a summary of the present calculation and a discussion of its implications.

II. DEFINITIONS AND VARIATIONAL FORMULATION

Our starting point is the linearized Boltzmann equation

$$\frac{\partial f(\vec{v},\vec{r},t)}{\partial t}+\vec{v}\cdot\frac{\partial f(\vec{v},\vec{r},t)}{\partial \vec{r}}=\hat{\mathcal{J}}[f(\vec{v},\vec{r},t)], \qquad (2.1)$$

where $\hat{\mathcal{J}}$ is a linearized collision operator. The perturbed distribution function $f(\vec{v},\vec{r},t)$ is defined according to

$$F(\vec{v},\vec{r},t)\equiv\Phi(v)+\delta F(\vec{v},\vec{r},t)\equiv\Phi(v)[1+f(\vec{v},\vec{r},t)] \qquad (2.2)$$

in terms of the total distribution function $F(\vec{v},\vec{r},t)$ and the Maxwellian distribution

$$\Phi(v)=(\beta/\pi)^{3/2}e^{-\beta v^2}, \qquad (2.3)$$

where $\beta=m/2k_BT$. We are interested in the density-density correlation function

$$C(k,t)=\langle\delta n^*(k,0)\delta n(k,t)\rangle_{\text{eq}} \qquad (2.4)$$

or more directly its transform

$$C(k,\sigma)\equiv\int_0^\infty dt\,e^{-\sigma t}C(k,t) \qquad (2.5)$$

to which $S(k,\omega)$ is related via

$$S(k,\omega)=2\,\text{Re}C(k,\sigma=i\omega)\,. \qquad (2.6)$$

The average denoted in (2.4) is over an equilibrium ensemble.

As is well known, the density-density correlation function may be calculated from a suitably defined initial-value problem for kinetic equations such as (2.1).[11,12] The initial-value problem appropriate to the calculation of $S(k,\omega)$ is [3,4]

$$\delta F(\vec{v},\vec{r},t=0)=\Phi(v)f(\vec{v},\vec{r},t=0)=\Phi(v)\delta^3(\vec{r})\,. \qquad (2.7)$$

This represents an excess thermalized particle located at the origin at $t=0$ and handles the problem of ensemble averaging. The density-density correlation function is then

$$C(\vec{k},t)=\int d^3\vec{v}\,\delta F(\vec{v},\vec{k},t)=\int d^3\vec{v}\,\Phi(v)f(\vec{v},\vec{k},t), \qquad (2.8)$$

so that

$$C(\vec{k},\sigma)=\int d^3\vec{c}\,\Phi(c)f(\vec{c},\vec{k},\sigma), \qquad (2.9)$$

where we've introduced the dimensionless velocity $c=\beta^{1/2}v$. The transformed distribution function is defined according to

$$f(\vec{c},\vec{k},\sigma)\equiv\int d^3\vec{r}\int_0^\infty dt\,e^{-i\vec{k}\cdot\vec{r}}e^{-\sigma t}f(\vec{c},\vec{r},t) \qquad (2.10)$$

and satisfies the transformed kinetic equation

$$\hat{\mathcal{L}}f(\vec{c},\vec{k},\sigma)=1\,, \qquad (2.11)$$

where

$$\hat{\mathcal{L}}\equiv(\sigma+\epsilon c_k)-\hat{\mathcal{J}}\,, \qquad (2.12)$$

with $\epsilon\equiv ik/\beta^{1/2}$. The initial condition (2.7) has been incorporated into (2.11).

In the present analysis, we shall bypass attempts to explicitly solve the transformed kinetic equation (2.11). Rather, we proceed directly to the physical quantity of interest, $C(k,\sigma)$ or $S(k,\omega)$ by a direct variational method. To do this we introduce the functional

$$I[\tilde{f}]\equiv\langle 1,\tilde{f}\rangle+\langle\tilde{f},1\rangle-\langle\tilde{f},\hat{\mathcal{L}},\tilde{f}\rangle\,, \qquad (2.13)$$

where $\tilde{f}$ denotes a trial solution of (2.11) and our scalar product is defined

$$\langle a,b\rangle\equiv\int d^3\vec{c}\,\Phi(c)a^*(c)b(c)\,. \qquad (2.14)$$

Our motivation for the use of (2.13) may be made clear by several observations. First we note that for $\tilde{f}=f$ $(\equiv f_{\text{exact}})$, we have by virtue of (2.11)

