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Very-Short-Wavelength Collective Modes in Fluids

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The existence of very-short-wavelength collective modes in fluids is discussed. These collective modes are the extensions of the five hydrodynamic (heat, sound, viscous) modes to wavelengths of the order of the mean free path in a gas or to a fraction of the molecular size in a liquid. They are computed here explicitly on the basis of a model kinetic equation for a hard sphere fluid. At low densities all five modes are increasingly damped with decreasing wavelength till each ceases to exist at a cutoff wavelength. At high densities the extended heat mode softens very appreciably for wavelengths of the order of the size of the particles and becomes a diffusion-like mode that persists till much shorter wavelengths than the other modes. Except for the shortest wavelengths these collective modes and in particular the heat mode dominate the dynamical structure factor $S(k, \omega)$ for all densities. The agreement of the theory with experimental $S(k, \omega)$ of liquid Ar seems to imply that very-short-wavelength collective modes also occur in real fluids.

KEY WORDS: Hydrodynamical modes; collective modes; fluids; kinetic theory; neutron scattering.

1. INTRODUCTION

The time evolution of small disturbances that vary slowly in space and time in a fluid in thermal equilibrium can be described in terms of hydrodynamic modes, i.e., in terms of the eigenvalues and eigenfunctions of the linearized equations of hydrodynamics.[1] These hydrodynamic modes are the heat mode, two sound modes, and two viscous modes, which corre-

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spond to the eigenvalues

$$\begin{aligned} z_H(k) &= -D_T k^2 \\ z_{\pm}(k) &= \pm ick - \Gamma k^2 \\ z_{\nu_i} &= -\nu k^2 \qquad (i = 1, 2) \end{aligned} \tag{1.1}$$

respectively.[2] In fact, the real parts of the $z(k)$ are the inverse decay times associated with the hydrodynamic modes each of which corresponds to a particular disturbance of the fluid. In (1.1) k is the (small) wave number describing the spatial variation of the disturbances, $D_T = \lambda / nc_p$ is the thermal diffusivity, $\nu = \eta / mn$ the kinematic viscosity, $\Gamma = \frac{2}{3}\nu + \frac{1}{2}\zeta/nm + \frac{1}{2}(\gamma - 1)D_T$ the sound damping constant, where λ is the thermal conductivity, η the shear viscosity, ζ the bulk viscosity, n the number density, m the mass of the particles, $\gamma = c_p / c_v$ the ratio of the specific heats per particle at constant pressure (c_p) and constant volume (c_v), and c the sound velocity.

The question we address ourselves here to is to what extent these hydrodynamic modes can be extended to larger values of k and then describe small disturbances with large values of k, i.e., disturbances with small amplitudes but with rapid spatial variations. We will call the hydrodynamic modes and their extensions collective modes.

The discussion of the existence of collective modes beyond the hydrodynamical regime can be based on kinetic theory.

For low densities, i.e., for dilute gases, one can use the linearized Boltzmann equation. In fact Foch and Ford[2] showed, on the basis of a model kinetic equation that approximates the linearized Boltzmann equation, that the sound modes could be extended to values of k such that $kl \approx 1$, where l is the mean free path in the gas.

Up until the present day one has not been able to generalize the Boltzmann equation in a systematic way to higher densities. Therefore, in that case—i.e., for dense gases or liquids—no well-founded kinetic equation of the same stature as the Boltzmann equation is available. Only for the special case of a fluid of hard spheres has an approximate kinetic equation been derived in a variety of ways by a number of authors.[3-7] We will show in Section 2 that, although approximate, the kinetic operator occurring in this equation possesses a number of desirable properties. Also, the equation reduces for small values of k to the linearized Boltzmann equation for hard spheres for low densities and to the linearized Enskog equation for high densities.[6,8] We will base our discussion of the existence of collective modes in fluids on what we will call this generalized Enskog equation. Like Foch and Ford we actually study a model kinetic equation that approximates this generalized Enskog equation. It will be argued later that the approximate equation we study appears to be a good approximation to the generalized Enskog equation.

In this paper we study in particular the collective modes of the generalized Enskog equation and their importance for the decay of small density disturbances in the fluid. In other words we compute the dynamical structure factor $S(k,\omega)$ or its Fourier transform, the intermediate scattering function given by

$$F(k,t) = \frac{1}{N}\left\langle \sum_{j=1}^{N} \exp(-i\mathbf{k}\cdot\mathbf{r}_j) \sum_{l=1}^{N} \exp[i\mathbf{k}\cdot\mathbf{r}_l(t)] \right\rangle_0 \tag{1.2}$$

and the intermediate self-scattering function

$$F^s(k,t) = \langle \exp\{-i\mathbf{k}\cdot[\mathbf{r}_1 - \mathbf{r}_1(t)]\}\rangle_0 \tag{1.3}$$

Here $\mathbf{r}_j(t)$ is the position of particle j ($j = 1, 2, \ldots, N$) in the fluid at time $t, \mathbf{r}_j \equiv \mathbf{r}_j(0)$, the brackets indicate an average over a canonical ensemble, and the bulk limit is supposed to be taken on the right-hand sides. We will show that for not too large values of ω, $S(k,\omega)$ of a hard sphere fluid computed on the basis of our generalized Enskog equation agrees well with $S(k,\omega)$ determined by the collective modes alone. In fact, we will derive an expression for $S(k,\omega)$ that is a generalization of the well-known Landau–Placzek formula for light scattering[1] [cf. Eq. (3.34)]

$$\begin{aligned} S(k,\omega) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}F(k,t) \\ &= \frac{1}{\pi}S(0)\left\{ \frac{\gamma-1}{\gamma}\mathrm{Re}\frac{1}{i\omega - z_H(k)} \right. \\ &\qquad \left. + \frac{1}{2\gamma}\mathrm{Re}\left[\frac{1}{i\omega - z_+(k)} + \frac{1}{i\omega - z_-(k)}\right]\right\} \\ &= \frac{1}{\pi}nk_BT\chi_T\left\{ \frac{\gamma-1}{\gamma}\frac{D_Tk^2}{\omega^2 + (D_Tk^2)^2} \right. \\ &\qquad \left. + \frac{1}{2\gamma}\left[\frac{\Gamma k^2}{(\omega - ck)^2 + (\Gamma k^2)^2} + \frac{\Gamma k^2}{(\omega + ck)^2 + (\Gamma k^2)^2}\right]\right\} \end{aligned} \tag{1.4}$$

Here we have used that $S(0) = \lim_{k\to 0} S(k) = nk_BT\chi_T$, where $S(k)$ is the static structure factor defined by

$$S(k) = 1 + n\int d\mathbf{r}\exp(-i\mathbf{k}\cdot\mathbf{r})[g(r) - 1] \tag{1.5}$$

with $\chi_T = (1/n)(\partial n/\partial p)_T$ the isothermal compressibility, p the pressure, T the absolute temperature, k_B Boltzmann's constant, and $g(r)$ the radial distribution function. Moreover, the experimental $S(k, \omega)$ for liquid Ar agrees with the $S(k, \omega)$ computed on the basis of the heat mode alone, if a simple adaptation of the hard sphere fluid to a real liquid is made. Therefore, we believe that the existence and importance of collective modes —in particular the extended heat mode—is not an artifact of our model kinetic equation for hard spheres, but is also true for real fluids. A very brief account of the main results contained in this paper has been given in a previous publication.[9] The details of the calculations to obtain these results are given here.

In Section 2 some general properties of the kinetic operator occurring in the generalized Enskog theory will be discussed. In particular a number of properties that are essential and should be kept in any meaningful kinetic model are mentioned. In Section 3 the model kinetic operator used in our calculations is derived and the way the collective modes can be identified and computed is outlined. In Section 4 the main results of the calculations are summarized. In *general* the collective modes become increasingly damped with increasing k and disappear when k is of the order of the inverse mean free path of the fluid. For low densities the extended hydrodynamic modes are smooth functions of k. For high densities a peculiar behavior manifests itself for values of k where the wavelength $\lambda = 2\pi/k \approx \sigma$, the hard sphere diameter. In particular the heat mode shows a very appreciable softening at $\lambda \approx \sigma$. That is, the heat mode eigenvalue $z_H(k)$ after an initial decrease according to Eq. (1) starts to increase appreciably till it reaches a maximum value close to zero at $\lambda \approx \sigma$. For larger values of k this mode continues as a diffusionlike mode. Also the sound modes show a complicated behavior around $\lambda \approx \sigma$. In Section 5 a number of comments, in particular about the implications of these results for neutron scattering of real fluids, are made.

2. THE ENSKOG KINETIC OPERATORS

In this section we discuss properties of the two kinetic operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$ that occur in the generalized Enskog theory. We do this not only to show that these operators are meaningful kinetic operators that satisfy a number of basic requirements, but also in view of the approximation procedure presented in Section 4 that will be based in part on these properties.

The operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$ are one-particle operators that replace in the generalized Enskog theory the N-particle Liouville operator as the operators that govern the evolution of time correlation functions like those defined in Eqs. (1.2) and (1.3). In fact, in the generalized Enskog theory one has for $F(k,t)$ and $F^s(k,t)$, respectively,[3,5,8,10] the expressions[3]

$$F_E(k,t) = S(k)\langle \exp[L(\mathbf{k})t]\rangle \tag{2.1}$$

$$F_E^s(k,t) = \langle \exp[L^s(\mathbf{k})t]\rangle \tag{2.2}$$

Here and in the rest of the paper the brackets denote a velocity average with the normalized Maxwell velocity distribution function

$$\langle \cdots \rangle = \int d\mathbf{v}\, \phi(v) \cdots \tag{2.3}$$

with

$$\phi(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right) \tag{2.4}$$

where $\mathbf{v}$ is the velocity of a hard sphere with speed $v = |\mathbf{v}|$. $L(\mathbf{k})$ and $L^s(\mathbf{k})$ are defined by

$$L(\mathbf{k}) = -i\mathbf{k}\cdot\mathbf{v} + n\chi\Lambda_{\mathbf{k}} + nA_{\mathbf{k}} \tag{2.5}$$

$$L^s(\mathbf{k}) = i\mathbf{k}\cdot\mathbf{v} + n\chi\Lambda^s \tag{2.6}$$

with $-i\mathbf{k}\cdot\mathbf{v}$ representing the free streaming of a particle and $\chi = g(\sigma)$ the radial distribution function at contact. $\Lambda_{\mathbf{k}}$ and Λ^s are binary collision operators that act on an arbitrary function $h(\mathbf{v})$ as

$$\Lambda_{\mathbf{k}} h(\mathbf{v}) = -\sigma^2 \int_{\mathbf{g}\cdot\hat{\boldsymbol{\sigma}}>0} d\hat{\boldsymbol{\sigma}} \int d\mathbf{v}'\, \phi(v')\mathbf{g}\cdot\hat{\boldsymbol{\sigma}} \times \{h(\mathbf{v}) - h(\mathbf{v}^*) + \exp(-i\mathbf{k}\cdot\hat{\boldsymbol{\sigma}}\sigma)[h(\mathbf{v}') - h(\mathbf{v}'^*)]\} \tag{2.7}$$

$$\Lambda^s h(\mathbf{v}) = -\sigma^2 \int_{\mathbf{g}\cdot\hat{\boldsymbol{\sigma}}>0} d\hat{\boldsymbol{\sigma}} \int d\mathbf{v}'\, \phi(v')\mathbf{g}\cdot\hat{\boldsymbol{\sigma}}[h(\mathbf{v}) - h(\mathbf{v}^*)] \tag{2.8}$$

where $\mathbf{g} = \mathbf{v} - \mathbf{v}'$ is the relative velocity of two colliding hard spheres and the velocities of the restituting collision $\mathbf{v}^*$ and $\mathbf{v}'^*$ are given by the relations $\mathbf{v}^* = \mathbf{v} - (\mathbf{g}\cdot\hat{\boldsymbol{\sigma}})\hat{\boldsymbol{\sigma}}$, $\mathbf{v}'^* = \mathbf{v}' + (\mathbf{g}\cdot\hat{\boldsymbol{\sigma}})\hat{\boldsymbol{\sigma}}$ with $\hat{\boldsymbol{\sigma}}$ a unit vector and $\sigma\hat{\boldsymbol{\sigma}}$ defining the geometry of the binary collision. The "mean field" operator $A_{\mathbf{k}}$ acts on an arbitrary function $h(\mathbf{v})$ as

$$A_{\mathbf{k}} h(\mathbf{v}) = [C(k) - \chi C_0(k)] \int d\mathbf{v}'\, \phi(v') i\mathbf{k}\cdot\mathbf{v}' h(\mathbf{v}') \tag{2.9}$$

where $C(k)$ is the direct correlation function that is related to the structure

[3] Equations (2.1) and (2.2) apply for positive times only. In order to determine Fourier transforms we will use that $F(k,t)$ and $F^s(k,t)$ are symmetric in t, also in the generalized Enskog theory.

factor $S(k)$ by the equation

$$C(k) = \frac{S(k) - 1}{nS(k)} \tag{2.10}$$

$C_0(k)$ is the low-density limit of $C(k)$ and according to Eq. (1.5) given by

$$C_0(k) = \int_{r<\sigma} d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r}) = -4\pi\sigma^3 \frac{j_1(k\sigma)}{k\sigma} \tag{2.11}$$

where $j_1(x)$ stands for the spherical Bessel function $j_n(x)$ with $n = 1$.[11]

In order to discuss some basic properties of the operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$, we first give some properties of the operators $A_\mathbf{k}$ and $\Lambda_\mathbf{k}$.

(1) The operator $A_\mathbf{k}$ has the properties

$$\lim_{n\to 0} A_\mathbf{k} = 0 \tag{2.12}$$

$$\lim_{\mathbf{k}\to 0} A_\mathbf{k} = 0 \tag{2.13}$$

$$\lim_{\mathbf{k}\to \infty} A_\mathbf{k} = 0 \tag{2.14}$$

To prove these properties one uses, in addition to Eq. (2.9), that in the limit of low densities $\chi = 1$, $C(k) = C_0(k)$ and that for large k both $C_0(k) \sim 1/k^2$ [cf. Eq. (2.11)] and $C(k) \sim 1/k^2$ [cf. Eq. (2.10)] and Eq. (1.5).

(2) The collision operator $\Lambda_\mathbf{k}$ has the properties

$$\lim_{k\to 0} \Lambda_\mathbf{k} = \Lambda_0 \tag{2.15}$$

$$\lim_{k\to \infty} \Lambda_\mathbf{k} = \Lambda^s \tag{2.16}$$

where Λ_0 is the linearized Boltzmann collision operator and Λ^s the Lorentz–Boltzmann collision operator.

The equation (2.16) follows from the equations (2.7) and (2.8). We note that both operators $A_\mathbf{k}$ and $\Lambda_\mathbf{k}$ depend on k through the parameter $k\sigma$ only. This follows for $\Lambda_\mathbf{k}$ directly from Eq. (2.7) and for $A_\mathbf{k}$ from Eqs. (2.9), (2.10), and (1.5) and that $g(r)$ depends on r/σ. Therefore, in addition to the equalities (2.13)–(2.16) one can say that for $k\sigma \ll 1$, $\Lambda_\mathbf{k} \simeq \Lambda_0$ and for $k\sigma \gg 1$, $\Lambda_\mathbf{k} \cong \Lambda^s$ and $A_\mathbf{k} \simeq 0$.

These properties of $A_\mathbf{k}$ and $\Lambda_\mathbf{k}$ imply the following properties for $L(\mathbf{k})$ and $L^s(\mathbf{k})$:

$$L(\mathbf{k}) \simeq L^s(\mathbf{k}) \qquad (k\sigma \gg 1) \tag{2.17}$$

For low densities one has

$$L(\mathbf{k}) \simeq -i\mathbf{k}\cdot\mathbf{v} + n\Lambda_0 \qquad (k\sigma \ll 1) \tag{2.18}$$

$$L^s(\mathbf{k}) \simeq -i\mathbf{k}\cdot\mathbf{v} + n\Lambda^s \tag{2.19}$$

Thus $L(\mathbf{k})$ tends to the inhomogeneous linearized Boltzmann operator

$-i\mathbf{k}\cdot\mathbf{v} + n\Lambda_0$ and $L^s(\mathbf{k})$ to the inhomogeneous Lorentz–Boltzmann operator $-i\mathbf{k}\cdot\mathbf{v} + n\Lambda^s$ for sufficiently low densities. For all densities and $k \to 0$ one has

$$L(0) = n\chi\Lambda_0 \tag{2.20}$$

$$L^s(0) = n\chi\Lambda^s \tag{2.21}$$

as follows from eqs. (2.5), (2.6), and (2.13).

The Boltzmann collision operator Λ_0 has five zero eigenfunctions, which are the five collision invariants 1, $\mathbf{v}$, v^2, while the Lorentz–Boltzmann collision operator Λ^s has only one zero eigenfunction 1. Thus

$$L(0)\varphi_j(\mathbf{v}) = 0 \qquad (j = 1, \ldots, 5) \tag{2.22}$$

has five nonzero solutions and

$$L^s(0)\varphi_1(\mathbf{v}) = 0 \tag{2.23}$$

has one nonzero solution, where the $\varphi_j(\mathbf{v})$ are the following orthonormal linear combinations of the collision invariants:

$$\varphi_1(\mathbf{v}) = 1 \tag{2.24}$$

$$\varphi_2(\mathbf{v}) = (\beta m)^{1/2} v_z \tag{2.25}$$

$$\varphi_3(\mathbf{v}) = \frac{1}{\sqrt{6}}(\beta m v^2 - 3) \tag{2.26}$$

$$\varphi_4(\mathbf{v}) = (\beta m)^{1/2} v_x \tag{2.27}$$

$$\varphi_5(\mathbf{v}) = (\beta m)^{1/2} v_y \tag{2.28}$$

Here $\beta = 1/k_B T$, $\langle \varphi_j \varphi_l \rangle = \delta_{jl}$ and the z axis of our coordinate system has been chosen parallel to the vector $\mathbf{k}$.

We are especially interested in the collective modes of the operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$. These will appear as particular terms in the spectral decomposition of these operators, i.e., in

$$L(\mathbf{k}) = \sum_j |\Psi_j\rangle z_j(k) \langle \Phi_j| \tag{2.29}$$

$$L^s(\mathbf{k}) = \sum_j |\Psi_j^s\rangle z_j^s(k) \langle \Phi_j^s| \tag{2.30}$$

Here the bra–ket notation refers to the inner product

$$\langle f | g \rangle \equiv \langle f^* g \rangle \tag{2.31}$$

and j runs over all eigenvalues $z_j(k)$ of $L(\mathbf{k})$ and $z_j^s(\mathbf{k})$ of $L^s(k)$ defined by

$$L(\mathbf{k})\Psi_j(\mathbf{k}, \mathbf{v}) = z_j(k)\Psi_j(\mathbf{k}, \mathbf{v}) \tag{2.32}$$

$$L^s(\mathbf{k})\Psi_j^s(\mathbf{k}, \mathbf{v}) = z_j^s(k)\Psi_j^s(\mathbf{k}, \mathbf{v}) \tag{2.33}$$

for the right eigenfunctions $\Psi_j(\mathbf{k}, \mathbf{v})$ and $\Psi_j^s(\mathbf{k}, \mathbf{v})$ and by

$$L^\dagger(\mathbf{k})\Phi_j(\mathbf{k}, \mathbf{v}) = z_j^*(k)\Phi_j(\mathbf{k}, \mathbf{v}) \tag{2.34}$$

$$L^{s\dagger}(\mathbf{k})\Phi_j^s(\mathbf{k}, \mathbf{v}) = z_j^{s*}(k)\Phi_j^s(\mathbf{k}, \mathbf{v}) \tag{2.35}$$

