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Kinetic models for the generalized Enskog equation

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The generalized Enskog equation is used to describe the dynamic structure factor $S(k,\omega)$ for a hard-sphere gas. The problem of constructing kinetic models for the calculation of $S(k,\omega)$ is considered and the minimum set of matrix elements of the exact collision operator required by hydrodynamics is identified. The source of existing discrepancies between kinetic-model calculations and light-scattering experiments is also found and removed. Sensitivity of $S(k,\omega)$ to the parameters of kinetic models is discussed and a simple model proposed. A preliminary comparison of the hard-sphere $S(k,\omega)$ calculated from this model with neutron-scattering data from gaseous krypton is given.

I. INTRODUCTION

Equilibrium time correlation functions may be described quite generally in terms of the solution to a linear kinetic equation. The structure of this equation is complicated and, although much progress has been made, the many-body analysis required for its application in most cases is prohibitively difficult. However, the exact short-time form of this equation may be determined explicitly in terms of the equilibrium properties of the fluid, such as the radial distribution function.[1] For continuous potentials the application of this short-time form is limited to times small compared to a collision time. In contrast, for a hard-sphere fluid the collision time is zero so that the short-time kinetic equation describes collisions as well as mean-field effects. The resulting equation is a generalization of the Enskog equation for hard spheres.[1,2] It is well known that the Enskog equation gives an adequate description of the transport properties for hard spheres.[2] Since the transport properties are determined in principle from the long-time form of the kinetic equation, this suggests that the generalized Enskog equation might be applicable for times considerably longer than that suggested from its derivation. A closer inspection of the hard-sphere kinetic equation shows that the generalized Enskog equation results from the neglect of dynamically correlated many-body collisions, while retaining the static correlations.[3] The time for the dynamic correlations to grow should be of the order of the time between collisions, and the error associated with the Enskog approximation at finite times should increase with density. This is in fact the case for transport coefficients.[4] On this basis, the generalized Enskog equation may be considered as a reasonable first approximation to calculate time correlation functions for a hard-sphere fluid, except perhaps at high densities.

The dynamic structure factor $S(k,\omega)$ is defined as the Fourier transform of the density-density time correlation function and contains a wealth of information about the static and dynamic properties of the fluid.[5] Furthermore, it is directly measurable by both neutron[6] and light scattering.[7] In recent years there have been several calculations[8-10] of $S(k,\omega)$ based on the generalized Enskog equation, providing the first detailed connection between the collision dynamics of particles in phase space and the dynamic structure of fluids at all frequencies and wavelengths. However, interpretation of these results is not entirely clear due to the approximations required to solve the generalized Enskog equation. These approximations are introduced by the construction of kinetic models[11] designed to preserve the most important properties of the kinetic equation, but also amenable to exact

solution. A given kinetic model is exact in some finite dimensional subspace of the functions on which it operates, but only approximate with respect to the complement of this subspace. The resulting kinetic equation may then be written as a finite dimensional matrix equation and solved by standard methods. For any transport process it is clear that the subspace of conserved quantities should be included; beyond this the number and choice of additional dimensions must be based on other properties expected to be important, such as frequency moments of $S(k,\omega)$ and transport coefficients. The kinetic-model calculations of Refs. 8—10 are constructed in this spirit but are all different in detail, and lead to somewhat different results for $S(k,\omega)$. In particular, comparison of the calculations of Furtado *et al.*, with neutron-scattering data for liquid argon suggests that hard spheres are not a good model for real fluids (without a phenomenological modification), whereas de Schepper and Cohen's comparison with the same data suggests somewhat better agreement. In summary, then, it is not entirely clear: (1) to what extent real fluids may be represented by a hard-sphere fluid, (2) how accurately the hard-sphere fluid may be described by the generalized Enskog equation, and (3) how well a given kinetic model represents the generalized Enskog equation. The latter two questions are currently being studied by comparison of kinetic models with molecular dynamics simulation of $S(k,\omega)$ for hard spheres.[12]

The objectives here are twofold—to clarify the constraints imposed by hydrodynamics on kinetic models for $S(k,\omega)$ and to give a comparison with neutron-scattering data in the gas phase where the accuracy of the generalized Enskog equation should be less questionable. Regarding the first objective, it is shown that many of the matrix elements of the generalized Enskog operator incorporated in the above kinetic models are not required for the description of $S(k,\omega)$ due to rotational invariance about the axis $\vec{k}$. Among these are the matrix elements associated with shear and bulk viscosities; instead, the viscous contribution to the sound damping constant is shown to be determined by different matrix elements constructed from functions with the proper symmetry. This difference is also shown to remove the recently observed discrepancies between the Brillouin peaks observed in light-scattering experiments and kinetic-model calculations.[13] The relevant hydrodynamics for $S(k,\omega)$, thermal diffusion and sound modes, is shown to be determined entirely by operation of the generalized Enskog operator in a five-dimensional subspace of functions symmetric about $\vec{k}$. On the basis of this identification, kinetic models are suggested that necessarily preserve the hydrodynamic limit of $S(k,\omega)$. A minimal model containing no additional information beyond that of this five-dimensional subspace is suggested here as a suitable compromise between the requirements of accuracy and tractability. It can be argued that the emphasis placed here on the hydrodynamic limit as a criterion for choosing the matrix elements for a kinetic model may not be appropriate for calculations at the relatively large frequencies and wave vectors observed by neutron scattering. However, de Schepper and Cohen have shown recently[9] (on the basis of their kinetic model) that the hydrodynamic part of $S(k,\omega)$, calculated by analytic continuation of the hydrodynamic modes to larger wave vectors, continues to be important over a wider range of k and ω values than might have been expected. Further comment on this point is given in the last section.

Much of the existing neutron-scattering results are limited to the liquid phase and the comparison with the kinetic models has been most extensive at correspondingly high densities, where the accuracy of the generalized Enskog equation is more questionable. More recently, high-flux reactors have made experiments in the gas phase feasible.[14—16] Here, a preliminary comparison is given of the kinetic-model calculation of $S(k,\omega)$ for hard spheres with neutron-scattering data for krypton in the gas phase.[15] A similar comparison with neutron-scattering data for gaseous argon was described recently by Postal and Pelizzari,[16] and for neon by Chen *et al.*[17]

II. KINETIC MODELING FOR $S(k,\omega)$

Since kinetic modeling has been discussed extensively elsewhere, only the basic ideas are described here to indicate the special simplifications associated with calculating $S(k,\omega)$. To formulate the problem it is convenient to consider solutions to the kinetic equation in a Hilbert space $\mathscr{H}$ with the scalar product

$$(a,b)\equiv\int d\vec{v}\,\phi(v)a^*(\vec{v})b(\vec{v})\,, \tag{2.1}$$

where the weight function $\phi(v)$ is the Maxwell-Boltzmann distribution and the symbol $*$ denotes complex conjugation. The dynamic structure factor is then given by[18]

$$\frac{S(k,\omega)}{S(k)} = 2\,\mathrm{Re}(1, R(k,\omega)1) . \tag{2.2}$$

Here $R(k,\omega)$ is the resolvent operator associated with the generalized Enskog equation

$$R(k,\omega) \equiv \lim_{\epsilon \to 0+} [-i\omega + \epsilon + L(k)]^{-1} \tag{2.3}$$

and $S(k)$ is the static structure factor. The operator $L(k)$ is defined by

$$L(k) \equiv i\vec{k}\cdot\vec{v} - B(k) , \tag{2.4}$$

and $B(k)$ is the generalized Enskog operator

$$B(k)h \equiv i\vec{k}\cdot\vec{v} n [C(k) - g(\sigma)C_0(k)](1,h) - ng(\sigma) \int d\vec{v}_1 \int_0^{2\pi} d\phi \int_0^{\sigma} db\, b\, |\vec{v} - \vec{v}_1|\, \phi(v_1)[h(\vec{v}) - h(\vec{v}') + e^{i\vec{k}\cdot\vec{\sigma}} h(\vec{v}_1) - e^{-i\vec{k}\cdot\vec{\sigma}} h(\vec{v}_1')] . \tag{2.5}$$

The functions $C(k)$ and $C_0(k)$ are the direct correlation function and its low-density limit, respectively; $g(\sigma)$ is the radial distribution function at the hard-sphere diameter σ. Also n is the density and the primes on the velocities denote the values of $\vec{v}$ and $\vec{v}_1$ after collision.