$$I[f]=\langle 1,f\rangle=C(k,\sigma) \qquad (2.15)$$

or

$$S(k,\omega)=2\,\text{Re}I[f(c,k,\sigma=i\omega)]\,. \qquad (2.16)$$

Thus the real part of our functional is physically equivalent to the dynamic structure function that we seek. Secondly, the functional $I[\tilde{f}]$ constitutes a variational principle, with the vanishing of first-order variations with respect to f implying the kinetic equation (2.11) as the associated Euler-Lagrange equation. To see this, we put $\tilde{f}=f+\delta f$, where δf is the error in our selected trial function, into (2.13). Using (2.11) we obtain the intermediate result

$$I[\tilde{f}]=\langle 1, f\rangle+\langle 1, \delta f\rangle-\langle f, \hat{\mathfrak{L}}\delta f\rangle-\langle \delta f, \hat{\mathfrak{L}}\delta f\rangle\,. \tag{2.17}$$

Using the fact that $\hat{\mathfrak{J}}$ is self-adjoint and that for $\sigma=i\omega$, $\sigma+\epsilon c_k$ is pure imaginary, we have $\hat{\mathfrak{L}}^{\dagger}f^*=1$, so that the second and third terms of (2.17) cancel, leaving

$$I[\tilde{f}]=C(k,\sigma)-\langle \delta f, \hat{\mathfrak{L}}\delta f\rangle\,. \tag{2.18}$$

Thus our functional is a variational principle whose Euler-Lagrange equation is the kinetic equation (2.11) and which approximates $C(k,\sigma)$ to within terms of second order in δf.

Though the functional $I[\tilde{f}]$ is not generally bounded, its real part, and thus $S(k,\omega)$, will in fact be bounded. To see this we rewrite (2.18) as

$$I[\tilde{f}]=\langle 1, f\rangle-\langle 1, (\sigma+\epsilon c_k)|\delta f^2|\rangle+\langle 1, (\delta f)^*\hat{\mathfrak{J}}(\delta f)\rangle\,. \tag{2.19}$$

Again with $\sigma+\epsilon c_k$ pure imaginary, we see that

$$\mathrm{Re}I[\tilde{f}]=\mathrm{Re}C(k,\sigma)+\langle 1, (\mathrm{Re}\delta f)\hat{\mathfrak{J}}(\mathrm{Re}\delta f)\rangle +\langle 1, (\mathrm{Im}\delta f)\hat{\mathfrak{J}}(\mathrm{Im}\delta f)\rangle\,. \tag{2.20}$$

Recalling the negative semidefinite character of the linearized Boltzmann collision operator,[13] we see that $\mathrm{Re}I[\tilde{f}]$ yields a lower bound to $S(k,\omega)$.

III. CHOICE OF VARIATIONAL TRIAL FUNCTIONS

As trial functions for our variational calculation we choose the general form,

$$\tilde{f}(\vec{c},k,\sigma)=\sum_{j=0}^{N}A_j(k,\sigma)\Psi_j(\vec{c})\,. \tag{3.1}$$

The complex quantities $A_j(k,\sigma)$ are wavelength- and frequency-dependent variational parameters which will be determined by the Rayleigh-Ritz parameter variation scheme. For the present calculation we specifically choose

$$\Psi_0(\vec{c})=1/(\sigma+\epsilon c_k), \tag{3.2}$$

which is the exact solution of (2.11) in the free-particle limit. We note that this form represents the limiting behavior of the fluctuations in the regimes of extremely high frequencies and/or extremely short wavelengths. For the remaining terms in the expansion (3.1) we employ the first five axially-symmetric Burnett polynomials $\Psi_{rl}(\vec{c})$:[14]

$$\Psi_1(c)\equiv\Psi_{00}(c)=1\,, \tag{3.3a}$$

$$\Psi_2(c)\equiv\Psi_{01}(c)=(2)^{1/2}c_k\,, \tag{3.3b}$$

$$\Psi_3(c)\equiv\Psi_{10}(c)=(\tfrac{2}{3})^{1/2}(\tfrac{3}{2}-c^2)\,, \tag{3.3c}$$

$$\Psi_4(c)\equiv\Psi_{02}(c)=(\tfrac{1}{3})^{1/2}(3c_k^2-c^2)\,, \tag{3.3d}$$

$$\Psi_5(c)\equiv\Psi_{11}(c)=(\tfrac{4}{5})^{1/2}(\tfrac{5}{2}-c^2)c_k\,, \tag{3.3e}$$

for which

$$\langle\Psi_i(c),\Psi_j(c)\rangle=\delta_{ij},\quad i,j>0\,. \tag{3.4}$$

These five polynomials lead to a hydrodynamic description of $S(k,\omega)$ in the Burnett approximation.[15] This contains as a limiting case the Navier-Stokes hydrodynamic description. Our results will first be formulated for a general interatomic force law. In any event however, the first three Burnett functions are eigenfunctions of $\hat{\mathfrak{J}}$ with zero eigenvalue, while the last two are eigenfunctions of $\hat{\mathfrak{J}}$ only for the case of the Maxwell molecule inverse-fifth-force law.