for the left eigenfunctions $\Phi_j(\mathbf{k}, \mathbf{v})$ and $\Phi_j^s(\mathbf{k}, \mathbf{v})$. The Hermitian conjugate $\mathcal{O}^\dagger$ of an operator $\mathcal{O}$ is defined with respect to the inner product (2.31), i.e., $\langle \mathcal{O}^\dagger f | g\rangle = \langle f | \mathcal{O} g\rangle$. The right and left eigenfunctions are orthonormal so that

$$\langle \Phi_j^* \Psi_l \rangle = \delta_{jl} \tag{2.36}$$

$$\langle \Phi_j^{s*} \Psi_l^s \rangle = \delta_{jl} \tag{2.37}$$

The collective modes in (2.29) and (2.30) are those eigenfunctions and eigenvalues appearing on the right-hand sides of Eqs. (2.29) and (2.30) for which the eigenvalues go to zero for $k \to 0$. For the hydrodynamic modes, i.e., the collective modes for small k, explicit expressions can be obtained by applying perturbation theory to the eigenfunctions and eigenvalues at $k = 0$, i.e., the φ_j of (2.24)–(2.28), using k as a small parameter. Or, with Eqs. (2.18) and (2.19) the hydrodynamic modes are the perturbed eigenvalues and eigenfunctions of the Eqs. (2.22) and (2.23), using $-i\mathbf{k} \cdot \mathbf{v}$ as a small perturbation. Since there are five eigenfunctions of Eq. (2.22) and one eigenfunction of Eq. (2.23), there are correspondingly five hydrodynamic modes for $L(\mathbf{k})$ and one for $L^s(\mathbf{k})$. We only give for later reference the results. Derivations can be found in the literature[7] and in Appendix C.

(1) There is one heat mode $j = H$ in (2.29) with eigenvalue $z_H(k)$ given by

$$z_H(k) = -D_{TE}k^2 + \mathcal{O}(k^4) \tag{2.38}$$

where D_{TE} is the thermal diffusivity as given by the Enskog dense gas transport theory.[12] To lowest order in k, the eigenfunctions are

$$\Psi_H(0, \mathbf{v}) = \tilde{c}\varphi_1 - \frac{1}{(\beta m)^{1/2}} \varphi_3 \tag{2.39}$$

$$\Phi_H(0, \mathbf{v}) = \frac{1}{c^2 S(0)} \left[\tilde{c} S(0) \varphi_1 - \frac{1}{(\beta m)^{1/2}} \varphi_3 \right] \tag{2.40}$$

where $\tilde{c}$ is proportional to the speed of sound c and given by

$$\tilde{c} = c\left[(\gamma - 1)/\gamma\right]^{1/2} \tag{2.41}$$

The orthonormality (2.36) of Ψ_H and Φ_H given by Eqs. (2.39) and (2.40) can easily be proved using the expression for $S(0)$ given below Eq. (1.4) and the thermodynamic relation $mnc^2 = \gamma/\chi_T$.

(2) There are two sound modes, $j = \pm$, in (2.29) with eigenvalues given by

$$z_{\pm}(k) = \pm ick - \Gamma_E k^2 + \mathcal{O}(k^3) \tag{2.42}$$

where Γ_E is the sound damping as given by the Enskog dense gas theory.[12] To lowest order in k, the right eigenfunctions are given by

$$\Psi_{\pm}(0, \mathbf{v}) = \frac{1}{(\beta m)^{1/2} S(0)} \varphi_1 \mp c\varphi_2 + \tilde{c}\varphi_3 \tag{2.43}$$

while the left eigenfunctions are given by

$$\Phi_{\pm}(0, \mathbf{v}) = \frac{1}{2c^2}\left[\frac{1}{(\beta m)^{1/2}} \varphi_1 \mp c\varphi_2 + \tilde{c}\varphi_3\right] \tag{2.44}$$

The orthonormality of $\Psi_{\pm}$ and $\Phi_{\pm}$ can be proved in a similar way as for Ψ_H and Φ_H.

(3) There are two shear modes, $j = \nu_1$ and $j = \nu_2$ in (2.29) with eigenvalues given by

$$z_{\nu_1}(k) = z_{\nu_2}(k) = z_{\nu}(k) = -\nu_E k^2 + \mathcal{O}(k^4) \tag{2.45}$$

where ν_E is the kinematic viscosity as given by the Enskog dense gas theory.[12] To lowest order in k, the eigenfunctions are

$$\Psi_{\nu_1}(0, \mathbf{v}) = \Phi_{\nu_1}(0, \mathbf{v}) = \varphi_4 \tag{2.46}$$

$$\Psi_{\nu_2}(0, \mathbf{v}) = \Phi_{\nu_2}(0, \mathbf{v}) = \varphi_5 \tag{2.47}$$

(4) The diffusion mode, $j = D$, in (2.30) has an eigenvalue given by

$$z_D^s(k) = -D_E k^2 + \mathcal{O}(k^4) \tag{2.48}$$

where D_E is the self-diffusion coefficient as given by the Enskog dense gas theory.[12] To lowest order in k, the eigenfunctions are

$$\Psi_D^s(0, \mathbf{v}) = \Phi_D^s(0, \mathbf{v}) = \varphi_1 \tag{2.49}$$

We remark that the equations (2.38), (2.42), and (2.45) for the hydrodynamic eigenvalues correspond to those derived from linearized hydrodynamics as given in Eq. (1.1) except that the transport coefficients have been replaced by their values according to the Enskog theory.

The collective modes associated with the operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$ are these five hydrodynamic modes and their continuous extensions to larger values of k as long as these extensions can be uniquely determined. Hence, there are five collective modes in (2.29) denoted in general by $j = H, \pm, \nu_1, \nu_2$ and one collective mode in (2.30) denoted in general by $j = D$.

In the next section approximate expressions will be introduced for $L(\mathbf{k})$ and $L^s(\mathbf{k})$ in order to be able to determine explicitly these collective modes for all k for which they exist.

We now mention five exact properties of the eigenvalues and eigenfunctions of $L(\mathbf{k})$ and $L^s(\mathbf{k})$ and in particular, therefore, also of their collective modes. These properties imply that $L(\mathbf{k})$ and $L^s(\mathbf{k})$ satisfy a number of basic conditions that every kinetic operator describing the time evolution of a fluid should have. In addition, however, we will use these five properties in the approximation procedure discussed in the next section in that we impose these five conditions on the approximations to $L(\mathbf{k})$ and $L^s(\mathbf{k})$ that we will use. This will ensure that also the operators that approximate $L(\mathbf{k})$ and $L^s(\mathbf{k})$ employed in the next section possess a number of desirable basic properties and that they contain collective modes of the same character as $L(\mathbf{k})$ and $L^s(\mathbf{k})$. These five properties are as follows:

(1) All eigenvalues in (2.32)–(2.35) satisfy for $k \neq 0$

$$\mathrm{Re}\, z_j(k) < 0 \tag{2.50}$$

$$\mathrm{Re}\, z_j^s(k) < 0 \tag{2.51}$$

Using (2.38), (2.42), (2.45), and (2.48), this implies that the transport coefficients as given by the Enskog theory are all positive. This property, which is closely related to an H theorem proved by Résibois,[13] also ensures that time correlation functions like (1.2) and (1.3) decay to zero for long times. A proof is given in Appendix B, where also the next three properties are derived.

(2) The right and left eigenfunctions of $L(\mathbf{k})$ and $L^s(\mathbf{k})$ are related for all $\mathbf{k}$ by

$$\Phi_j^*(\mathbf{k}) = \frac{\Psi_j(\mathbf{k}) + [S(k) - 1]\langle \Psi_j(\mathbf{k})\rangle}{\langle [\Psi_j(\mathbf{k})]^2\rangle + [S(k) - 1]\langle \Psi_j(\mathbf{k})\rangle^2} \tag{2.52}$$

$$\Phi_j^{s*}(\mathbf{k}) = \frac{\Psi_j^s(\mathbf{k})}{\langle [\Psi_j^s(\mathbf{k})]^2\rangle} \tag{2.53}$$

These equations are not only generalizations to larger values of $\mathbf{k}$ of known relations between right and left eigenfunctions of the Boltzmann operators defined in (2.18) and (2.19), i.e., left eigenfunctions are proportional to the complex conjugates of right eigenfunctions, but also of the hydrodynamic modes [cf. Eqs. (2.38)–(2.49)].

(3) Each right eigenfunction $\Psi_j(\mathbf{k})$ is for all values of $\mathbf{k}$ either even or odd in v_x and either even or odd in v_y. In addition, upon interchange of v_x and v_y, each eigenfunction changes into an eigenfunction with the same

eigenvalue. The same properties hold for the left eigenfunctions due to the Eqs. (2.52) and (2.53).

As a consequence, in particular the extended heat and sound modes as well as the extended diffusion mode will be even in v_x and v_y since the corresponding hydrodynamic modes have this property. Similarly, one extended shear mode will be odd in v_x and even in v_y, while one will be even in v_y and odd in v_x, where the second mode can be obtained from the first by interchanging v_x and v_y, because the corresponding hydrodynamic modes have these properties. Furthermore, the extended shear mode eigenvalues are equal for all k, i.e.,

$$z_{\nu_1}(k) = z_{\nu_2}(k) = z_\nu(k) \tag{2.54}$$

(4) If $z_j(k)$, $\Psi_j(\mathbf{k}, \mathbf{v})$ and $z_j^s(k)$, $\Psi_j^s(\mathbf{k}, \mathbf{v})$ satisfy (2.32) and (2.33), respectively, then one has that

$$L(\mathbf{k})\Psi_j^*(\mathbf{k}, v_x, v_y, -v_z) = z_j^*(k)\Psi_j^*(\mathbf{k}, v_x, v_y, -v_z) \tag{2.55}$$

$$L^s(\mathbf{k})\Psi_j^{s*}(\mathbf{k}, v_x, v_y, -v_z) = z_j^{s*}(k)\Psi_j^{s*}(\mathbf{k}, v_x, v_y, -v_z) \tag{2.56}$$

This means that the eigenvalues in the spectral decompositions (2.29) and (2.30) appear in complex conjugate pairs and that the eigenfunctions are related by Eqs. (2.32), (2.33), (2.55), and (2.56). Thus also the extended sound modes will have complex conjugate eigenvalues and the extended heat, shear, and diffusion eigenvalues will always be real. For, if any of these quantities were complex, one would have more than five hydrodynamic modes, as would follow from Eqs. (2.55) and (2.56) and the properties discussed under point 3.