The operator, $L(k)$, is invariant under rotations about the axis, $\hat{k}$. Let $\mathscr{H}_s$ denote the subspace of $\mathscr{H}$ composed of functions with cylindrical symmetry about $\hat{k}$, and let $\mathscr{H}_\perp$ denote its orthogonal complement. As a result of the rotational invariance, $L(k)$ maps each of these subspaces into itself, and may be represented as

$$L(k) = L_s(k) + L_\perp(k) , \tag{2.6}$$

with

$$L_s(k) = \mathscr{P} L(k) \mathscr{P} , \qquad L_\perp(k) = Q L(k) Q , \tag{2.7}$$

where $\mathscr{P}$ is the projection onto $\mathscr{H}_s$ and $Q = (1 - \mathscr{P})$. It is then straightforward to show that $S(k,\omega)$ is entirely determined by L_s,

$$\frac{S(k,\omega)}{S(k)} = 2\,\mathrm{Re}(1, R_s(k,\omega)1) , \qquad R_s(k,\omega) \equiv \lim_{\epsilon \to 0+} [-i\omega + \epsilon + L_s(k)]^{-1} . \tag{2.8}$$

Consequently, any kinetic-model calculation of $S(k,\omega)$ need only contain an adequate representation of L_s; conversely, any features of the model based on $L_\perp$ are either extraneous or inappropriate.

A given kinetic model is defined in terms of a representation of $B(k)$ with respect to a chosen basis set. If $\{ u_\alpha^s \}$ denotes a complete orthonormal set in $\mathscr{H}_s$ and $\{ u_\alpha^\perp \}$ denotes a corresponding set for $\mathscr{H}_\perp$, then

$$L_s = \mathscr{P} i\vec{k}\cdot\vec{v}\mathscr{P} - \sum_{\alpha,\beta} P_\alpha^s B P_\beta^s \equiv \mathscr{P} i\vec{k}\cdot\vec{v}\mathscr{P} - B_s , \qquad L_\perp = Q i\vec{k}\cdot\vec{v} Q - \sum_{\alpha,\beta} P_\alpha^\perp B P_\beta^\perp \equiv Q i\vec{k}\cdot\vec{v} Q - B_\perp , \tag{2.9}$$

where P_α^s and $P_\alpha^\perp$ are the projection operators onto u_α^s and $u_\alpha^\perp$, respectively. A kinetic model for L_s is obtained by selecting a finite subset of the $\{ u_\alpha^s \}$, for example, $\alpha \le N$, and making the following approximations:

$$(u_\alpha^s, B u_\beta^s) = 0 \quad \text{for } \alpha \le N, \beta > N;\ \alpha > N, \beta \le N$$

and

$$(u_\alpha^s, B u_\beta^s) = \lambda_s \delta_{\alpha\beta} \quad \text{for } \alpha > N, \beta > N . \tag{2.10}$$

These approximations correspond to a decomposition of $\mathscr{H}_s$ into a finite dimensional subspace and its complement, such that L_s is given exactly in the subspace but is proportional to the identity operator in the complement and represented there by the single degenerate value, λ_s. The spirit of this approximation is that if the subspace is suitably chosen, the quantity to be calculated will be relatively insensitive to the details outside that subspace. Following a similar procedure for $L_\perp$, kinetic models for Eqs. (2.9) are given by

$$L_s = \mathscr{P} i\vec{k}\cdot\vec{v}\mathscr{P} - \sum_{\alpha,\beta}^{N} P_\alpha^s B P_\beta^s - \lambda_s \left[\mathscr{P} - \sum_{\alpha=1}^{N} P_\alpha^s \right] , \qquad L_\perp = Q i\vec{k}\cdot\vec{v} Q - \sum_{\alpha,\beta}^{N} P_\alpha^\perp B P_\beta^\perp - \lambda_\perp \left[Q - \sum_{\alpha=1}^{N} P_\alpha^\perp \right] . \tag{2.11}$$

The parameters λ_s and $\lambda_\perp$ are usually chosen as one of the diagonal matrix elements of B in the

complement to the corresponding subspace chosen, e.g.,

$$\lambda_s=(u^s_{N+1},Bu^s_{N+1})\,,\qquad \lambda_\perp=(u^\perp_{N+1},Bu^\perp_{N+1})\,. \tag{2.12}$$

More systematic methods for choosing these λ's have been suggested[18] but will not be discussed here.

For small k the spectrum of $L(k)$ contains eigenvalues corresponding to the five hydrodynamic modes. Three of these, thermal diffusion and the two sound modes, are associated entirely with $L_s(k)$. The twofold degenerate shear modes are associated entirely with $L_\perp(k)$. In the next section, it is shown that a five-dimensional subspace is required for a representation of $L_s(k)$ that preserves the thermal diffusion and sound modes. An orthonormal basis set spanning this space is given by

$$\begin{aligned}
u^s_1&=1\,,\\
u^s_2&=\sqrt{2}\frac{\hat{k}\cdot\vec{v}}{v_0}\,,\\
u^s_3&=\sqrt{2/3}\left[\frac{v^2}{v_0^2}-\tfrac{3}{2}\right],\\
u^s_4&=\frac{2}{\sqrt{5}}\frac{\hat{k}\cdot\vec{v}}{v_0}\left[\frac{v^2}{v_0^2}-\tfrac{5}{2}\right],\\
u^s_5&=\sqrt{3}\left[\left[\frac{\hat{k}\cdot\vec{v}}{v_0}\right]^2-\frac{1}{3}\left[\frac{v}{v_0}\right]^2\right],
\end{aligned} \tag{2.13}$$

where $v_0\equiv(2/\beta m)^{1/2}$ and where $\beta=(k_BT)^{-1}$. The first three members of this basis set are eigenvectors of $L_s(0)$, with zero eigenvalue, corresponding to conservation of particle number, component of momentum along $\vec{k}$, and energy. The function u^s_4 is required to describe the thermal conductivity, and u^s_5 is required for the sound damping constant. Although the hydrodynamic analysis of the next section is limited to the modes of $L_s(k)$, a similar analysis of the shear modes for $L_\perp(k)$ would indicate that a three-dimensional subspace in $\mathscr{H}_\perp$ is required. The orthonormal basis set is

$$\begin{aligned}
u^\perp_1&=\sqrt{2}\frac{\hat{e}_1\cdot\vec{v}}{v_0}\,,\\
u^\perp_2&=\sqrt{2}\frac{\hat{e}_2\cdot\vec{v}}{v_0}\,,\\
u^\perp_3&=2\frac{(\hat{e}_1\cdot\vec{v})(\hat{e}_2\cdot\vec{v})}{v_0^2}\,,
\end{aligned} \tag{2.14}$$

where $\hat{e}_1$ and $\hat{e}_2$ are unit vectors orthogonal to $\vec{k}$ and to each other. The first two functions are the two components of momentum orthogonal to $\vec{k}$, providing the remaining conservation laws. The last member is required for the shear viscosity.

A possible confusion arises from the dependence of the sound damping constant on shear and bulk viscosities. For example, in the low-density limit the bulk viscosity vanishes and the sound damping constant is given by

$$\Gamma^{(0)}=\frac{\lambda_T^{(0)}}{\rho C_p}\frac{1}{2}\left[\frac{C_p}{C_v}-1\right]+\frac{1}{2\rho}\left(\tfrac{4}{3}\eta_s^{(0)}\right) \tag{2.15}$$

where $\lambda_T^{(0)}$ and $\eta_s^{(0)}$ are the low-density thermal conductivity and shear viscosity, respectively, ρ is the mass density, and C_p and C_v are the specific heats at constant pressure and volume. Since $\lambda_T^{(0)}$ is described by matrix elements with respect to u^s_4, and $\eta_s^{(0)}$ is described by the matrix elements with respect to $u^\perp_3$, it may be expected that $\Gamma^{(0)}$ is determined and the dimension u^s_5 is therefore extraneous. However, the sound modes are properties of $L_s(k)$ which has vanishing matrix elements with respect to $u^\perp_3$ (and all other members of $\mathscr{H}_\perp$). Consequently, the viscous contribution to the sound modes arises from entirely different matrix elements of $L(k)$ than those that determine the viscosity in the shear modes. As will be seen below, the relevant function in $\mathscr{H}_s$ for the determination of both shear and bulk viscosity contributions to sound damping is u^s_5. This function has not appeared in the construction of previous kinetic models.

In summary, none of the matrix elements of $L(k)$ with respect to functions in $\mathscr{H}_\perp$ [in particular, those of Eq. (2.14)] is relevant for the calculation of $S(k,\omega)$. Anticipating the results of the next section, a kinetic model for $S(k,\omega)$ consistent with the hydrodynamics of the generalized Enskog equation at all densities is given by Eq. (2.8) with

$$[L_s(k)]_5=\mathscr{P}(i\vec{k}\cdot\vec{v}-\lambda)\mathscr{P}-\sum_{\alpha=1}^{5}\sum_{\beta=1}^{5}P^s_\alpha[B(k)-\lambda\delta_{\alpha\beta}]P^s_\beta \tag{2.16}$$

and λ is arbitrary.