The judiciousness of our choice of trial function will of course ultimately be determined by the accuracy of the calculations. Nonetheless, the choice may be intuitively motivated. Basically (3.1), along with (3.2) and (3.3), represents a mixture of free-particle and hydrodynamic behavior. Intuitively then, the variational procedure, through the wavelength-frequency-dependent variational parameters, admixes hydrodynamic and free-particle behavior in some optimal fashion at each point in the (k,ω) domain of $S(k,\omega)$.[8] As we shall see, the free-particle contribution to the trial function will give increasingly weighted modifications of the $S(k,\omega)$ results in those specific regions in which the Boltzmann equation itself is intrinsically defective, i.e., the regions of high frequency and short wavelength. It may be noted that our choice of trial functions is akin in spirit to the choice of an admixture of the asymptotic up-stream and down-stream solutions made by Mott-Smith in a variational calculation of shock-wave structure.[16]

IV. CALCULATION OF $S(k,\omega)$

With the choice (3.1) of trial functions, our functional becomes

$$I=\sum_{j=0}^{5}A_j\langle 1,\Psi_j\rangle+\sum_{j=0}^{5}A_j^*\langle\Psi_j,1\rangle -\sum_{j=0}^{5}\sum_{l=0}^{5}A_l^*A_j\langle\Psi_l,\hat{\mathfrak{L}}\Psi_j\rangle\,. \tag{4.1}$$

Writing the complex parameters as

$$A_j=B_j+D_j\,, \tag{4.2}$$

where $D_j^* = -D_j$, we obtain

$$I = 2\sum_j (B_j\gamma_j + D_j\bar{\gamma}_j) - \sum_j \sum_l (B_jB_l - D_jD_l + D_jB_l - B_jD_l)\Gamma_{lj}, \quad (4.3)$$

where

$$2\gamma_j \equiv \langle 1, \Psi_j\rangle + \langle \Psi_j, 1\rangle , \quad (4.4)$$

$$2\bar{\gamma}_j \equiv \langle 1, \Psi_j\rangle - \langle \Psi_j, 1\rangle , \quad (4.5)$$

and

$$\Gamma_{lj} \equiv \langle \Psi_l, \hat{\mathfrak{L}}\Psi_j\rangle . \quad (4.6)$$

For complex parameters A_j, our parameter variation scheme becomes

$$\frac{\partial I[\tilde{f}]}{\partial B_j} = 0, \quad j = 0, 1, \ldots, 5 \quad (4.7)$$

and

$$\frac{\partial I[\tilde{f}]}{\partial D_j} = 0, \quad j = 0, 1, \ldots, 5 . \quad (4.8)$$

This yields the set of algebraic equations

$$\sum_{l=0}^{5} (B_l\Lambda_{lj} + D_l\Delta_{jl}) = \gamma_j, \quad j = 0, 1, \ldots, 5 \quad (4.9)$$

and

$$\sum_{l=0}^{5} (B_l\Delta_{jl} + D_l\Lambda_{lj}) = -\bar{\gamma}_j, \quad j = 0, 1, \ldots, 5, \quad (4.10)$$

where

$$2\Delta_{lj} \equiv \Gamma_{lj} - \Gamma_{jl} \quad \text{and} \quad 2\Lambda_{lj} \equiv \Gamma_{lj} + \Gamma_{jl} \quad (4.11)$$

for determining the parameters $\{B_j, D_j\}$. We note that the inclusion of $\Psi_0(c)$ as defined by (3.2) in our trial function means that the expansion (3.1) is not completely in terms of orthonormal functions. As a result, the algebraic equations given by (4.9) and (4.10) are not identical to the algebraic equations that would be obtained by a moment-method solution based upon a finite set of orthogonal polynomials[8] as employed, for example, in Ref. 6. It's clear that $\Psi_0(c)$ contains the complete set of such orthogonal polynomials. With the conditions (4.9) and (4.10) we find