(5) Since for $k\sigma \gg 1$, $L(\mathbf{k}) \simeq L^s(\mathbf{k})$, the eigenvalues and the right and left eigenfunctions of $L(\mathbf{k})$ will approach the corresponding ones of $L^s(\mathbf{k})$ for $k\sigma \gg 1$. Also, for low densities, the eigenvalues and eigenfunctions of $L(\mathbf{k})$ will approach the corresponding ones of the inhomogeneous Boltzmann operator defined on the right-hand side of Eq. (2.18).

We remark that this operator as well as the operator defined on the right-hand side of Eq. (2.19) depend on k through the paramenter kl_0, where $l_0 = 1/\pi n\sigma^2\sqrt{2}$ is the low-density value of the mean free path l. For higher densities the operator $L^s(\mathbf{k})$ depends on k through kl_E, while $L(\mathbf{k})$ depends on k through kl_E and $k\sigma$ [cf. the discussion below Eq. (2.16)]. Here $l_E = l_0/\chi$ is the mean free path in the Enskog theory. Associated with l_0 and l_E are mean free times $t_0 = l_0/\langle v\rangle$ and $t_E = l_E/\langle v\rangle$, respectively, where $\langle v\rangle = 2\sqrt{2}/(\beta m\pi)^{1/2}$ is the average value of the speed v.

We now outline the procedure we follow to determine the collective modes of $L(\mathbf{k})$ and $L^s(\mathbf{k})$. First we use the following inverse Laplace transform representations of the evolution operators $\exp[L(\mathbf{k})t]$ and

$\exp[L^s(\mathbf{k})t]$

$$\exp[L(\mathbf{k})t] = \int_{-i\infty}^{i\infty} \frac{dz}{2\pi i} \frac{e^{zt}}{z - L(\mathbf{k})}$$

$$= \int_{-i\infty}^{i\infty} \frac{dz}{2\pi i} \frac{e^{zt}}{z + i\mathbf{k}\cdot\mathbf{v} - n\chi\Lambda_{\mathbf{k}} - nA_{\mathbf{k}}} \tag{2.57}$$

$$\exp[L^s(\mathbf{k})t] = \int_{-i\infty}^{i\infty} \frac{dz}{2\pi i} \frac{e^{zt}}{z - L^s(\mathbf{k})}$$

$$= \int_{-i\infty}^{i\infty} \frac{dz}{2\pi i} \frac{e^{zt}}{z + i\mathbf{k}\cdot\mathbf{v} - n\chi\Lambda^s} \tag{2.58}$$

These representations can be used in view of the Eqs. (2.50) and (2.51). It will be clear that by locating the poles in the complex z plane of the integrands on the right-hand sides of the Eqs. (2.57) and (2.58) and performing the integrals around the poles, eigenvalues and eigenfunctions in the spectral representations (2.29) and (2.30) of $L(\mathbf{k})$ and $L^s(\mathbf{k})$ are obtained. In particular the collective modes can be identified from those poles that go to zero for $k \to 0$. Thus the collective modes of the operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$ can be found by inverting the operators $[z - L(\mathbf{k})]$ and $[z - L^s(\mathbf{k})]$. Writing the operator $(z - L)$ as an $\infty \times \infty$ matrix with respect to a complete set of functions of $\mathbf{v}$, one finds the collective modes among the singularities of the inverse matrix and similarly for $(z - L^s)$ [cf. next section, below Eq. (3.18)]. The approximation discussed in the next section consists in replacing the actual ∞ matrix by a simpler matrix that can be explicitly inverted. The approximation we use will only approximate the collision operators $\Lambda_{\mathbf{k}}$ and Λ^s but will treat the operators $-i\mathbf{k}\cdot\mathbf{v}$ and $A_{\mathbf{k}}$ [in $L(\mathbf{k})$ and $L^s(\mathbf{k})$] exactly.

3. EVALUATION OF THE ENSKOG OPERATORS

As pointed out in the previous section, in order to determine the inverses of the operators $[z - L(\mathbf{k})]$ and $[z - L^s(\mathbf{k})]$ we approximate the operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$ by infinite matrices that can be inverted. In fact we introduce a series of approximate expressions $L^{(M)}(\mathbf{k})$ and $L^{s(M)}(\mathbf{k})$, labeled with an index M, for the exact Enskog operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$, respectively, such that (a) for increasing $M, L^{(M)}(\mathbf{k}) \to L(\mathbf{k})$ and $L^{s(M)}(\mathbf{k}) \to L^s(\mathbf{k})$; (b) for each M, $L^{(M)}(\mathbf{k})$ and $L^{s(M)}(\mathbf{k})$ satisfy the five basic properties discussed in Section 2, so that $L^{(M)}(\mathbf{k})$ possesses for each M five collective modes and $L^{s(M)}(\mathbf{k})$ one collective mode of the proper character.

We define $L^{(M)}(\mathbf{k})$ and $L^{s(M)}(\mathbf{k})$ each as sums of multiplication operators proportional to $-i\mathbf{k}\cdot\mathbf{v}$ and matrix operators characterized by M, where M refers to M functions of a complete set of orthonormal polynomials $\{\varphi_j\}$. This set $\{\varphi_j\}$ contains, in addition to the polynomials $\varphi_1 \ldots \varphi_5$

defined by Eqs. (2.24)–(2.28), polynomials of increasing order in v_x, v_y, and v_z (cf. Appendix A).

$L^{(M)}(\mathbf{k})$ and $L^{s(M)}(\mathbf{k})$ are given by the relations

$$L^{(M)}(\mathbf{k}) = -i\mathbf{k}\cdot\mathbf{v} + n\chi\Lambda_{\mathbf{k}}^{(M)} + nA_{\mathbf{k}} \tag{3.1}$$

$$L^{s(M)}(\mathbf{k}) = -i\mathbf{k}\cdot\mathbf{v} + n\chi\Lambda^{s(M)} \tag{3.2}$$

with

$$\Lambda^{s(M)} = \lim_{k\to\infty} \Lambda_{\mathbf{k}}^{(M)} \tag{3.3}$$

Thus for each $M, L^{(M)}(\mathbf{k}) \simeq L^{s(M)}(\mathbf{k})$ for $k\sigma \gg 1$, similarly as in Eq. (2.17) for $L(\mathbf{k})$ and $L^s(\mathbf{k})$. In Eq. (3.1) no approximation for $A_{\mathbf{k}}$ was introduced, since $A_{\mathbf{k}}$ can be written, with Eqs. (2.9) and (2.11) in the form of a one-term matrix operator

$$A_{\mathbf{k}} = |\varphi_1\rangle \frac{i\sqrt{\pi}}{nt_E}\left[j_1(k\sigma) + \frac{kC(k)}{4\pi\sigma^2\chi}\right]\langle\varphi_2| \tag{3.4}$$

The approximations $\Lambda^{(M)}(\mathbf{k})$ to $\Lambda_{\mathbf{k}}$ that we use here follow from the matrix operator representation

$$\Lambda_{\mathbf{k}} = \sum_{j=1}^{\infty}\sum_{l=1}^{\infty} |\varphi_j\rangle\Omega_{j,l}(k\sigma)\langle\varphi_l| \tag{3.5}$$

by considering

$$\begin{aligned}\Lambda_{\mathbf{k}}^{(M)} = {} & \sum_{j=1}^{M}\sum_{l=1}^{M} |\varphi_j\rangle\Omega_{jl}(k\sigma)\langle\varphi_l| \\ & + \left[g_+(k)(\varphi_2 - P_M\varphi_2P_M) + h_+(k)(1-P_M)\right]P_+ \\ & + \left[g_-(k)(\varphi_2 - P_M\varphi_2P_M) + h_-(k)(1-P_M)\right]P_- \end{aligned} \tag{3.6}$$

In the Eqs. (3.5) and (3.6) the matrix elements $\Omega_{jl} = \langle\varphi_j\Lambda_{\mathbf{k}}\varphi_l\rangle$ are discussed in Appendix A, the projection operator P_M projects on the M functions $\varphi_1 \ldots \varphi_M$, the projection operator P_+ projects on functions that are even in both v_x and v_y, the projection operator $P_- = 1 - P_+$ and the four functions $g_\pm(k)$ and $h_\pm(k)$ are discussed below. We remark that in our calculations P_+ and P_- always act on functions that are either even or odd in v_x and either even or odd in v_y, so that P_+ and P_- result in multiplication of these functions by 0 or 1. In particular each polynomial φ_j in the set $\{\varphi_j\}$ is either even or odd in v_x, in v_y, and in v_z. Therefore, the expression (3.6) for $\Lambda_{\mathbf{k}}^{(M)}$ is such that the $M \times M$ blocks of matrix elements of $\Lambda_{\mathbf{k}}$ in (3.5) and of $\Lambda_{\mathbf{k}}^{(M)}$ in (3.6) with $j, l \leqslant M$ are identical. Since all matrix elements of the terms in (3.6) involving $g_\pm$ and $h_\pm$ taken between φ_j and φ_l with $j, l \leqslant M$ vanish, the terms in (3.6) containing $g_\pm$ and $h_\pm$ are approximations to the matrix operator representation (3.5) outside the $M \times M$ block with $j, l \leqslant M$.

We also note that one cannot replace $\Lambda_{\mathbf{k}}$ by the $M \times M$ block on the right-hand side of Eq. (3.6) alone, since this would introduce an infinite number of conserved quantities of $\Lambda_{\mathbf{k}}^{(M)}$, in particular also of $L^{(M)}(0) = n\chi\Lambda_0^{(M)}$, viz., all polynomials orthogonal to $\varphi_1 \ldots \varphi_M$. This would lead to a model with an infinite number of hydrodynamic modes that does not satisfy the five basic properties of $L(\mathbf{k})$ mentioned in the previous section. Usually in approximations of the type discussed here—first introduced by Bhatnagar, Gross, and Krook[14] and Gross and Jackson[15]—the part of the matrix operator representing $\Lambda_{\mathbf{k}}$ outside the $M \times M$ block is approximated by an operator of the form $a(1 - P_M)$, where a is an adjustable parameter. Such an approximation will lead to $L^{(M)}(\mathbf{k})$ operators that satisfy for $M \geqslant 5$ and for $a < 0$ all the five basic properties mentioned in Section 2 but give for $M = 5$ the correct value for one transport coefficient only at low densities. In our work we have chosen the more complicated form (3.6) based on the following considerations.