III. HYDRODYNAMIC LIMIT

To determine the matrix elements of $L_s(k)$ that are important for the hydrodynamic limit of $S(k,\omega)$, i.e., the behavior for small k and ω, the

hydrodynamic modes and corresponding transport coefficients may be determined from the eigenvalues of $L_s(k)$. In particular, the three modes associated with $L_s(k)$ are identified, for sufficiently small k, by

$$\begin{aligned} L_s(k)\psi_1 &= \frac{\lambda_T}{\rho C_p}k^2\psi_1 , \\ L_s(k)\psi_2 &= (iC_sk+\Gamma k^2)\psi_2 , \\ L_s(k)\psi_3 &= (-iC_sk+\Gamma k^2)\psi_3 , \end{aligned} \tag{3.1}$$

where λ_T, Γ, and C_s are the thermal conductivity, sound damping constant, and sound speed associated with the generalized Enskog equation. It is now possible to determine the eigenvalues and eigenvectors of Eq. (3.1) by expanding the operator $L_s(k)$ and the eigenfunctions in powers of k,

$$\begin{aligned} L_s(k) &= L_s(0)+kL_1+k^2L_2+\cdots , \\ \psi_\alpha(k) &= \psi_\alpha^{(0)}+k\psi_\alpha^{(1)}+\cdots , \end{aligned} \tag{3.2}$$

and treating the k-dependent terms as a small perturbation. The perturbation theory is straightforward, although complicated by the degeneracy of the unperturbed zero eigenvalue and the fact that the perturbation is not Hermitian. Only the results will be discussed here (further details are given in Appendix A). The sound velocity is obtained by first-order perturbation theory and is found from

$$(\phi_\alpha^{(0)},L_1\psi_\beta^{(0)}) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & iC_s & 0 \\ 0 & 0 & -iC_s \end{bmatrix} , \tag{3.3}$$

where $\{\phi_\alpha^{(0)}\},\{\psi_\beta^{(0)}\}$ are bi-orthogonal sets of three vectors formed from linear combinations of u_1^s, u_2^s, and u_3^s [see Eqs. (A11) and (A13) for a precise definition]. Direct calculation of the matrix elements on the left side of Eq. (3.3) gives

$$C_s = \frac{v_0}{\sqrt{2}}[1-nC(0)+\tfrac{2}{3}(1+4\eta g)^2]^{1/2} , \tag{3.4}$$

where $C(0)$ is the $k=0$ limit of the direct correlation function, $g=g(\sigma)$ is the pair-correlation function at contact, and $\eta\equiv\pi n\sigma^3/6$ is the packing fraction. This is the usual Enskog result. Consequently, any kinetic model incorporating the exact properties of the generalized Enskog operator in a subspace spanned by u_1^s, u_2^s, and u_3^s will necessarily give the correct sound speed.

The thermal conductivity and sound damping constant are found from second-order perturbation theory. Consider first the thermal conductivity, which is found to be [see Eq. (A23)]

$$\lambda_T = \frac{\lambda_T^{(0)}}{g}\left[(1+\tfrac{12}{5}\eta g)^2+\frac{24k_B(\eta g)^2}{\pi\sigma^2\lambda_T^{(0)}\sqrt{\pi\beta m}}+\Delta\right] . \tag{3.5}$$

Δ represents terms proportional to $PB_1u_1^s$ and $PB_1u_3^s$ and where $\lambda_T^{(0)}$ is the usual Boltzmann result,

$$\lambda_T^{(0)} = \tfrac{5}{4}k_Bngv_0^2(u_4^s,X) \tag{3.6}$$

and X is the solution to

$$B(0)X = -u_4^s , \tag{3.7}$$

with the condition that $(X,u_\alpha^s)=0$ for $\alpha=1-3$. The operator P in the last term of Eq. (3.5) denotes a projection orthogonal to $\{u_\alpha^s\}$, $\alpha=1-4$. To obtain Eq. (3.5), matrix elements of the form $(u_4^s, L_1u_\alpha^s)$ have been evaluated for $\alpha=1-3$. The first two terms in Eq. (3.5) are the exact Enskog result, since the terms $PB_1u_1^s$ and $PB_1u_3^s$ are found to vanish by direct calculation. This latter property implies

$$(u_\alpha^s,B_1u_\beta^s)=0, \quad \alpha>4 \quad \beta=1,3 . \tag{3.8}$$

Finally, for practical purposes Eq. (3.7) may be solved by an expansion of X in the set $\{u_\alpha^s\}$. The first approximation is accurate to within a few percent[2] and is given by

$$X\sim -u_4^s[(u_4^s,B(0)u_4^s)]^{-1} . \tag{3.9}$$

This approximation is equivalent to the condition,

$$(u_4^s,B(0)u_\alpha^s)\sim 0, \quad \alpha>4 . \tag{3.10}$$

With Eq. (3.9) $\lambda_T^{(0)}$ may be evaluated. Substitution in Eq. (3.5) then gives the final result

$$\lambda_T = \frac{75}{64}\frac{k_B}{\sigma^2g\sqrt{\pi m\beta}}[1+1.2(4\eta g)+0.767(4\eta g)^2] . \tag{3.11}$$

The above shows that the thermal conductivity is accurately given[19] if the exact properties of B are given in the subspace spanned by u_α^s for $\alpha=1-4$. Further, the matrix elements of B_1 between u_1^s or u_3^s and the space orthogonal to this four-dimensional subspace must vanish.

Similarly, the sound damping constant is found to be

$$\Gamma=\frac{\lambda_T}{\rho C_p}\frac{1}{2}\left[\frac{C_p}{C_v}-1\right]+\frac{1}{2\rho}(\tfrac{4}{3}\eta_s+\xi), \quad (3.12)$$

where λ_T is given by Eq. (3.11) and [see Eq. (A28)]

$$(\tfrac{4}{3}\eta_s+\xi)=\tfrac{4}{3}\eta_s^{(0)}\frac{1}{g}(1+\tfrac{8}{5}\eta g)^2 + \frac{9}{5\pi\sigma^2 g}\sqrt{m/\pi\beta}(4\eta g)^2+\Delta', \quad (3.13)$$

where Δ' represents terms proportional to $\bar{P}B_1u_2^s$. Here $\eta_s^{(0)}$ is the Boltzmann shear viscosity

$$\eta_s^{(0)}=\frac{\rho v_0^2}{2}g(u_5^s,Y), \quad (3.14)$$

and Y is the solution to

$$-B(0)Y=u_5^s, \quad (3.15)$$

with the condition $(Y,u_\alpha^s)=0$ for $\alpha=1-3$. The projection operator $\bar{P}$ in the last term of Eq. (3.13) denotes projection orthogonal to u_α^s for $\alpha=1-5$. To obtain Eq. (3.13) use was made of the matrix element $(u_2^s,B_1u_5^s)=(u_5^s,B_1u_2^s)$. Evaluation of $\bar{P}B_1u_2^s$ shows that this term is zero, or

$$(u_\alpha^s,B_1u_2^s)=0, \quad \alpha>5. \quad (3.16)$$

Just as with Eq. (3.7), the first approximation in the expansion of the solution to Eq. (3.15) is very accurate, with the result,

$$Y\sim -u_5^s[(u_5^s,B(0)u_5^s)]^{-1}. \quad (3.17)$$

Equivalently, this would result from the condition

$$(u_5^s,B_1u_\alpha^s)=0, \quad \alpha>5. \quad (3.18)$$

Equation (3.17) now allows evaluation of $\eta_s^{(0)}$, and Eq. (3.13) becomes

$$(\tfrac{4}{3}\eta_s+\xi)=\tfrac{5}{12}\sqrt{m/\pi\beta}\frac{1}{\sigma^2 g} \times[1+0.8(4\eta g)+1.54(4\eta g)^2], \quad (3.19)$$

which is the Enskog result.[19]

To summarize, the hydrodynamic modes and transport coefficients relevant for $S(k,\omega)$ will be accurately reproduced[18] by any kinetic model that retains certain matrix elements of $B(k)$ in the five-dimensional subspace spanned by the basis set of (2.13). More specifically, the matrix elements in this subspace are

$$(u_\alpha^s,B(k)u_\beta^s)\leftrightarrow\begin{bmatrix}0&0&0&0&0\\B_{21}&B_{22}&B_{23}&B_{24}&B_{25}\\0&B_{23}&B_{33}&B_{34}&0\\0&B_{24}&B_{34}&B_{44}&0\\0&B_{25}&0&0&B_{55}\end{bmatrix}, \quad (3.20)$$

where the symmetry $B_{\alpha\beta}=B_{\beta\alpha}$ for $(\alpha,\beta)\neq(1,2)$ has been noted. The zeros in the fifth row and column are due to the conditions (3.8) and (3.10). Also, conditions (3.8), (3.10), (3.16), and (3.18) require the matrix elements between u_4^s or u_5^s and the orthogonal complement to this subspace must vanish. No other properties of the collision operator, $B(k)$, are necessary to determine the hydrodynamic limit of $S(k,\omega)$.