$$I[\tilde{f}] = \sum_j (B_j\gamma_j + D_j\bar{\gamma}_j). \quad (4.12)$$

Evaluation of the γ_j's and the $\bar{\gamma}_j$'s gives

$$\gamma_0 = -(i/\epsilon)\pi^{1/2}\exp(-\sigma^2/\epsilon^2), \quad \gamma_0 = 1, \qquad \bar{\gamma}_0 = n_F + (i/\epsilon)\pi^{1/2}\exp(-\sigma^2/\epsilon^2), \quad (4.13)$$

and

$$\gamma_j = 0, \quad j \neq 1, 0; \quad \bar{\gamma}_j = 0, \quad j \neq 0, \quad (4.14)$$

where $n_F(k,\sigma)$ is the free-particle density response, related to the tabulated plasma dispersion function[17] Z according to

$$n_F(k,\sigma) = \langle 1, (\sigma + \epsilon c_k)^{-1}\rangle = (1/\epsilon)Z(-\sigma/\epsilon) . \quad (4.15)$$

Thus only three terms contribute to the summation in (3.12), giving

$$I[\tilde{f}] = \gamma_0B_0 + B_1 + \bar{\gamma}_0D_0 . \quad (4.16)$$

The set of 12 equations, (4.9) and (4.10), determining $\{B_j, D_j\}$ has a relatively simple structure owing to the vanishing of many of the coefficients. Specifically, we find that[18]

$$\Delta_{10} = -\Delta_{01} = \Gamma_{10} = -\Gamma_{01} = 1 , \quad (4.17)$$

$$\Gamma_{04} = -\langle\Psi_0, \hat{\mathfrak{J}}\Psi_4\rangle + \langle\Psi_0, (\sigma + \epsilon c_k)\Psi_4\rangle , \quad (4.18)$$

and

$$\Gamma_{05} = -\langle\Psi_0, \hat{\mathfrak{J}}\Psi_5\rangle + \langle\Psi_0, (\sigma + \epsilon c_k)\Psi_5\rangle . \quad (4.19)$$

The remaining nonvanishing elements Δ_{ij} are $\Delta_{04} = -\Delta_{40}$ and $\Delta_{05} = -\Delta_{50}$. For the matrix elements Γ_{ij} we find

$$\Gamma_{02} = \Gamma_{20} = \Gamma_{03} = \Gamma_{30} = \Gamma_{13} = \Gamma_{31} = \Gamma_{14} = \Gamma_{41} = \Gamma_{15} = \Gamma_{51} = \Gamma_{25} = \Gamma_{52} = \Gamma_{34} = \Gamma_{43} = 0 . \quad (4.20)$$

Thus Eqs. (4.13) and (4.14) have the form

$$\vec{\Gamma} \cdot \vec{A} = \vec{X} , \quad (4.21)$$

where

$$A_0, \ldots, A_5 = B_0, \ldots, B_5 \quad (4.22)$$

and

$$A_6, \ldots, A_{11} = D_0, \ldots, D_5 . \quad (4.23)$$

Also

$$X_0 = \gamma_0, \quad X_1 = 1, \quad X_6 = -\gamma_0, \quad X_j = 0, \quad \text{for } j \neq 0, 1, 6, \quad (4.24)$$

and

$$\bar{\Gamma}=\begin{pmatrix}
\Gamma_{00} & 0 & 0 & 0 & \Lambda_{40} & \Lambda_{50} & 0 & -1 & 0 & 0 & \Delta_{04} & \Delta_{05}\\
0 & \sigma & \Gamma_{12} & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0\\
0 & \Gamma_{12} & \sigma & \Gamma_{23} & \Gamma_{24} & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & \Gamma_{23} & \sigma & 0 & \Gamma_{35} & 0 & 0 & 0 & 0 & 0 & 0\\
\Lambda_{04} & 0 & \Gamma_{24} & 0 & \Gamma_{44} & \Gamma_{45} & \Delta_{40} & 0 & 0 & 0 & 0 & 0\\
\Lambda_{05} & 0 & 0 & \Gamma_{35} & \Gamma_{45} & \Gamma_{55} & \Delta_{50} & 0 & 0 & 0 & 0 & 0\\
0 & -1 & 0 & 0 & \Delta_{04} & \Delta_{05} & \Gamma_{00} & 1 & 0 & 0 & \Lambda_{40} & \Lambda_{50}\\
1 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma & \Gamma_{12} & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \Gamma_{12} & \sigma & \Gamma_{23} & \Gamma_{24} & 0\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \Gamma_{23} & \sigma & 0 & \Gamma_{35}\\
\Delta_{40} & 0 & 0 & 0 & 0 & 0 & \Lambda_{04} & 0 & \Gamma_{24} & 0 & \Gamma_{44} & \Gamma_{45}\\
\Delta_{50} & 0 & 0 & 0 & 0 & 0 & \Lambda_{05} & 0 & 0 & \Gamma_{35} & \Gamma_{45} & \Gamma_{55}
\end{pmatrix}, \qquad (4.25)$$