Firstly, all the properties of $L^{(M)}(\mathbf{k})$ mentioned in the beginning of this section will be satisfied by $L^{(M)}(\mathbf{k})$ of the form (3.6) if $M \geqslant 5$, the functions $h_\pm$ are strictly negative and the functions $g_\pm$ purely imaginary and vanishing for $k = 0$ as well as $k = \infty$. This is shown in Appendix B. Secondly, the matrix inversion that has to be carried out is not more complicated for the form (3.6) of $L^{(M)}(\mathbf{k})$ than for the simple form $a(1 - P_M)$ mentioned above, since this inversion depends mainly on the number M of polynomials that occur in the first part of $L^{(M)}(\mathbf{k})$ in (3.6). The smallest value of M that allows the requirements mentioned in the beginning of this section to be satisfied is $M = 5$. Taking $M = 5$ in (3.6), the four functions $g_\pm(k)$ and $h_\pm(k)$ are used to obtain as good approximations as possible to the three hydrodynamic eigenvalues ν, D_T, and Γ of $L(\mathbf{k})$ for small k. Now for low densities, the kinematic viscosity ν_0, i.e., the value of the kinematic viscosity as given by the Boltzmann equation (in first Enskog approximation), is determined by the matrix element $\Omega_{6,6}(0)$, where φ_6 represents a normalized shear current [cf. Appendix C Eq. (C.21a)]. Similarly, the Boltzmann value (in first Enskog approximation) for the thermal diffusivity D_{T_0} is determined by $\Omega_{7,7}(0)$, where φ_7 represents a normalized heat current [cf. Appendix C Eq. (C.21b)], while the Boltzmann value (in first Enskog approximation) of the sound damping Γ_0 is determined by $\Omega_{8,8}(0)$, where φ_8 represents a normalized longitudinal current. The Boltzmann value (in first Enskog approximation) for the self-diffusion coefficient D_0 is obtained from $\Omega_{2,2}(k\sigma)$ for $k \to \infty$. For high densities, however, there are additional contributions to the transport coefficients and therefore to the hydrodynamic eigenvalues, due to collisional transfer of momentum and energy. We want to incorporate also these contributions and obtain the transport coefficients as proper combinations of kinetic and collisional transfer contributions. These collisional transfer contributions arise from $\Omega_{j,j}(k\sigma)$ with $j = 2, 3, 4$ and from the off-diagonal matrix elements $\Omega_{2,8}$, $\Omega_{3,7}$, and $\Omega_{4,6}$ for small k. With the form (3.6) with $M = 5$ and only four functions at our disposal it is not possible to get all the hydrodynamical eigenvalues correctly. We have made the following choice:

$$h_+(k) = \Omega_{7,7}(k\sigma) \tag{3.7a}$$

$$h_-(k) = \Omega_{6,6}(k\sigma) \tag{3.7b}$$

$$g_+(k) = \frac{\sqrt{15}}{5}\,\Omega_{3,7}(k\sigma) \tag{3.7c}$$

$$g_-(k) = \Omega_{4,6}(k\sigma) \tag{3.7d}$$

implying that 29 matrix elements of $\Lambda_{\mathbf{k}}$ and $\Lambda_{\mathbf{k}}^{(M)}$ are now the same: viz., those for $j, l \leqslant 5$; $j = l = 6$; $j = l = 7$; $j = 3, l = 7$; and $j = 4$ and $l = 6$. We note that $h_\pm(k)$ is real, while $g_\pm(k)$ is purely imaginary.

With this choice, it is shown in Appendix B that Eqs. (3.1), (3.6), and (3.7) give the Enskog values for the kinematic viscosity ν_E, thermal diffusivity D_{T_E}, and self-diffusion coefficient D_E (in first Enskog approximation) for all densities. It is not possible with $M = 5$ and the choices (3.7) to obtain the correct Enskog value for the sound absorption Γ_E, although the actual value obtained for Γ in our approximation is not too far from Γ_E. To obtain Γ in the same approximation as the other hydrodynamic eigenvalue ν and D_T, one would have to choose $M = 6$. While the hydrodynamic eigenvalues, i.e., the transport coefficients, are obtained approximately from (3.6), (3.7) with $M = 5$, the thermodynamic quantities and the speed of sound c are the same as for $L(\mathbf{k})$. Also the hydrodynamic eigenfunctions to lowest order in k, as given in Eqs. (2.39)–(2.49) in Section 2 are obtained correctly.

Now that we have defined the approximations to $L(\mathbf{k})$ and $L^s(\mathbf{k})$ that we have used in our explicit calculations, we will sketch how approximate collective modes to $L(\mathbf{k})$ and $L^s(\mathbf{k})$ can be found using the Eqs. (3.1), (3.6) with $M = 5$ and (3.7). For brevity we will call the approximate operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$ defined this way $\bar{L}(\mathbf{k})$ and $\bar{L}^s(\mathbf{k})$, respectively. We first discuss the collective modes of $\bar{L}(k)$. For the inversion of the operator $[z - \bar{L}(\mathbf{k})]$ to be carried out below, it is convenient to write $\bar{L}(\mathbf{k})$ in the form

$$\bar{L}(\mathbf{k}) = \left[f_+(k, \mathbf{v}) + F_+(k)\right]P_+ + \left[f_-(k, \mathbf{v}) + F_-(k)\right]P_- \tag{3.8}$$

where $f_\pm(k, \mathbf{v})$ are functions of k and $\mathbf{v}$ defined by

$$\begin{aligned} f_\pm(k, \mathbf{v}) &= -i\mathbf{k}\cdot\mathbf{v} + n\chi h_\pm(k) + n\chi\, g_\pm(k)\varphi_2(\mathbf{v}) \\ &= n\chi h_\pm(k) + \left[n\chi\, g_\pm(k) - \frac{ik}{(\beta m)^{1/2}}\right]\varphi_2(\mathbf{v}) \end{aligned} \tag{3.9}$$

while $F_\pm(k)$ are finite matrix operators given by

$$F_+(k) = \sum_{j=1}^{3} \sum_{l=1}^{3} |\varphi_j\rangle F_{jl}(k) \langle \varphi_l| \tag{3.10a}$$

$$F_-(k) = \sum_{j=4,5} |\varphi_j\rangle F_\nu(k) \langle \varphi_j| \tag{3.10b}$$

with matrix elements given by

$$F_{jl}(k) = n\chi \Omega_{j,l}(k\sigma) - n\chi\, g_+(k) \langle \varphi_j \varphi_2 \varphi_l \rangle$$
$$- n\chi h_+(k)\delta_{j,l} + \frac{i\sqrt{\pi}}{t_E}\left[j_1(k\sigma) + \frac{kC(k)}{4\pi\sigma^2\chi} \right] \delta_{j,1}\delta_{l,2} \tag{3.11a}$$

$$F_\nu(k) = n\chi\Omega_{4,4}(k\sigma) - n\chi h_-(k) \tag{3.11b}$$

We remark that $f_\pm(k, \mathbf{v})$ and $F_\pm(k)$ only depend on $k = |\mathbf{k}|$ because of the particular choice of our coordinate system. $f_\pm(k, \mathbf{v})$ incorporates the contributions of $h_\pm(k)P_\pm$ and $g_\pm(k)\varphi_2 P_\pm$ in (3.6) and of the free-streaming term $-i\mathbf{k}\cdot\mathbf{v}$ in (3.1), which can also be written, with Eq. (2.25), as $i\mathbf{k}\cdot\mathbf{v} = ik\varphi_2(\mathbf{v})/(\beta m)^{1/2}$. The matrix operators $F_\pm(k)$ incorporate the contributions of the first term in Eq. (3.6) as well as the terms proportional to $P_M \varphi_2 P_M P_\pm$, $P_M P_\pm$ in this equation and the operator $A_\mathbf{k}$ in (3.1). With Eq. (3.8), the operator $[z - \bar{L}(k)]^{-1}$ can be written as the sum of two operators that can each independently be inverted

$$\frac{1}{z - \bar{L}(\mathbf{k})} = \frac{1}{z - f_+(k,\mathbf{v}) - F_+(k)} P_+ + \frac{1}{z - f_-(k,\mathbf{v}) - F_-(k)} P_- \tag{3.12}$$

where we used that the operators $P_\pm$ and $F_\pm$ all commute with each other and that $P_+ f_\pm(k) P_- = P_- f_\pm(k) P_+ = 0$.