IV. COMPARISON OF MODELS

A kinetic model for $S(k,\omega)$ consistent with the conditions of Sec. III is that given by Eq. (2.16). The properties of the generalized Enskog operator are primarily represented by its matrix elements in the five-dimensional subspace. The matrix elements $B_{\alpha\beta}(k)$ for $\alpha,\beta=1-4$ have been calculated by Furtado *et al.*, and it is straightforward to determine the additional two elements, B_{25} and B_{55}. The results are given in Appendix B. Substitution of Eq. (2.16) in (2.8) then gives the kinetic model for $S(k,\omega)$

$$\frac{S(k,\omega)}{S(k)}=2\,\mathrm{Re}\bar{C}_1(k,\omega), \quad (4.1)$$

where $\bar{C}_1$ is the solution to a coupled set of five equations,

$$\bar{C}_\alpha=\bar{C}_\alpha^{(0)}+\sum_{\beta=1}^{5}\sum_{\gamma=1}^{5}\bar{D}_{\alpha\beta}(B_{\beta\gamma}-\lambda\delta_{\beta\alpha})\bar{C}_\gamma. \quad (4.2)$$

The functions $\bar{C}_\alpha^{(0)}$ and $\bar{D}_{\alpha\beta}$ may be calculated in terms of the complex plasma dispersion function and are also given in Appendix B.

The parameter λ in Eq. (4.2) is still arbitrary. As indicated in Sec. II its role is to represent $L(k)$ in the complement to the five-dimensional subspace required by hydrodynamics. To suggest a simple choice, it is convenient to rewrite Eq. (2.16) as

$$[L_s(k)]_5=[L_s(k)]_4 +(\lambda-B_{55})P_5^s-(P_5^sBP_2^s+P_2^sBP_5^s). \quad (4.3)$$

Here $[L_s(k)]_4$ is the kinetic model based on representation of $B(k)$ in only the four-dimensional subspace spanned by $\{u_\alpha^s\}$ for $\alpha=1-4$,

$$[L_s(k)]_4=\mathscr{P}(i\vec{k}\cdot\vec{v}-\lambda)\mathscr{P} -\sum_{\alpha=1}^{4}\sum_{\beta=1}^{4}P_\alpha^s(B-\lambda)P_\beta^s. \quad (4.4)$$

This four-dimensional model results from the five-dimensional one if λ is chosen to be the matrix element B_{55}, and the matrix element B_{25} is neglected.

The choice $\lambda=B_{55}$ is simply that of Eq. (2.12) for the four-dimensional model, but the neglect of B_{25} leads to an incorrect sound damping constant as calculated from (4.4). Closer inspection of the results in Appendix A shows that B_{25} is responsible only for some of the density corrections to the viscous contributions of Γ. Consequently the model $[L_s(k)]_4$ is consistent with hydrodynamics at low density. It is important to note that this agreement with hydrodynamics at low density is only obtained if the choice $\lambda=B_{55}$ is made. The kinetic model used by Furtado *et al.* is, in fact, that of Eq. (4.4), although with a different choice for λ [Eq. (2) of Ref. 8]. The resulting hydrodynamics is therefore in error even at low densities. In particular, the sound damping constant is almost 30% too large. Since the amplitudes of the Brillouin peaks are inversely proportional to Γ, this error is seen to be responsible for the recently discussed discrepancies at low-density light-scattering data or hydrodynamics and calculations using the kinetic model of Furtado *et al.*[13] In constrast, a comparison of the kinetic model using $\lambda=B_{55}$ with a hydrodynamic calculation shows good agreement.[20] At higher densities the five-dimensional model is required, as described below. Interestingly, for values of k and ω well outside the hydrodynamic range the results of Furtado *et al.*, and those obtained using $\lambda=B_{55}$ are essentially the same, indicating a surprising insensitivity to λ. Further comment on this will be given below.

The kinetic model of Eq. (4.4) fails to give the correct hydrodynamics at higher densities. This is due to the neglect of B_{25} in passing from (4.3) to (4.4). Returning to the model $[L_s(k)]_5$, it is noted that by construction the hydrodynamic modes are correct at all densities, for arbitrary choice of λ. One possibility is that of Eq. (2.12),

$$\lambda=(u_6^s,B(k)u_6^s)\,, \tag{4.5}$$

where $(u_6^s,u_\alpha^s)=0$ for $\alpha=1-5$. Instead of adding any new information to the model it is useful first to determine just how sensitive $S(k,\omega)$ is to this free parameter. To do so, let λ be a multiple of B_{55},

$$\lambda=\nu B_{55}(k)\,, \tag{4.6}$$

where ν is to be varied. The comparison of kinetic models obtained by increasing the dimension of the subspace of matrix elements $B_{\alpha\beta}$ is discussed in Ref. 12, and indicates convergence is slowest for $S(k,\omega)$ at $\omega=0$. The variation of ν in the $[L_s(k)]_5$ model gives a similar measure of the importance of the collision operator in the subspace orthogonal to the chosen five-dimensional space. Table I gives $S(k,\omega=0)/S(k)$ as calculated for $\nu=0.5$, 1.0, and 5.0. Table II shows a similar comparison for calculation of the full width of $S(k,\omega)$ at half maximum. The insensitivity of these results to changes of λ by an order of magnitude suggests that the structure of $L_s(k)$ that is important for $S(k,\omega)$ is largely contained in the matrix elements of $[L_s(k)]_5$.

The wave vectors considered in Tables I and II are those typical for neutron-scattering results. Somewhat surprisingly even the four-dimensional model $[L_s(k)]_4$ agrees reasonably well (within 10%) with the five-dimensional models in this range. Furthermore, a certain insensitivity to variation of λ in the four-dimensional model is also found, suggesting that for sufficiently large wave vectors the dominant behavior of $S(k,\omega)$ is determined from the matrix elements of $B(k)$ with respect to only the four functions $\{u_\alpha^s\}$ for $\alpha=1-4$. This is in substantial accord with the relative agreement between the single- and triple-relaxation time models of Ref. 8. Similarly the results of de Schepper and Cohen suggest that the analytic continuation of the hydrodynamic heat mode dominates in this range of wave vectors. Since this mode is determined by the matrix elements of $B(k)$ with respect to these same four functions, an insensitivity to higher-order dimensions is again indicated.

TABLE I. Comparison of $S(k,\omega=0)/S(k)$ at $n\sigma^3=0.47$ as calculated from Eqs. (4.3) and (4.6) for $\nu=0.5$, $\nu=1.0$, and $\nu=5.0$; $\sigma=3.52$ Å.

k (Å^{-1})	$\nu=0.5$	$\nu=1.0$	$\nu=5$
0.1	1.10×10^{-11}	1.09×10^{-11}	1.08×10^{-11}
0.3	0.239	0.232	0.224
0.5	0.160	0.157	0.151
0.7	0.136	0.134	0.130
0.9	0.129	0.128	0.124
1.1	0.130	0.129	0.126
1.3	0.136	0.135	0.132
1.5	0.138	0.137	0.134
1.7	0.124	0.123	0.120
1.9	0.990×10^{-12}	0.987×10^{-12}	0.952×10^{-12}
2.1	0.798	0.794	0.760
2.3	0.685	0.680	0.649
2.5	0.623	0.618	0.588
2.7	0.587	0.583	0.554
2.9	0.564	0.559	0.532

TABLE II. Same as Table I, except for the full width at half maximum.

k (Å^{-1})	$\nu=0.5$	$\nu=1$	$\nu=5$
0.1	0.208×10^{12}	0.212×10^{12}	0.216×10^{12}
0.3	2.30	2.38	2.48
0.5	3.38	3.44	3.53
0.7	3.91	3.96	4.08
0.9	4.10	4.15	4.19
1.1	4.05	4.09	4.21
1.3	3.89	3.92	4.04
1.5	3.90	3.91	4.04
1.7	4.48	4.48	4.60
1.9	5.76	5.75	5.77
2.1	7.24	7.22	7.26
2.3	8.39	8.38	8.45
2.5	9.12	9.13	9.30
2.7	9.45	9.61	9.87
2.9	9.96	9.99	10.30

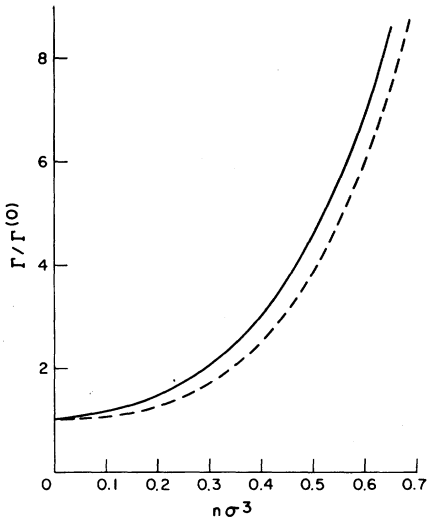

FIG. 1. Sound damping constant as calculated from Eq. (4.4) (— — —), and the MM model, Eq. (4.7) (——). Both are normalized to the low-density Boltzmann result $\Gamma^{(0)}$.