where we've used

$$\Gamma_{11}=\Gamma_{22}=\Gamma_{33}=\sigma\,. \qquad (4.26)$$

The nonzero matrix elements with respect to the Burnett functions, i.e., Γ_{ij} for $i,j>0$, are obtained from the standard kinetic-theory literature.[14] They are

$$\Gamma_{12}=\Gamma_{21}=(1/\sqrt{2})\epsilon\,,\quad \Gamma_{23}=\Gamma_{32}=-(1/\sqrt{3})\epsilon\,,$$
$$\Gamma_{24}=\Gamma_{42}=\sqrt{\tfrac{2}{3}}\epsilon\,,\quad \Gamma_{35}=\Gamma_{53}=\sqrt{\tfrac{5}{6}}\epsilon\,,$$
$$\Gamma_{45}=\Gamma_{54}=-\sqrt{\tfrac{4}{15}}\epsilon\,,\quad \Gamma_{44}=\sigma-J_{44},\quad \Gamma_{55}=\sigma-J_{55}\,, \qquad (4.27)$$

where J_{44} and J_{55} are standard kinetic-theory collision integrals defined as[19]

$$J_{44}=\langle\Psi_4,\hat{\mathcal{J}}\Psi_4\rangle \qquad (4.28)$$

and

$$J_{55}=\langle\Psi_5,\hat{\mathcal{J}}\Psi_5\rangle \qquad (4.29)$$

and formally related to the viscosity η and the thermal conductivity κ according to[14]

$$J_{44}=-mn/2\beta\eta \qquad (4.30)$$

and

$$J_{55}=-\tfrac{5}{4}nk_B/\beta\kappa\,. \qquad (4.31)$$

These are also tabulated for various intermolecular forces.[14] The remaining matrix elements for which expressions are required are

$$\Gamma_{00}=-n_F-(i/\epsilon)2\pi^{1/2}\exp(-\sigma^2/\epsilon^2)-J_F\,, \qquad (4.32)$$

where

$$J_F=\langle\Psi_0,\hat{\mathcal{J}}\Psi_0\rangle\,, \qquad (4.33)$$

Γ_{40}, and Γ_{50}. The evaluation of these integrals requires the choice of a specific model and subsequent representation of the collision operator $\hat{\mathcal{J}}$. For present purposes a convenient representation of $\hat{\mathcal{J}}$ is

$$\hat{\mathcal{J}}=\sum_i\sum_j|\Psi_i\rangle J_{ij}\langle\Psi_j|,\quad i,j>0 \qquad (4.34)$$

in terms of the Burnett function used in the representation of our trial function. The matrix elements are tabulated for various collision models. The first nonvanishing matrix element is J_{44}. Higher-order matrix elements may be related to J_{44}. This relationship between higher-order matrix elements and J_{44} is the same for all molecular models through seventh order. Thus to obtain results which are model dependent, we require a representation of $\hat{\mathcal{J}}$ of dimension 8 or greater. As we'll see the nine-dimensional representation is sufficient to give accurate results for $S(k,\omega)$. Our remaining integrals then become

$$\Gamma_{40}=-J_{44}\langle\Psi_4,\Psi_0\rangle-J_{48}\langle\Psi_8,\Psi_0\rangle\,, \qquad (4.35)$$

$$\Gamma_{50}=-J_{55}\langle\Psi_5,\Psi_0\rangle\,, \qquad (4.36)$$

and

$$J_F=\sum_{j=4}^{9}J_{jj}|\langle\Psi_j,\Psi_0\rangle|^2$$
$$+J_{48}(\langle\Psi_0,\Psi_4\rangle\langle\Psi_8,\Psi_0\rangle+\langle\Psi_0,\Psi_8\rangle\langle\Psi_4,\Psi_0\rangle), \qquad (4.37)$$

where we've used the fact that the only nonvanishing off-diagonal matrix element of $\hat{\mathscr{J}}$ through ninth order is $J_{48} = J_{84}$. Noting that

$$\frac{c_k}{\sigma + \epsilon c_k} = \frac{1}{\epsilon} - \frac{\sigma}{\epsilon}\frac{1}{\sigma + \epsilon c_k} \tag{4.38}$$

the scalar products $\langle \Psi_j, \Psi_0 \rangle$ may be evaluated by partial fraction expansion, each scalar product being expressed in terms of the plasma dispersion function.