In Appendix D the inversion of $[z - \bar{L}(k)]$ based on Eq. (3.12) is carried out explicitly, resulting in the equation

$$\frac{1}{z - \bar{L}(\mathbf{k})} = \frac{1}{z - f_+(k,\mathbf{v})} \left\{ 1 + \sum_{j,l=1}^{3} |\varphi_j\rangle \left[\mathsf{F}(k)\{1 - \mathsf{A}(k,z)\mathsf{F}(k)\}^{-1} \right]_{jl} \times \langle \varphi_l | \frac{1}{z - f_+(k,\mathbf{v})} \right\} P_+$$
$$+ \frac{1}{z - f_-(k,\mathbf{v})} \left\{ 1 + \sum_{j=4,5} |\varphi_j\rangle \left[F_\nu(k)\{1 - A_\nu(k,z)F_\nu(k)\}^{-1} \right] \times \langle \varphi_j | \frac{1}{z - f_-(k,\mathbf{v})} \right\} P_- \tag{3.13}$$

Here $\mathsf{F}(k)$ is a 3×3 matrix with matrix elements $F_{jl}(k)$ given by Eq. (3.11a), $\mathsf{A}(k,z)$ is a 3×3 matrix with matrix elements $A_{jl}(k,z)$ given by $(j,l = 1,2,3)$

$$A_{jl}(k,z) = \left\langle \varphi_j \frac{1}{z - f_+(k,\mathbf{v})} \varphi_l \right\rangle$$
$$= \int d\mathbf{v}\, \phi(v) \frac{\varphi_j(\mathbf{v})\varphi_l(\mathbf{v})}{z + i\mathbf{k}\cdot\mathbf{v} - n\chi h_+(k) - n\chi g_+(k)(\beta m)^{1/2}\mathbf{v}\cdot\hat{k}} \tag{3.14}$$

$[\ ]_{jl}$ is the jl-matrix element of the matrix $[\ ]$, $F_\nu(k)$ is defined by Eq. (3.11b), and $A_\nu(k,z)$ by

$$A_\nu(k,z) = \left\langle \varphi_4 \frac{1}{z - f_-(k,\mathbf{v})} \varphi_4 \right\rangle$$
$$= \int d\mathbf{v}\, \phi(v) \frac{[\varphi_4(\mathbf{v})]^2}{z + i\mathbf{k}\cdot\mathbf{v} - n\chi h_-(k) - n\chi g_-(k)(\beta m)^{1/2}\mathbf{v}\cdot\hat{k}} \tag{3.15}$$

where the unit vector $\hat{k} = \mathbf{k}/k$. In Appendix D it is also shown that the functions $A_{jl}(k,z)(j,l = 1,2,3)$ and $A_\nu(k,z)$ can all be expressed in terms of the plasma dispersion function $Z(z)$, which for $\mathrm{Im}\, z > 0$ is defined as[2,16]

$$Z(z) = -\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx\, \frac{e^{-x^2}}{z - x} \tag{3.16}$$

As discussed in Section 2, the collective modes of $\bar{L}(\mathbf{k})$ are associated with those values of z for which poles appear on the right-hand side of Eq. (3.13) that go to zero for $k \to 0$. In order to determine these poles we remark the following. For a given value of k, all functions $A_{jl}(k,z)$ in (3.14) and the function $[z - f_+(k,\mathbf{v})]^{-1}$ are analytic in the complex z plane for values of z for which $\mathrm{Re}\, z > n\chi h_+(k)$. This follows from Eqs. (3.9) and (3.14), using that $g_+(k)$ is a purely imaginary function of k. Also, it follows from the explicit form for $h_+(k)$ given by Eq. (3.7a) and Appendix A, that $h_+(k)$ is always smaller than its value for $k = 0$, $h_+(0) = (-8/15)(nt_0)^{-1}$ and oscillates to a constant value for $k \to \infty$, $h_+(\infty) = (-59/60)(nt_0)^{-1}$. Therefore, the functions $A_{jl}(k,z)$ and $[z - f_+(k,\mathbf{v})]^{-1}$ in (3.13) are analytic in a region of the complex plane to the right of $\mathrm{Re}\, z = n\chi h_+(k)$, which includes the origin for all k. Similarly, the functions $A_\nu(k,z)$ in (3.15) and $[z - f_-(k,\mathbf{v})]^{-1}$ are analytic for all z for which $\mathrm{Re}\, z > n\chi h_-(k)$, a region of the complex plane that includes the origin for all k, as follows from Eq.

(3.7b) and Appendix A. Hence, the collective modes are associated with values of z for which the matrix $\mathsf{1} - \mathsf{A}(k,z)\mathsf{F}(k)$ and the function $1 - A_\nu(k, z)F_\nu(k)$ cannot be inverted. Now the inverse of the matrix $\mathsf{1} - \mathsf{AF}$ is given by

$$\left[\mathsf{1} - \mathsf{A}(k,z)\mathsf{F}(k)\right]^{-1} = \frac{1}{D(k,z)}\mathsf{H}(k,z) \tag{3.17}$$

where the matrix $\mathsf{H}(k,z)$ is the transpose of the matrix of minors of the matrix $\mathsf{1} - \mathsf{AF}$ and

$$D(k,z) = \det\left[\mathsf{1} - \mathsf{A}(k,z)\mathsf{F}(k)\right] \tag{3.18}$$

Since the functions in $\mathsf{H}(k,z)$ are analytic for $\operatorname{Re} z > n\chi h_+(k)$, the matrix $\mathsf{1} - \mathsf{AF}$ cannot be inverted for those values of z for which the determinant $D(k,z)$ vanishes. Similarly, the function $D_\nu(k,z) = 1 - A_\nu(k,z)F_\nu(k)$ cannot be inverted for those values of z for which this function vanishes.

Thus, the (extended) heat mode eigenvalue $z_H(k)$ and the (extended) sound mode eigenvalues $z_\pm(k)$ are determined by the implicit equations

$$D(k, z_H(k)) = 0; \qquad z_H(k) \text{ real} \tag{3.19a}$$

$$D(k, z_\pm(k)) = 0; \qquad z_\pm(k) \text{ c.c.} \tag{3.19b}$$

while the (extended) shear mode eigenvalue $z_\nu(k)$ is determined by the equation

$$D_\nu(k, z_\nu(k)) = 0 \tag{3.20}$$

In order to find the eigenfunctions corresponding to these eigenvalues, one substitutes (3.13) into Eq. (2.57) with $L(\mathbf{k})$ replaced by $\bar{L}(\mathbf{k})$. Carrying out the integration around the five (extended) hydrodynamic poles in the complex z plane yields then

$$\begin{aligned} e^{\bar{L}(\mathbf{k})t} = & \sum_{j=H,\pm} e^{z_j(k)t} \frac{1}{D'(k,z_j(k))\left[z_j(k) - f_+(k,\mathbf{v})\right]} \\ & \times \sum_{l,m=1}^{3} |\varphi_l\rangle\left[\mathsf{F}(k)\mathsf{H}(k,z_j(k))\right]_{lm}\langle\varphi_m| \frac{1}{z_j(k) - f_+(k,\mathbf{v})} P_+ \\ & + \sum_{j=4,5} e^{z_\nu(k)t} \frac{1}{z_\nu(k) - f_-(k,\mathbf{v})} |\varphi_j\rangle \frac{F_\nu(k)}{D_\nu'(k,z_\nu(k))} \\ & \times \langle\varphi_j| \frac{1}{z_\nu(k) - f_-(k,\mathbf{v})} P_- + \cdots \end{aligned} \tag{3.21}$$

In (3.21) the remaining terms, indicated by $\ldots$, can be represented by integrals over z along the lines $\operatorname{Re} z = n\chi h_\pm(k)$, but are not written down explicitly here; $D'(k,z) = dD(k,z)/dz$ and $D_\nu'(k,z) = dD_\nu(k,z)/dz$. The eigenfunctions of the collective modes can be determined as follows. The shear mode eigenfunctions can be read off directly from the terms $j = 4$ and $j = 5$ in Eq. (3.21). The heat and sound mode eigenfunctions are contained in the first term on the right-hand side of Eq. (3.21). Explicit expressions for these eigenfunctions can be obtained by diagonalizing the matrix $\mathsf{F}(k)\mathsf{H}(k, z_j(k))$ for $j = H$ and for $j = \pm$. However, since the time correlation functions in which we are interested, like $F(k, t)$, can be computed without explicit knowledge of the collective eigenfunctions, we will not give these eigenfunctions here.

We remark that $\bar{L}(\mathbf{k})$ has been constructed in such a way that it satisfies the five basic properties mentioned in Section 2. Consequently, the eigenvalues and eigenfunctions of the collective modes found here must satisfy these conditions.

We now consider eigenvalues and eigenfunctions of the operator $\bar{L}^s(\mathbf{k})$ that approximates $L^s(\mathbf{k})$ in a similar fashion as the operator $\bar{L}(\mathbf{k})$ approximates $L(\mathbf{k})$. In this case we are not only interested in the collective mode, i.e., the diffusion mode, but in general in the modes that correspond to the five collective modes of $\bar{L}(\mathbf{k})$, which must be present in $\bar{L}^s(\mathbf{k})$ in view of the relation $\bar{L}(\mathbf{k}) \to \bar{L}^s(\mathbf{k})$ for $k\sigma \gg 1$. Because of Eq. (3.3), the operator $\bar{L}^s(\mathbf{k})$ can be constructed in a very similar way as the operator $\bar{L}(\mathbf{k})$. We only indicate the main steps. Similarly to Eq. (3.8), $\bar{L}^s(\mathbf{k})$ can be written in the form

$$\bar{L}^s(\mathbf{k}) = \left[f^s_+(k, \mathbf{v}) + F^s_+ \right] P_+ + \left[f^s_-(k, \mathbf{v}) + F^s_- \right] P_- \tag{3.22}$$

where the functions $f^s_\pm(\mathbf{k}, \mathbf{v})$ are given by

$$f^s_\pm(k, \mathbf{v}) = -i\mathbf{k} \cdot \mathbf{v} + n\chi h_\pm(\infty) \tag{3.23}$$

and the matrix operators $F^s_\pm$ by

$$F^s_+ = \sum_{j=1}^{3} \sum_{l=1}^{3} |\varphi_j\rangle F_{jl}(\infty)\langle\varphi_l| \tag{3.24a}$$

$$F^s_- = \sum_{j=4,5} |\varphi_j\rangle F_\nu(\infty)\langle\varphi_j| \tag{3.24b}$$

where, with Eq. (3.11)

$$F_{jl}(\infty) = \lim_{k\to\infty} F_{jl}(k) = n\chi\Omega_{jl}(\infty) - n\chi h_+(\infty)\delta_{jl} \tag{3.25a}$$

$$F_\nu(\infty) = \lim_{k\to\infty} F_\nu(k) = n\chi\Omega_{4,4}(\infty) - n\chi h_-(\infty) \tag{3.25b}$$

since $g_\pm$, j_1 and $kC(k)$ vanish for $k \to \infty$.