At smaller wave vectors the full five-dimensional model, $[L_s(k)]_5$, is required as the hydrodynamic limit of $S(k,\omega)$ is approached. However, since $S(k,\omega)$ is independent of λ in this limit and insensitive to λ otherwise, this parameter of the model may be chosen for convenience and simplicity. Consideration of Eq. (4.3) suggests the choice $\lambda=B_{55}$. The model then contains only the minimum information about $B(k)$ required by hydrodynamics and no additional matrix elements. This will be referred to as the minimum matrix element model (MM) and is given by

$$[L_s(k)]_5=[L_s(k)]_4-(P_5^sBP_2^s+P_2^sBP_5^s)\,, \tag{4.7}$$

where $[L_s(k)]_4$ is defined by Eq. (4.4) with $\lambda=B_{55}$. The model differs from the four-dimensional model only by the matrix element $B_{52}=B_{25}$. As noted above the latter is required to give certain collisional transfer contributions to the viscous part of the sound damping constant. Figure 1 compares the sound damping constant as calculated from Eqs. (4.4) and (4.7). The error associated with the four-dimensional model can be as much as 18%. Similarly the Brillouin peaks in $S(k,\omega)$ will have a corresponding error if B_{52} is neglected, except at very low density.[20] In contrast, since Eq. (4.7) predicts the correct Enskog sound damping constant at *all* densities the discrepancies between hydrodynamics and kinetic models discussed in Ref. 13 are removed at all densities.

V. COMPARISON WITH EXPERIMENT

Neutron-scattering experiments on gaseous krypton were performed recently[15] at twelve densities along the 297 K isotherm for wave vectors in the range $0.4\leq k\leq3.5$ Å^{-1}. This allows determination of the density derivatives of $S(k,\omega)$ and $S(k)$ in addition to the functions themselves, and should provide a more severe test of kinetic theories and potential models used to describe the results.[21] In this section a preliminary comparison of the MM kinetic model with the experimental results is made at only a single density, $n=1.07\times10^{22}$ cm^{-3}; a more complete analysis will be given elsewhere. The only free parameter of the kinetic model is the hard-sphere diameter, σ. This is chosen by requiring that the hard-sphere static structure factor be similar to the experimental result for the k range of interest. The hard-sphere structure factor is calculated from Percus-Yevick theory.[5] Figure 2 shows a comparison of $S(k)$ for hard spheres at $\sigma=3.52$ Å with the corresponding experimental results. At least in the region of the peak the structure of the hard-sphere fluid is seen to be qualitatively similar to that of xenon. All of the following kinetic-model results are based on the choice $\sigma=3.52$ Å.

Figure 3 shows $S(k,\omega)/S(k)$ at $\hbar\omega=0$, 1, and 2 meV. The static structure factor has been divided out to emphasize the dynamical effects, and the theory has been convoluted with an instrument profile. The agreement is seen to be reasonably good at $\hbar\omega=1$ and 2 meV, although significant

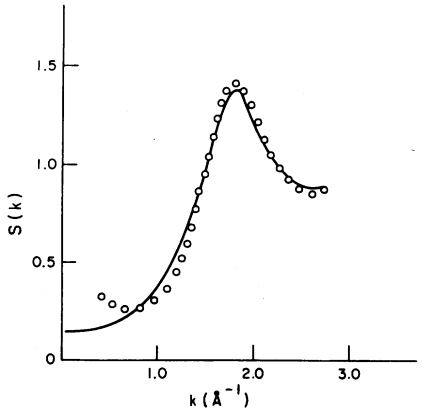

FIG. 2. Comparison of $S(k)$ for hard spheres with $\sigma=3.52$ Å (——), and from neutron-scattering data for krypton gas at $T=297$ K (o o o); both are at $n\sigma^3=0.47$.

differences in detail are evident. At $\hbar\omega=0$ the disagreement between the kinetic-model calculation and experimental results is clearly larger. This difference could be due to either the failure of hard spheres to represent xenon, or errors associated with the MM kinetic model. However, the latter explanation is unlikely in light of the results of the last section, showing that the kinetic model is insensitive to variations of the collision rate outside the five-dimensional subspace. Furthermore, hard-sphere molecular dynamics results at this density[12] are in substantial agreement with the $\hbar\omega=0$ MM results of Fig. 3. Consequently, it is likely that the discrepancies should be attributed to the unrealistic nature of the hard-sphere potential model.

A more graphic representation of the failure of hard spheres to accurately model xenon gas is shown in Fig. 4. The full width at half maximum for hard spheres is seen to be too large for $k \lesssim 1$ and too small for $1 < k \lesssim 1.5$. Interestingly, for $k < 1$ the hard-sphere width is also larger than that for an ideal gas, a point that has been observed recently elsewhere.[22] The fact that the deviations in widths changes sign with k suggests that the difference in potential model is responsible for more than an overall change in collision rate, as might be expected from comparison of transport coefficients. Instead it appears that a detailed description of the spatial dependence of particles interacting via continuous potentials is required. The situation should clarify when molecular dynamics results for continuous potentials are available for comparison with both experimental results and hard-sphere molecular dynamics results. A practical kinetic theory of dense gases for continuous potentials with accuracy comparable to the Enskog theory is still lacking.

VI. DISCUSSION

The kinetic model for $S(k,\omega)$ suggested above, Eq. (4.7), has been obtained by requiring that sufficient information about the exact generalized Enskog operator be maintained for the accurate representation of the hydrodynamic limit, i.e., small k and ω. At larger k and ω the k dependence of these same matrix elements provides the exact low-order frequency moments of $S(k,\omega)$. Consequently, the model is accurate at the limits of

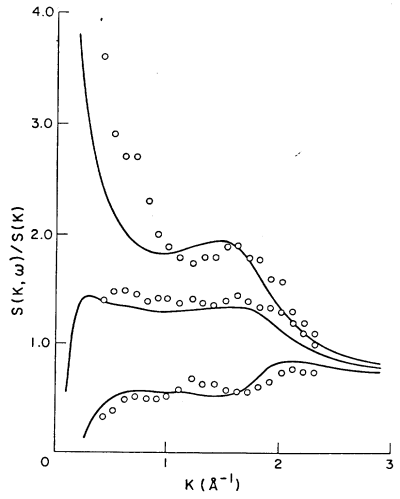

FIG. 3. Comparison of $S(k,\omega)/S(k)$ for the MM model, Eq. (4.7) (——), and neutron-scattering data for krypton gas (o o o); for 0, 1, and 2 meV, respectively, from top to bottom.

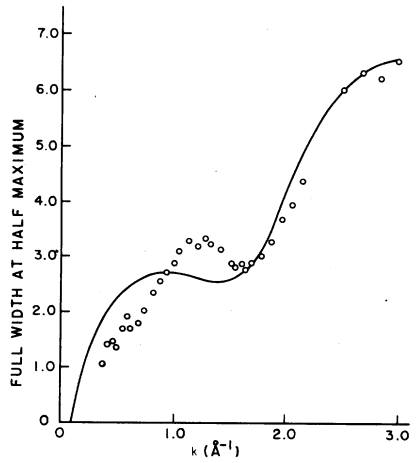

FIG. 4. Same as Fig. 3, except for the full width at half maximum.

small k,ω and large k,ω for all densities, and interpolates between them. The relative accuracy of the model for intermediate values of k and ω is expected on the basis of the results in Tables I and II, which show that $S(k,\omega)$ is quite insensitive to variations of the model in that portion of the subspace for which the approximations have been introduced. As will be shown elsewhere[12] these expectations are generally confirmed by comparison with molecular dynamics simulations. The constraints of hydrodynamics require that only matrix elements of the collision operator in a five-dimensional subspace need to be retained. However, this should not be confused with retaining only the hydrodynamic part of $S(k,\omega)$. The kinetic models discussed above all describe both hydrodynamic and microscopic modes. As noted in the Introduction de Schepper and Cohen have recently suggested that the further approximation of retaining only the hydrodynamic modes of a kinetic model may also be a good description, if these models are suitably extended to larger k than those of Appendix A. See also Ref. 23 for further discussion of this suggestion.