V. RESULTS AND DISCUSSION

The system of equations (4.21) are such that they may be partially reduced with moderate effort. Since, however, our interest here is in numerical results we solve the system of 12 complex equations directly. The expression (4.16) for $I[\bar{f}]$ may be expressed as a ratio of determinants, i.e.,

$$\begin{aligned} I[\bar{f}] = [&\gamma_0(\gamma_0 M_{00} - M_{10} - \bar{\gamma}_0 M_{60}) \\ &+ (\gamma_0 M_{01} - M_{11} - \gamma_0 M_{61}) \\ &+ \bar{\gamma}_0(\gamma_0 M_{06} - M_{16} - \bar{\gamma}_0 M_{66})]/|\Gamma| , \end{aligned} \tag{5.1}$$

where the M_{ij}'s are minors of $|\Gamma|$. These determinants may be evaluated by computer. Because of the availability of other first-principles calculations which can be used to test the accuracy of the present one, we consider the case of hard spheres. For the purpose of performing calculation and for making comparisons with previous ones, we introduce the dimensionless variables

$$x = -\sigma/\epsilon , \quad y = -iJ_{44}/\epsilon . \tag{5.2}$$

The variable x is the dimensionless frequency, and y is a collision parameter which is a measure of the ratio of fluctuation wavelength to collision mean free path. Further, we introduce the dimensionless dynamic structure function $R(x,y)$ defined

$$R(x,y) = \frac{\epsilon}{i}\frac{S(x,y)}{\pi} = \frac{\epsilon}{i}\frac{2}{\pi}\,\mathrm{Re}[I(x,y)] . \tag{5.3}$$

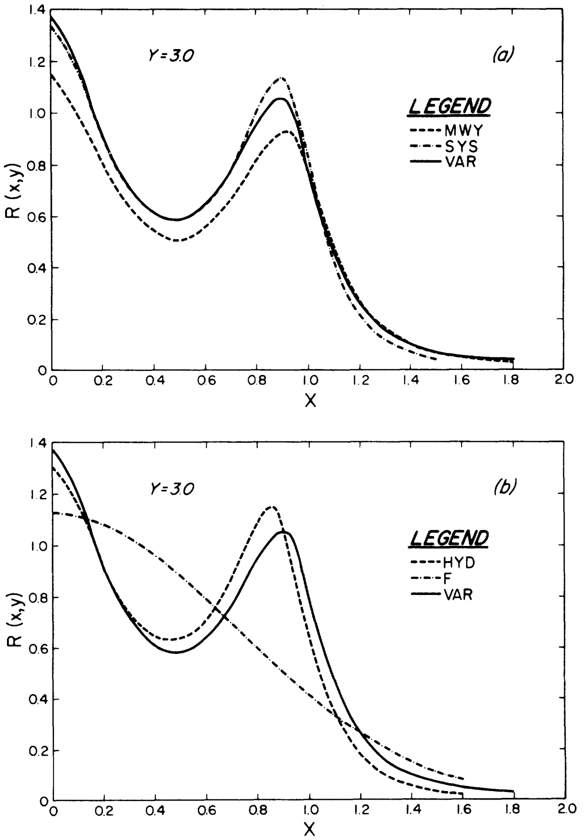

FIG. 1. Dimensionless dynamic structure function $R(x,y)$ for hard-sphere molecules as a function of the dimensionless frequency x for $y = 3.0$. (a) The variational results (——) are compared to those of SYS (-·-·) and MWY (---). (b) The variational results are compared to the Navier-Stokes (---) and free-molecule results (-·-·).