An expression for the operator $[z - \bar{L}^s(\mathbf{k})]^{-1}$ can then be obtained similar in form to Eq. (3.13) for $[z - L(\mathbf{k})]^{-1}$:

$$\frac{1}{z - \bar{L}^s(\mathbf{k})} = \frac{1}{z - f_+^s(k,\mathbf{v})} \left\{ 1 + \sum_{j,l=1}^{3} |\varphi_j\rangle \left[\mathsf{F}^s \{ 1 - \mathsf{A}^s(k,z)\mathsf{F}^s \}^{-1} \right]_{jl} \right.$$
$$\left. \times \langle \varphi_l | \frac{1}{z - f_+^s(k,\mathbf{v})} \right\} P_+$$
$$+ \frac{1}{z - f_-^s(k,\mathbf{v})} \left\{ 1 + \sum_{j=4,5} |\varphi_j\rangle F_\nu(\infty) \left[1 - A_\nu^s(k,z) F_\nu(\infty) \right]^{-1} \right.$$
$$\left. \times \langle \varphi_j | \frac{1}{z - f_-^s(k,\mathbf{v})} \right\} P_- \tag{3.26}$$

Here F^s denotes a 3×3 matrix with elements $F_{jl}(\infty)$ and $\mathsf{A}^s(k,z)$ a 3×3 matrix of functions $A_{jl}^s(k,z)$ defined by

$$A_{jl}^s(k,z) = \left\langle \varphi_j \frac{1}{z - f_+^s(k,\mathbf{v})} \varphi_l \right\rangle \tag{3.27a}$$

while

$$A_\nu^s(k,z) = \left\langle \varphi_4 \frac{1}{z - f_-^s(k,\mathbf{v})} \varphi_4 \right\rangle \tag{3.27b}$$

which, like $A_{jl}(k,z)$ in (3.14) and $A_\nu(k,z)$ in (3.15) can be completely expressed in terms of the plasma dispersion function (3.16), as discussed in Appendix D.

The modes we are interested in are associated with values of z for which the matrix $\mathsf{1} - \mathsf{A}^s(k,z)\mathsf{F}^s$ and the function $1 - A_\nu^s(k,z)F_\nu(\infty)$ cannot be inverted. Writing

$$\left[\mathsf{1} - \mathsf{A}^s(k,z)\mathsf{F}^s \right]^{-1} = \frac{1}{D^s(k,z)} \mathsf{H}^s(k,z) \tag{3.28}$$

where $\mathsf{H}^s(k,z)$ is the transpose of the matrix of minors of the matrix $\mathsf{1} - \mathsf{A}^s\mathsf{F}^s$ and $D^s(k,z)$ is defined by

$$D^s(k,z) = \det\left[\mathsf{1} - \mathsf{A}^s(k,z)\mathsf{F}^s \right] \tag{3.29a}$$

and defining similarly

$$D_\nu^s(k,z) = 1 - A_\nu^s(k,z)F_\nu(\infty) \tag{3.29b}$$

the modes of interest are obtained for those values of z for which $D^s(k,z)$ and $D_\nu^s(k,z)$ vanish. The diffusion mode eigenvalue follows from the equation

$$D^s(k, z_D^s(k)) = 0, \qquad z_D^s(k) \text{ real} \tag{3.30a}$$

while there are two other solutions of the equation $D^s(k,z) = 0$

$$D^s(k, z_\pm^s(k)) = 0, \qquad z_\pm^s(k) \text{ c.c.} \tag{3.30b}$$

that are each others' complex conjugate. In addition there is a solution of the equation $D_\nu^s(k,z) = 0$

$$D_\nu^s(k, z_\nu^s(k)) = 0, \qquad z_\nu^s(k) \text{ real} \tag{3.31}$$

that is real.

Substitution of Eq. (3.26) into Eq. (2.58), with $L^s(\mathbf{k})$ replaced by $\overline{L}^s(\mathbf{k})$, and integration around the four poles yields, similarly as before,

$$\begin{aligned} e^{\overline{L}^s(\mathbf{k})t} &= \sum_{j=D,\pm} e^{z_j^s(k)t} \frac{1}{D^{s'}(k, z_j^s(k))\left[z_j^s(k) - f_+^s(k,\mathbf{v})\right]} \\ &\times \sum_{l,m=1}^{3} |\varphi_l\rangle \left[\mathsf{F}^s\mathsf{H}^s(k, z_j^s(k))\right]_{lm} \langle\varphi_m| \frac{1}{z_j^s(k) - f_+^s(k,\mathbf{v})} P_+ \\ &+ \sum_{j=4,5} e^{z_\nu^s(k)t} \frac{1}{z_\nu^s(k) - f_-^s(k,\mathbf{v})} |\varphi_j\rangle \frac{F_\nu(\infty)}{D_\nu^{s'}(k, z_\nu^s(k))} \\ &\times \langle\varphi_j| \frac{1}{z_\nu^s(k) - f_-^s(k,\mathbf{v})} P_- + \cdots \end{aligned} \tag{3.32}$$

where the integral representation of the remaining terms is again omitted.

From Eq. (3.32) one can obtain explicit expressions for five eigenfunctions of $\overline{L}^s(\mathbf{k})$. Two eigenfunctions can be read off directly from the terms with $j = 4$ and $j = 5$ and belong to the same real eigenvalue $z_\nu^s(k)$. Since they are even in v_x, odd in v_y and vice versa, they appear as the analogs of the two shear modes of $\overline{L}(\mathbf{k})$ and they are indeed very similar to these modes for $k\sigma \gg 1$ as will be discussed in the next section. The first term in (3.32) contains the diffusion mode $j = D$ and two modes $j = \pm$ with complex conjugate eigenvalues. Explicit expressions for the eigenfunctions could be obtained by diagonalizing the matrix $\mathsf{F}^s\mathsf{H}^s(z^s, k)$. We will not do so for the reason discussed below Eq. (3.21). We only note that, just as the heat mode and the sound mode, the eigenfunctions corresponding to z_D^s and $z_\pm^s$ are even in v_x and in v_y. This follows from Eq. (3.32), since φ_l and φ_m have this property for $l, m = 1, 2, 3$. Therefore, since both $z_D^s(k)$ and $z_H^s(k)$ are real, the heat mode would appear to tend to the self-diffusion mode for $k\sigma \gg 1$ and the sound modes to the modes of $\overline{L}^s(\mathbf{k})$ corresponding to the eigenvalues $z_\pm^s(k)$. This is further discussed in the next section. We remark that the four modes corresponding to $z^s_\pm(k)$ and $z^s_\nu(k)$ are all of a kinetic type, i.e., they all tend to a nonzero value $-\frac{2}{3}t_E^{-1}$ for $k\to 0$, while the corresponding four eigenfunctions tend in this limit to linear combinations of $\mathbf{v}$ and v^2, which are *not* collisional invariants for the Lorentz–Enskog equation. These results follow directly from properties of the operator $L^s(0)=n\chi\Lambda^s$.

Finally, we can compute explicitly on the basis of the results obtained in this section the functions $F(k,t)$ and $F^s(k,t)$ defined in Section 1 or rather, using Eqs. (2.1), (2.2), and (2.24) their Fourier transforms

$$S_E(k,\omega)=\frac{1}{\pi}S(k)\mathrm{Re}\left\langle \varphi_1 \frac{1}{i\omega-\bar{L}(\mathbf{k})}\varphi_1\right\rangle \tag{3.33a}$$

and

$$S_E^s(k,\omega)=\frac{1}{\pi}\mathrm{Re}\left\langle \varphi_1 \frac{1}{i\omega-\bar{L}^s(\mathbf{k})}\varphi_1\right\rangle \tag{3.33b}$$

In fact we will compute $S_E(k,\omega)$ and $S_E^s(k,\omega)$ using the contributions of the collective modes alone as well as using the contributions of all modes: the collective modes and all other modes. In comparing the results of these two calculations, we can assess the importance of the collective modes in the calculation of $S_E(k,\omega)$ and $S_E^s(k,\omega)$.

The contribution of the collective modes alone to $S(k,\omega)$ leads to the expression

$$S_E(k,\omega)=\frac{1}{\pi}S(k)\sum_{j=H,\,\pm}\mathrm{Re}\,\frac{M_j(k)}{i\omega-z_j(k)} \tag{3.34}$$

where

$$M_j(k)=\frac{1}{D'(k,z_j(k))}\left[\mathsf{H}(k,z_j(k))\mathsf{A}(k,z_j(k))\right]_{1,1} \tag{3.35}$$

as derived in Appendix D. We note that owing to their symmetry in v_x and v_y, the shear modes do not contribute to $S_E(k,\omega)$. On the other hand an expression containing *all* contributions to $S_E(k,\omega)$ can also be obtained and reads

$$S_E(k,\omega)=\frac{1}{\pi}S(k)\mathrm{Re}\frac{1}{D(k,i\omega)}\left[\mathsf{H}(k,i\omega)\mathsf{A}(k,i\omega)\right]_{1,1} \tag{3.36}$$

This is also derived in Appendix D.

Comparing the expressions (3.34) and (3.36) for $S_E(k,\omega)$ leads to the following.

For $k\to 0$, the collective (i.e., hydrodynamic) modes *are* the dominant contributions to $S_E(k,\omega)$. This follows immediately from Eq. (3.33a), that

φ_1 is an eigenfunction of $L(0)$, so that all contributions present in (3.36) but not in (3.34) tend to zero for $k \to 0$ and that $M_H(0) = 1 - 1/\gamma$ and $M_\pm(0) = 1/2\gamma$, as discussed in Appendix D. Thus for small k the hydrodynamic modes determine the dynamical scattering function $S_E(k, \omega)$ and Eq. (3.34) reduces to the Landau–Placzek formula (1.4) given in Section 1, with the correct values for the thermodynamic properties such as c, γ, and $S(0)$ and approximate values D_{TE}, ν_E, and Γ_E for the hydrodynamic eigenvalues (transport coefficients) of a hard sphere fluid described by the generalized Enskog theory. The importance of the contributions of the collective modes to $S_E(k, \omega)$ for larger values of k is discussed in the next section.