The comparison of the kinetic-model calculations with xenon data suggests that significant differences between the dynamics of hard spheres and that for real fluids may be studied via $S(k,\omega)$. These differences are expected to be enhanced at lower temperatures and in the gas phase. Further analysis is called for before any substantive conclusions can be drawn, but $S(k,\omega)$ continues to prove a good testing ground for many-body theories of the dynamic structure of fluids.

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APPENDIX A: HYDRODYNAMIC MODES OF $L_s(k)$

The discrete eigenvalues and corresponding eigenfunctions of $L_s(k)$ may be determined from

$$L_s(k)\psi_\alpha(k)=\lambda_\alpha(k)\psi_\alpha(k)\ . \tag{A1}$$

For $k=0$ there is a threefold degenerate eigenvalue at $\lambda_\alpha(0)=0$, corresponding to conservation of particle number, energy, and momentum along $\vec{k}$. The corresponding eigenfunctions are u_α^s of Eq. (2.13) for $\alpha=1-3$,

$$L_s(0)u_\alpha^s=0,\quad \alpha=1-3\ . \tag{A2}$$

This degeneracy is removed at $k\neq 0$, yielding the hydrodynamic modes of Eq. (3.1). For sufficiently small k these eigenvalues may be determined by perturbation theory. Assuming that $L_s(k)$, $\psi_\alpha(k)$, and $\lambda_\alpha(k)$ are analytic in k,

$$\begin{aligned} L_s(k)&=L_0+kL_1+k^2L_2+\cdots\ ,\\ \psi_\alpha(k)&=\psi_\alpha^{(0)}+k\psi_\alpha^{(1)}+\cdots\ ,\\ \lambda_\alpha(k)&=0+k\lambda_\alpha^{(1)}+k^2\lambda_\alpha^{(2)}+\cdots\ . \end{aligned} \tag{A3}$$

Substitution of (A3) in (A1) then gives the equations of the first- and second-order perturbation expansion,

$$L_1\psi_\alpha^{(0)}+L_0\psi_\alpha^{(1)}=\lambda_\alpha^{(1)}\psi_\alpha^{(0)}\ , \tag{A4}$$

$$L_2\psi_\alpha^{(0)}+L_1\psi_\alpha^{(1)}+L_0\psi_\alpha^{(2)}=\lambda_\alpha^{(1)}\psi_\alpha^{(1)}+\lambda_\alpha^{(2)}\psi_\alpha^{(0)}\ . \tag{A5}$$

1. First order

The operator L_0 is symmetric with respect to the scalar product, Eq. (2.1), so that taking the scalar product of Eqs. (A4) with u_α^s for $\alpha=1-3$ gives

$$\lambda_\beta^{(1)}(u_\alpha^s,\psi_\beta^{(0)})=(u_\alpha^s,L_1\psi_\beta^{(0)})\ . \tag{A6}$$

The $\psi_\alpha^{(0)}$ are solutions to $L_s(0)\psi_\alpha^{(0)}=0$ and must be of the form

$$\psi_\alpha^{(0)}=\sum_{\beta=1}^{3}C_{\alpha\beta}u_\beta^s \tag{A7}$$

so that the first-order eigenvalues are solutions to

$$\sum_{\gamma=1}^{3}C_{\beta\gamma}[(u_\alpha^s,[i\hat{k}\cdot\vec{v}-B_1]u_\gamma^s)-\lambda_\beta^{(1)}\delta_{\alpha\gamma}]=0\ . \tag{A8}$$

The matrix elements of B_1 may be calculated from the expansion of the generalized Enskog operator, Eq. (2.5), to first order in k. The condition for solutions to Eq. (A8) is then found to be

$$\begin{vmatrix} -\lambda^{(1)} & \frac{iv_0}{\sqrt{2}} & 0 \\ \frac{iv_0}{\sqrt{2}}[1-nC(0)] & -\lambda^{(1)} & \frac{iv_0}{\sqrt{3}}(1+4\eta g) \\ 0 & \frac{iv_0}{\sqrt{3}}(1+4\eta g) & -\lambda^{(1)} \end{vmatrix} = 0 \tag{A9}$$

with $v_0 \equiv (2/\beta m)^{1/2}$. The solutions are

$$\lambda_1^{(1)} = 0 , \tag{A10}$$

$$\lambda_{2,3}^{(1)} = \pm iC_s \equiv \pm \frac{iv_0}{\sqrt{2}}[1-nC(0)+\tfrac{2}{3}(1+4\eta g)^2]^{1/2} .$$

The corresponding eigenfunctions are

$$\psi_1^{(0)} = N_1 \left[u_1^s - \sqrt{3/2}\frac{[1-nC(0)]}{(1+4\eta g)} u_3^s \right] , \tag{A11}$$

$$\psi_{2,3}^{(0)} = N_{2,3} \left[u_1^s \pm \sqrt{2}\frac{C_s}{v_0} u_2^s + \sqrt{2/3}(1+4\eta g) u_3^s \right] ,$$

where the N_α are normalization constants. This set $\{ \psi_\alpha^{(0)} \}$ is not pairwise orthogonal, due to the fact that the perturbation is not Hermitian. However, a second set $\{ \phi_\alpha^{(0)} \}$ may be found such that $\{ \phi_\alpha^{(0)} \}$ and $\{ \psi_\alpha^{(0)} \}$ are biorthogonal, i.e.,

$$(\phi_\alpha^{(0)}, \psi_\beta^{(0)}) = \delta_{\alpha\beta} . \tag{A12}$$

This set is given by

$$\phi_1^{(0)} = N_1' \left[u_1^s - \sqrt{3/2}\frac{1}{1+4\eta g} u_3^s \right] ,$$

$$\phi_{2,3}^{(0)} = N_{2,3}' \left[u_1^s \pm \frac{\sqrt{2}}{1-nC(0)}\frac{C_s}{v_0} u_2^s + \sqrt{2/3}\frac{(1+4\eta g)}{[1-nC(0)]} u_3^s \right] , \tag{A13}$$

and the normalization condition gives

$$N_1 N_1' = \frac{1}{3}\left[\frac{v_0}{C_s}\right]^2 (1+4\eta g)^2 ,$$

$$N_2 N_2' = N_3 N_3' = \frac{1}{4}\left[\frac{v_0}{C_s}\right]^2 [1-nC(0)] . \tag{A14}$$

The eigenvalues to first order may then be written

$$\lambda_\alpha^{(1)} \delta_{\alpha\beta} = (\phi_\alpha^{(0)}, L_1 \psi_\beta^{(0)}) \tag{A15}$$

with

$$(\phi_\alpha^{(0)}, L_1 \psi_\beta^{(0)}) = iC_s \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} . \tag{A16}$$

This verifies the first result quoted in Sec. III, namely that the sound velocity is completely determined by the properties of L_s in the subspace spanned by $\{ u_\alpha \}$, $\alpha = 1-3$.