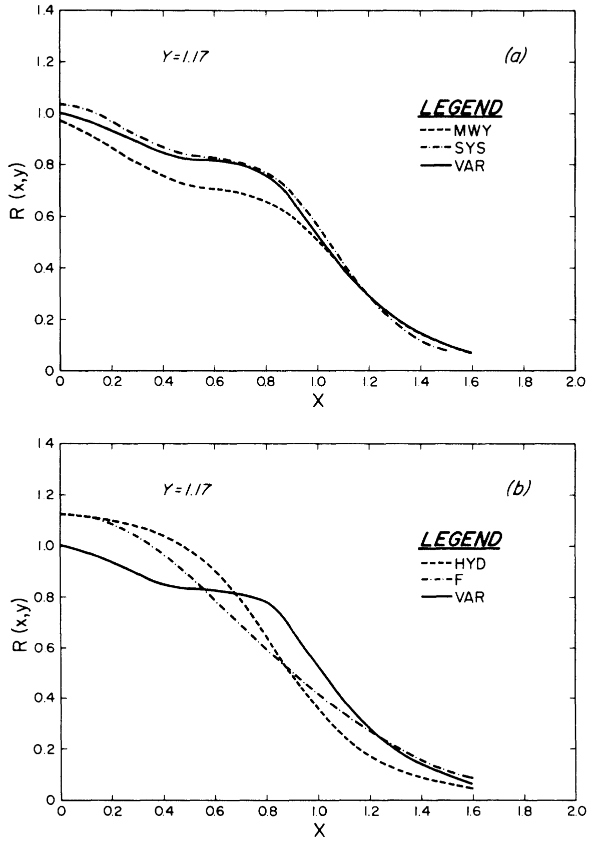

FIG. 2. Same as Fig. 1 except that $y = 1.17$.

Its dependence upon x for various values of the collision parameter y is given in Figs. 1–4. In part (a) of each, our results are compared to the corresponding results of Sugawara, Yip, and Sirovich (SYS)[6] and to those of Mazenko, Wei, and Yip (MWY).[7] In part (b) of each figure our results are compared to the Navier-Stokes hydrodynamic (H) and free-molecule (F) results. The MWY calculations are based upon the kinetic equations of Mazenko[20] which include memory effects. In that calculation a representation of the memory function is employed analogous to the representation of $\hat{\mathcal{J}}$ in the present calculation. There the dimensionality of the matrix representation was 35 with Hermite polynomials used as basis functions. In the SYS calculation, based upon the linearized Boltzmann equation, Sonine polynomials were employed to construct a matrix representation of the linearized Boltzmann collision operator of dimension 23.

Our results are seen generally to be in good agreement with those of the MWY and SYS calculations. In particular, we note that our results agree at short wavelengths, e.g., $y = 0.067$. This feature is particularly significant since our calculation is based upon the Boltzmann collision operator itself rather than a kinetic model. The problem of convergence, at short wavelengths, of orthogonal polynomial expansion solutions of the Boltzmann equation is widely known.[21] For the present problem, orthogonal polynomial expansions up to 60 terms have been shown to be seriously defective at wavelength to mean-free-path ratios as low as 0.067.[6] It has been shown that the convergence of orthogonal polynomial solutions tends to be slowest at $x = 0$. In the present variational calculation, based upon Ψ_0 and the first five Burnett polynomials, the $x = 0$ and $y = 0.067$ result differs from the analogous SYS result by only a few percent.

We also note that the variational results lie closer to the MWY results at higher frequency. The shift of the variational results from those of SYS is in fact towards the exact free-molecule results in this limit. It is interesting that except for the low-frequency limit, the variational results tend generally to lie closer to the MWY results than do those of SYS to the MWY results.

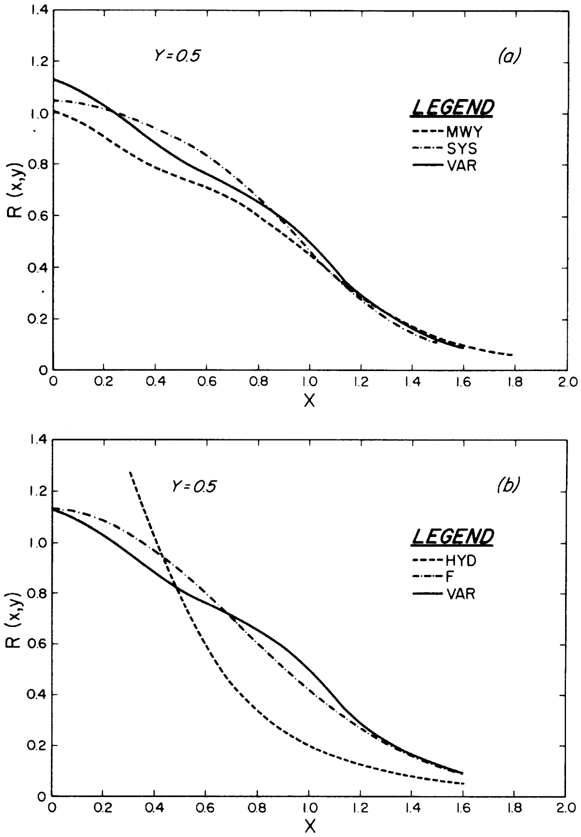

FIG. 3. Same as Fig. 1 except that $y = 0.5$.