2. Second order

The first-order eigenfunctions are given by Eq. (A4) with $\lambda_\alpha^{(1)}$ given by (A15),

$$\psi_\alpha^{(1)} = L_0^{-1}(\lambda_\alpha^{(1)} - L_1)\psi_\alpha^{(0)} + \sum_{\beta=1}^{3} d_{\alpha\beta}\psi_\beta^{(0)} . \tag{A17}$$

The coefficients $d_{\alpha\beta}$ are arbitrary at this point. Substituting (A17) into the second-order equation, (A5), and taking its scalar product with respect to $\phi_\beta^{(0)}$, we obtain

$$\lambda_\alpha^{(2)}\delta_{\alpha\beta} = (\phi_\beta^{(0)}, L_2\psi_\alpha^{(0)}) - (\phi_\beta^{(0)}, [L_1 - \lambda_\alpha^{(1)}]L_0^{-1}[L_1 - \lambda_\alpha^{(1)}]\psi_\alpha^{(0)}) + (\lambda_\beta^{(1)} - \lambda_\alpha^{(1)})d_{\alpha\beta} \tag{A18}$$

or, more explicitly,

$$\lambda_1^{(2)} = (\phi_1^{(0)}, L_2\psi_1^{(0)}) - (\phi_1^{(0)}, L_1 L_0^{-1} L_1 \psi_1^{(0)}) ,$$

$$\lambda_{2,3}^{(2)} = (\phi_{2,3}^{(0)}, L_2\psi_{2,3}^{(0)}) - (\phi_{2,3}^{(0)}, (L_1 \mp iC_s)L_0^{-1}(L_1 \mp iC_s)\psi_{2,3}^{(0)}) . \tag{A19}$$

Consider first the expression for $\lambda_1^{(2)}$. The term $L_1\psi_1^{(0)}$ is orthogonal to u_α^s, for $\alpha = 1-3$. It may be decomposed further into its component along u_4^s and the component orthogonal to u_α^s, $\alpha = 1-4$. Then $\lambda_1^{(2)}$ becomes

$$\lambda_1^{(2)} = (\phi_1^{(0)}, L_2\psi_1^{(0)}) - (\phi_1^{(0)}, L_1 L_0^{-1} u_4^s)(u_4^s, L_1\psi_1^{(0)}) - (\phi_1^{(0)}, L_1 L_0^{-1} P L_1 \psi_1^{(0)}) . \tag{A20}$$

The projection operator P projects orthogonal to u_α^s, $\alpha = 1-4$. The first two terms in Eq. (A20) may now

be evaluated to give,

$$\lambda_1^{(2)}=\frac{\lambda_T}{\rho C_p}\ , \tag{A21}$$

where C_p and C_v are the specific heats at constant pressure and volume,

$$C_p=C_v\left[1+\frac{2}{3}\frac{(1+4\eta g)^2}{[1-nC(0)]}\right],\quad C_v=\frac{3}{2}\frac{k_B}{m} \tag{A22}$$

and the thermal conductivity λ_T is identified as

$$\lambda_T=\frac{\lambda_T^{(0)}}{g}\left[(1+\tfrac{12}{5}\eta g)^2+\frac{24k_B(\eta g)^2}{\pi\sigma^2\lambda_T^{(0)}\sqrt{\pi\beta m}}\right]+\frac{N_1 i v_0\sqrt{5}}{2}\frac{[1-nC(0)]}{(1+4\eta g)}(1+\tfrac{12}{5}\eta g)(\phi_1^{(0)},B_1PL_0^{-1}u_4^s)$$
$$-(\phi_1^{(0)},L_1L_0^{-1}PL_1\psi_1^{(0)})\ . \tag{A23}$$

Here $\lambda_T^{(0)}$ is the Boltzmann thermal conductivity,

$$\lambda_T^{(0)}=g\tfrac{5}{4}k_B n v_0^2(u_4^s,L_0^{-1}u_4^s)\ . \tag{A24}$$

Equation (A23) is the result used in Sec. III, Eqs. (3.5) and (3.6). The last two terms in Eq. (A23) vanish, and with the approximation (3.9), the Enskog result, (3.11), for λ_T is obtained. Consequently, the thermal conductivity is seen to be determined by the properties of L_s in the space spanned by u_α^s, $\alpha=1-4$.

Next consider the expressions for $\lambda_{2,3}^{(2)}$, Eq. (A19). A similar decomposition of $L_1\psi_{2,3}^{(0)}$ into its component along u_4^s and that orthogonal to u_α^s, $\alpha=1-4$, leads eventually to

$$\lambda_2^{(2)}=\lambda_3^{(2)}=\Gamma\ , \tag{A25}$$

where the sound damping constant is defined by

$$\Gamma=\frac{\lambda_T}{2\rho C_p}\left[\frac{C_p}{C_v}-1\right]+\frac{1}{2\rho}(\tfrac{4}{3}\eta_s+\xi) \tag{A26}$$

and $(\frac{4}{3}\eta_s+\xi)$ is identified as

$$(\tfrac{4}{3}\eta_s+\xi)=\frac{9}{5\pi\sigma^2 g}\sqrt{m/\pi\beta}(4\eta g)^2$$
$$-2\rho(\phi_2^{(0)},L_1L_0^{-1}PL_1\psi_2^{(0)})\ . \tag{A27}$$

To evaluate the last term in Eq. (A27) one last decomposition is useful, dividing $PL_1\psi_2^{(0)}$ into its projection along u_5^s and its component orthogonal to u_α^s, $\alpha=1-5$. This gives,

$$(\tfrac{4}{3}\eta_s+\xi)=\tfrac{4}{3}\eta_s^{(0)}\frac{1}{g}(1+\tfrac{8}{5}\eta g)^2+\frac{9}{5\pi\sigma^2 g}\sqrt{m/\pi\beta}(4\eta g)^2-2\rho(\phi_2^{(0)},L_1L_0^{-1}\bar{P}L_1\psi_2^{(0)}) \tag{A28}$$

where $\bar{P}$ projects orthogonal to u_α^s, $\alpha=1-5$, and $\eta_s^{(0)}$ is the Boltzmann shear viscosity

$$\eta_s^{(0)}=\frac{\rho}{2}g v_0^2(u_5^s,L_0^{-1}u_5^s)\ . \tag{A29}$$

Equation (A28) is the result used in Sec. III, Eq. (3.13). Direct calculation shows that the term $\bar{P}L_1\psi_2^{(0)}=0$, so that with the approximation (3.17) the Enskog result (3.19) is obtained. Therefore, the sound damping constant is determined from the properties of L_s in the subspace spanned by u_α^s, $\alpha=1-5$.

In summary, to second order in k the eigenvalues are

$$\lambda_1(k)=\frac{\lambda_T}{\rho C_p}k^2$$

$$\lambda_{2,3}(k)=\pm iC_s k+\Gamma k^2 \tag{A30}$$

with λ_T and Γ given by Eqs. (3.11), (3.12), and (3.19).

APPENDIX B: DETAILS OF THE KINETIC MODEL

In this appendix the equations (4.2) determining $S(k,\omega)$ are described in more detail. For practical purposes it is better to consider the dimensionless equations

$$kv_0\frac{S(k,\omega)}{S(k)}=2\,\mathrm{Im}C_1(k,\omega)\ , \tag{B1}$$

where C_1 is the solution to the set of five coupled equations,

$$C_\alpha = C_\alpha^{(0)} - iy \sum_{\beta=1}^{5} \sum_{\gamma=1}^{5} D_{\alpha\beta} E_{\beta\gamma} C_\gamma \ . \tag{B2}$$

Here the functions C_α, $C_\alpha^{(0)}$, $D_{\alpha\beta}$, and $E_{\alpha\beta}$ are defined by

$$\begin{aligned} C_\alpha &\equiv ikv_0(u_\alpha^s, R\,1) \ , \\ C_\alpha^0 &\equiv ikv_0(u_\alpha^s, R_0 1) \ , \\ D_{\alpha\beta} &\equiv ikv_0(u_\alpha^s, R_0 u_\beta^s) \ , \\ E_{\alpha\beta} &\equiv (u_\alpha^s, (B^* - \lambda^*) u_\beta^s) \ . \end{aligned} \tag{B3}$$

Also,

$$\begin{aligned} R_0 &\equiv (-i\omega + i\vec{k}\cdot\vec{v} - \lambda)^{-1} \ , \\ B^* &\equiv B(k)/\lambda_0 \ , \\ \lambda^* &\equiv \lambda(k)/\lambda_0 \ , \\ y &\equiv \lambda_0/kv_0 \ , \end{aligned} \tag{B4}$$

and λ_0 is an arbitrary normalization constant introduced to scale $B(k)$. A useful choice is

$$\lambda_0 \equiv |B_{55}(0)| = \frac{12v_0}{5\sigma}\sqrt{2/\pi}(4\eta g) \ . \tag{B5}$$

The matrix elements, $B_{\alpha\beta}^*(k) \equiv (u_\alpha^s, B(k) u_\beta^s)/\lambda_0$ are given by

$$\begin{aligned} B_{1\alpha}^* &= 0 , \quad \alpha = 1-5, \\ B_{\alpha 1}^* &= 0 , \quad \alpha = 1,3-5, \\ B_{21}^* &= \frac{5ikC(k)}{16\sqrt{\pi} g\sigma^2} \ , \\ B_{22}^* &= -\frac{5}{2}\left[\tfrac{1}{3} - j_0(x) + \frac{2}{x} j_1(x)\right] , \\ B_{23}^* &= B_{32}^* = -i\tfrac{5}{4}\sqrt{\pi/6}\, j_1(x) \ , \\ B_{24}^* &= B_{42}^* = \frac{1}{2\sqrt{10}} B_{22}^* \ , \\ B_{25}^* &= B_{52}^* = -i\tfrac{5}{12}\sqrt{3\pi}\left[\frac{3}{x} j_0(x) + \left[1 - \frac{9}{x^2}\right] j_1(x)\right] , \\ B_{33}^* &= -\tfrac{5}{6}[1 - j_0(x)] \ , \\ B_{34}^* &= B_{43}^* = \frac{3}{\sqrt{10}} B_{23}^* \ , \\ B_{35}^* &= B_{53}^* = 0 , \\ B_{44}^* &= -\tfrac{2}{3}\left(1 - \tfrac{81}{80} B_{22}^*\right) , \\ B_{45}^* &= B_{54}^* = 0 , \\ B_{55}^* &= -\frac{4}{3}\left[1 - \frac{5}{4}\left[1 - \frac{18}{x^2}\right] j_0(x) + \frac{15}{2x}\left[1 - \frac{9}{x^2}\right] j_1(x)\right] , \end{aligned} \tag{B6}$$

where $x = k\sigma$. It is also straightforward to determine the functions $C_\alpha^{(0)}$ and $D_{\alpha\beta}$ in terms of the plasma dispersion function

$$\phi(z) \equiv \int_{-\infty}^{\infty} \frac{dv}{\sqrt{\pi}} \frac{e^{-v^2}}{v - z} \tag{B7}$$

with

$$z \equiv w - i\lambda^* y \ , \quad w \equiv \omega/kv_0 \ . \tag{B8}$$

The results are

$$\begin{aligned} C_1^0 &= \phi(z) \ , \\ C_2^0 &= \sqrt{2}[1 + z\phi(z)] \ , \\ C_3^{(0)} &= \sqrt{2/3}[z + (z^2 - \tfrac{1}{2})\phi(z)] \ , \\ C_4^{(0)} &= \frac{2}{\sqrt{5}}[(z^2 - 1) + z(z^2 - \tfrac{3}{2})\phi(z)] \ , \\ C_5^{(0)} &= \sqrt{2} C_3^{(0)} \ , \end{aligned} \tag{B9}$$

and

$$\begin{aligned} D_{\alpha\beta} &= D_{\beta\alpha} , \quad \alpha,\beta = 1-5 \ , \\ D_{1\alpha} &= C_\alpha^{(0)} , \quad \alpha = 1-5 \ , \\ D_{2\alpha} &= \sqrt{2} z C_\alpha^{(0)} , \quad \alpha = 2-5 \ , \\ D_{33} &= \tfrac{2}{3}[C_1^{(0)} + \sqrt{3/2}(z^2 - \tfrac{1}{2}) C_3^{(0)}] \ , \\ D_{34} &= \sqrt{6/5}[1 + \tfrac{2}{3} z C_1^{(0)} + \sqrt{2/3} z (z^2 - \tfrac{3}{2}) C_3^{(0)}] \ , \\ D_{35} &= \frac{2}{\sqrt{3}}\left[(z^2 - \tfrac{1}{2}) C_3^{(0)} - \frac{1}{\sqrt{6}} C_1^{(0)}\right] , \\ D_{44} &= \tfrac{6}{5} z \left[1 + \tfrac{2}{3} z C_1^{(0)} + \sqrt{2/3} z (z^2 - \tfrac{3}{2}) C_3^{(0)} - \frac{\sqrt{5}}{3} C_4^{(0)}\right] , \\ D_{45} &= \sqrt{3/5}[-1 - \tfrac{2}{3} z C_1^{(0)} - \sqrt{2/3} z (z^2 - \tfrac{3}{2}) C_3^{(0)} + \sqrt{5}(z^2 - \tfrac{1}{2}) C_4^{(0)}] \ , \\ D_{55} &= \sqrt{3}\left[\frac{1}{3\sqrt{3}} C_1^{(0)} - \frac{\sqrt{2}}{3}(z^2 - \tfrac{1}{2}) C_3^{(0)} + (z^2 - \tfrac{1}{2}) C_5^{(0)}\right] . \end{aligned} \tag{B10}$$

Equations (B2) may be written in matrix form

$$AC = C^{(0)}, \tag{B11}$$

where $C^{(0)}$ is the five-dimensional column matrix with elements $C_\alpha^{(0)}$, and A is the five-by-five square matrix elements

$$A_{\alpha\beta} = \delta_{\alpha\beta} + iy \sum_{\gamma=1}^{5} D_{\alpha\gamma} E_{\gamma\beta} . \tag{B12}$$

The matrix multiplication of Eq. (B11) and inversion of (B10) were done numerically in complex arithmetic. A detailed listing of the program is available on request. The hard-sphere equilibrium properties used are those of the Percus-Yevick theory, i.e.,

$$g(\sigma) = (1 - \tfrac{1}{2}\eta - \tfrac{1}{2}\eta^2)/(1-\eta)^3 , \tag{B13}$$

$$nC(k) = \frac{-24\eta}{(1-\eta)^4}\left[(1+2\eta)^2\frac{1}{x^3}(\sin x - x\cos x) - 6\eta(1+\tfrac{1}{2}\eta)^2\frac{1}{x^4}[2x\sin x - (x^2-2)\cos x - 2]\right.$$
$$\left. + \tfrac{1}{2}\eta(1+2\eta)^2\frac{1}{x^6}[(4x^3-24x)\sin x - (x^4-12x^2+24)\cos x + 24]\right] . \tag{B14}$$

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[1] J. L. Lebowitz, J. K. Percus, and J. Sykes, Phys. Rev. 188, 487 (1969).

[2] J. Ferziger and H. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).

[3] J. R. Dorfman and E. G. D. Cohen, Phys. Rev. A 12, 292 (1975).

[4] T. Reed and K. Gubbins, *Applied Statistical Mechanics* (McGraw-Hill, New York, 1973).

[5] J. P. Hansen and I. MacDonald, *Theory of Simple Fluids* (Academic, New York, 1976).

[6] S. Yip, Annu. Rev. Phys. Chem. 30, 547 (1979).

[7] V. Ghaem-Maghami and A. D. May, Phys. Rev. A 22, 692 (1980).

[8] P. M. Furtado, G. F. Mazenko, and S. Yip, Phys. Rev. A 12, 1653 (1975); 13, 1641 (1976).

[9] I. M. de Schepper and E. G. D. Cohen, Phys. Rev. A 22, 287 (1980).

[10] J. W. Dufty and M. J. Lindenfeld [unpublished; see however, results in L. Groome, A. Teitsma, P. Egelstaff, and H. Mook, J. Chem. Phys. 73, 1393 (1980)].

[11] E. P. Gross and E. A. Jackson, Phys. Fluids 2, 432 (1959); A. Sugawara, S. Yip, and L. Sirovich, *ibid.* 11, 925 (1968).

[12] S. Yip, W. Alley, and B. Alder (unpublished); B. Alder (private communication).

[13] V. Ghaem-Maghami and A. D. May, Phys. Rev. A 22, 1686 (1980).

[14] C. D. Andriesse, Physica (Utrecht) 48, 61 (1970); 49, 502 (1970); A. Hasman, *ibid.* 63, 499 (1973).

[15] P. A. Egelstaff, W. Gläser, D. Litchinsky, E. Schneider, and J. B. Suck (unpublished).

[16] T. A. Postol and C. A. Pelizarri, Phys. Rev. 18, 2321 (1978).

[17] S.-H. Chen, H. C. Teh, and S. Yip in *Neutron Inelastic Scattering 1977,* Vol. II (International Atomic Energy Agency, Vienna, 1978).

[18] L. Groome, J. W. Dufty, and M. Lindenfeld, Phys. Rev. A 19, 304 (1979).

[19] Strictly speaking, the transport coefficients determined from the matrix elements of $B(k)$ in the five-dimensional subspace are not exact, due to the approximations (3.9) and (3.17). These are the usual first Sonine polynomial approximations used to calculate transport coefficients and have an error of the order of 2%.

[20] J. W. Dufty and M. J. Lindenfeld, Phys. Rev. A 24, 1132 (1981).

[21] P. Egelstaff, Annu. Rev. Phys. Chem. 24, 159 (1973).

[22] L. Groome, A. Teitsma, P. Egelstaff, and H. Mook, J. Chem. Phys. 73, 1393 (1980).

[23] M. C. Marchetti, G. E. Garland, and J. W. Dufty (to be published).