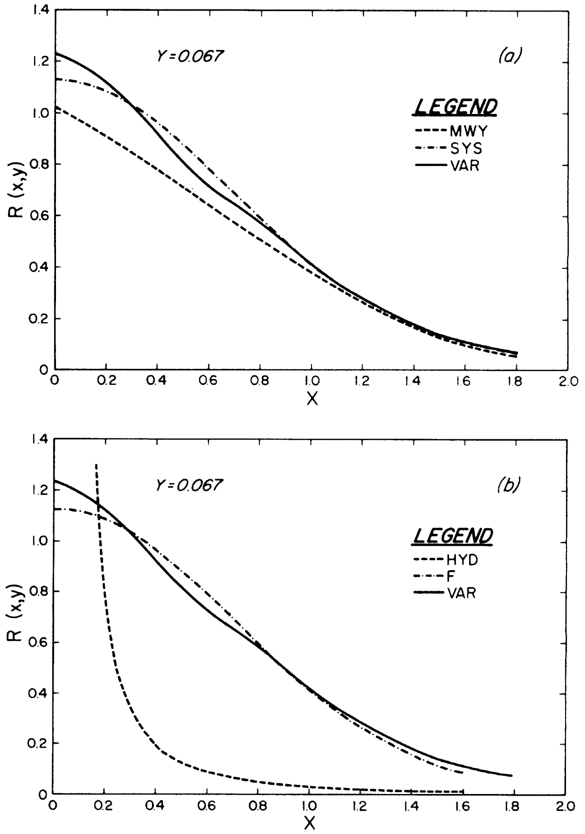

FIG. 4. Same as Fig. 1 except that $y = 0.067$.

This is due principally to the inclusion of Ψ_0 in our variational trial function. The form of the chosen trial function in effect constrains the results to approach $n_F(k,\sigma)$ in the high-frequency or short-wavelength region. A result of this is a distortion of the contribution of the chosen collision operator $\hat{\mathcal{J}}$ in the intermediate regimes of frequency and wavelength. This distortion is generally towards the results of the non-Markovian theory of MWY. As will be shown elsewhere, our results in the moderately-long-wavelength region may be recast into the Navier-Stokes form with frequency- and wavelength-dependent transport coefficients as in the non-Markovian generalized hydrodynamic theory of Oppenheim and Selwyn.[22]

VI. SUMMARY AND CONCLUSIONS

In this paper, we have introduced a direct variational method for calculating the dynamic structure function of a linear system described by a kinetic equation. The real part of the functional introduced approximates $S(k,\omega)$. Using as a trial distribution function a linear combination of the exact free-molecule solution and the first five axially symmetric Burnett functions, we've developed a general system of equations (4.21) for evaluating $S(k,\omega)$. Alternately, $S(k,\omega)$ may be expressed in a generalized determinantal form (5.1). Numerical results are obtained for the case of a gas of hard spheres and shown to be in excellent agreement with the results of previous first-principles calculations.[6,7]

The dimensionality of the system of equations (4.21), or of the determinants in (5.1), used in the present calculation is considerably less than those used in the calculations to which the present one is compared. Herein lies the principle virtue of the variational approach. This achievement of accuracy with reduced computational complexity suggests that the method may be a useful practical tool for performing calculations for more complex systems. The good agreement between the present claculation and that of MWY suggests that although the use of a non-Markovian kinetic description is formally correct, the present type of variational calculation is desirable from a computational point of view. It should, however, be emphasized that the variational approach itself is also applicable to calculations based on kinetic equations with memory effects incorporated.

The application of the variational method to first-principles calculations for more complex many-body systems will be discussed in subsequent works. There we shall discuss the problems of utilizing the variational method for treating dense gases and liquids, multicomponent systems, systems that are bounded and systems that are nonlinear. Further, there is the more fundamental problem of understanding in more detail whether the closeness of our variational results, with no memory effects having been explicitly included in our starting kinetic description, and those of MWY is an instance of accidental degeneracy or whether there is some more formal connection between the mechanics of the variational method and the mechanics of the techniques employed by Mezenko and others[20,23] in the microscopic calculation of memory functions. This matter will also be discussed in subsequent work.

Finally, it is perhaps useful to reemphasize the differences between the variational method employed here and Zwanzig's use of variational methods.[24,25] The essential distinction is that we have used a "direct" method in which the functional is equivalent to a measurable macroscopic property of the system. In the work of Zwanzig, the variational method is used to calculate eigenfuctions and eigenvalues of the Liouville operator. These may then be used to calculate macroscopic quantities via standard nonvariational formulas.[26] Results obtained from this two-step approach, however, are first order, rather than second or higher order, in the errors of the variationally determined eigenfunctions of the Liouville operator.

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