Similarly, the contributions of the diffusion mode and the kinetic modes corresponding to $z_\pm^s(k)$ alone to $S_E^s(k, \omega)$ give

$$S_E^s(k, \omega) = \frac{1}{\pi} \sum_{j=D,\pm} \operatorname{Re} \frac{M_j^s(k)}{i\omega - z_j^s(k)} \tag{3.37}$$

with

$$M_j^s(k) = \frac{1}{D^{s'}(k, z_j^s(k))} \left[\mathsf{H}^s(k, z_j^s(k)) \mathsf{A}^s(k, z_j^s(k)) \right]_{1,1} \tag{3.38}$$

while the contribution of all modes to $S_E^s(k, \omega)$ is given by

$$S_E^s(k, \omega) = \frac{1}{\pi} \operatorname{Re} \frac{1}{D^s(k, i\omega)} \left[\mathsf{H}^s(k, i\omega) \mathsf{A}^s(k, i\omega) \right]_{1,1} \tag{3.39}$$

Again the relative importance of the contribution of the collective diffusion mode to $S_E^s(k, \omega)$ will be discussed in the next section.

4. RESULTS

We have computed explicitly the extensions of the hydrodynamic eigenvalues $z_H(k)$, $z_\nu(k)$, $z_\pm(k)$ as given by Eqs. (2.38), (2.45), and (2.42) to larger values of k on the basis of the kinetic model described in Section 3 for two different densities. Also we have computed the extension of the self-diffusion eigenvalue $z_D^s(k)$ given by Eq. (2.48) to larger values of k as well as the behavior of the three kinetic eigenvalues $z_\nu^s(k)$ and $z_\pm^s(k)$ introduced in Section 3.

These eight eigenvalues were obtained as functions of k by solving Eqs. (3.19), (3.20), (3.30), and (3.31) numerically, using the 3–3 Padé approximation of Ree and Hoover[17] for the equation of state of the hard sphere fluid and the expression of Henderson and Grundke[18] for $S(k)$.

The various $z(k)$ are plotted as a function of k for a typical low density ($V_0/V = n\sigma^3/\sqrt{2} = 0.055$; $V_0 = N\sigma^3/\sqrt{2}$ is the volume of close packing) in Fig. 1 and for a typical high (liquid) density ($V_0/V = n\sigma^3/\sqrt{2} = 0.625$) in Fig. 2. We first discuss the low-density case, i.e., Fig. 1.

(1) $z_D^s(k)$ is a smooth, monotonically decreasing function of k, behaving for small k as $z_D^s(k) = -D_E k^2$ and extending till a limiting value k_D^{s*} of k, where Eq. (3.30a) no longer has a unique solution. Deviations of $z_D^s(k)$ from $-D_E k^2$ grow as large as 30% for $k \approx k_D^{s*}$, and are such that $|z_D^s(k)| \leqslant D_E k^2$ for all $0 \leqslant k \leqslant k_D^{s*}$. Thus the diffusion mode exhibits a softening with increasing k when compared to its hydrodynamic behavior, i.e., the decay of the diffusion mode for large k tends to be slower than predicted by the self-diffusion equation.

(2) $z_\nu^s(k)$ and the real part of $z_\pm^s(k)$, as obtained from Eqs. (3.31) and (3.30b), respectively, are also smooth monotonically decreasing functions of k, extending till limiting values k_ν^{s*} and $k_\pm^{s*}$, respectively, beyond which Eqs.

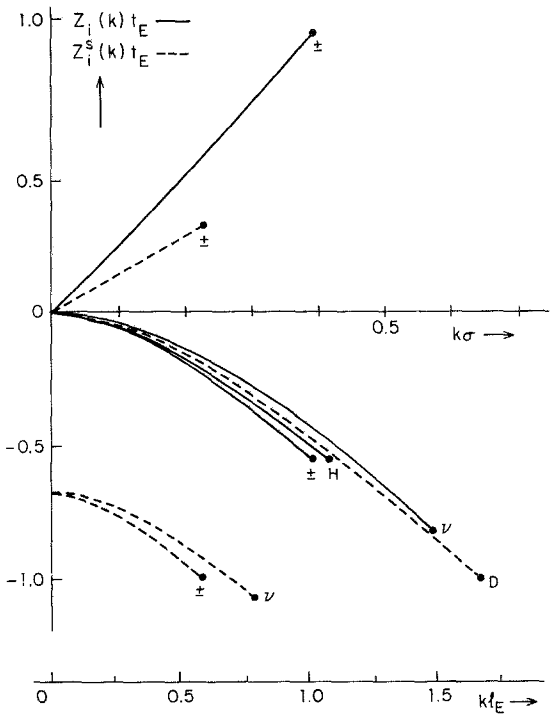

Fig. 1. Eigenvalues z_i of $\bar{L}(\mathbf{k})$ (drawn lines) and eigenvalues z_i^s of $\bar{L}^s(\mathbf{k})$ (dotted lines) as functions of $k\sigma$ and kl_E for a hard sphere fluid at a typical low density $V_0/V = 0.055$. t_E denotes the mean free time between collisions and $l_E = 2.56\sigma$ the mean free path. i stands for heat (—H), shear (—ν), sound (—$\pm$), diffusion (---D,) shearlike (---ν), and soundlike (---$\pm$) modes. Positive values refer to the absolute value of the imaginary parts of $z_i(k)$ and of $z_i^s(k)$, negative values refer to real parts.

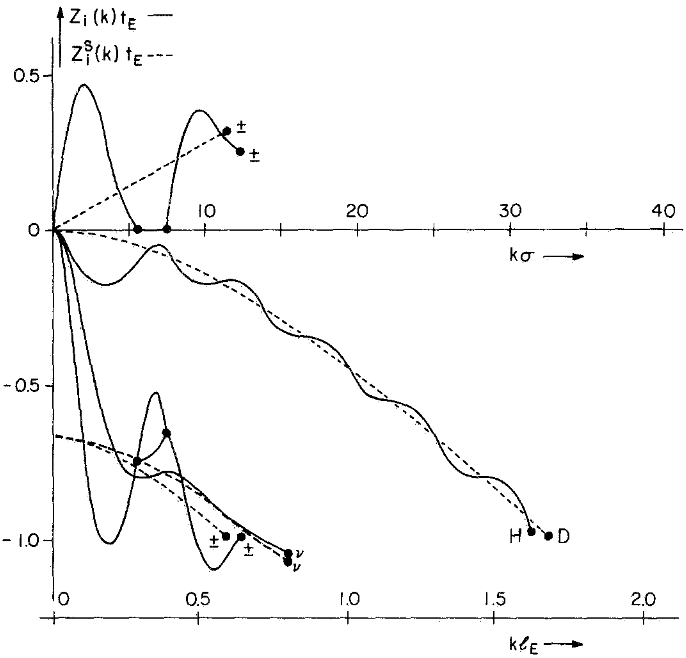

Fig. 2. Eigenvalues of $\bar{L}(\mathbf{k})$ (drawn lines) and $\bar{L}^s(\mathbf{k})$ (dotted lines) as functions of $k\sigma$ and kl_E for a hard sphere fluid at a density $V_0/V=0.625$, typical for liquids. The notation is as in Fig. 1, $l_E=0.052\sigma$ and the results for $z_i^s(k)t_E$ on the scale kl_E are the same as in Fig. 1.

(3.31) and (3.30b) no longer have unique solutions. For small k, the imaginary part of $z_{\pm}^s(k)$ behaves like a linear function of k, while the real parts of $z_{\pm}^s(k)$ and $z_\nu^s(k)$ tend to $-(2/3)t_E^{-1}$ for $k\to 0$.

The limiting values k_D^{s*}, k_ν^{s*}, and $k_{\pm}^{s*}$ are determined as follows. The functions occurring in $D^s(k,z)$ and $D_\nu^s(k,z)$ are only well-defined analytic functions of z for values of z to the right of $\mathrm{Re}\,z=n\chi h_+(\infty)=-(59/60)t_E^{-1}$ and $\mathrm{Re}\,z=n\chi h_-(\infty)=-(16/15)t_E^{-1}$, respectively, in the complex plane. However, for that value of k for which a solution $z_j^s(k)$ $(j=D,\nu,\pm)$ of the equations (3.31) and (3.30b) reaches these limiting values, the solution of these equations can no longer be obtained. Thus the limit wave vectors $k_j^{s*}(j=D,\nu,\pm)$ are determined from the implicit equations

$$z_j^s(k_j^{s*})=n\chi h_+(\infty)=-(59/60)t_E^{-1} \tag{4.1a}$$

for $j=D,\pm$ and

$$z_\nu^s(k_\nu^{s*})=n\chi h_-(\infty)=-(16/15)t_E^{-1} \tag{4.1b}$$

for $j=\nu$.

While one can determine $k_\nu^{s*} = 0.8 l_E^{-1}$ analytically, $k_D^{s*} = 1.67 l_E^{-1}$ and $k_\pm^{s*} = 0.585 l_E^{-1}$ were obtained numerically. We remark that if the z_j^s are measured in units t_E^{-1} and the wave vectors k in units l_E^{-1}, the z_j^s become universal functions of k, independent of the density. This follows directly from the eigenvalue equation (2.33). This implies that the values of k_j^{s*} given above are valid for all densities (cf. Fig. 3) and can also be used in Fig. 2.

(3) The real parts of $z_j(k)$ ($j = H, \pm, \nu$) are all smooth monotonically decreasing functions of k, while $\operatorname{Im} z_\pm(k)$ is monotonically increasing, extending to limiting values k_H^*, $k_\pm^*$, and k_ν^*, respectively, where Eqs. (3.19) and (3.20) no longer have unique solutions. For small k they behave as $z_H = -D_{TE}k^2$, $z_\pm = \pm ick - \Gamma_E k^2$ and $z_\nu = -\nu_E k^2$, respectively. Deviations from this behavior for larger k typically do not exceed 30% and are such that $|z_H(k)| \leqslant D_{TE}k^2$, $|\operatorname{Re} z_\pm(k)| \leqslant \Gamma_E k^2$ and $|z_\nu(k)| \leqslant \nu_E k^2$. Thus also these modes exhibit a softening for large k and decay slower than

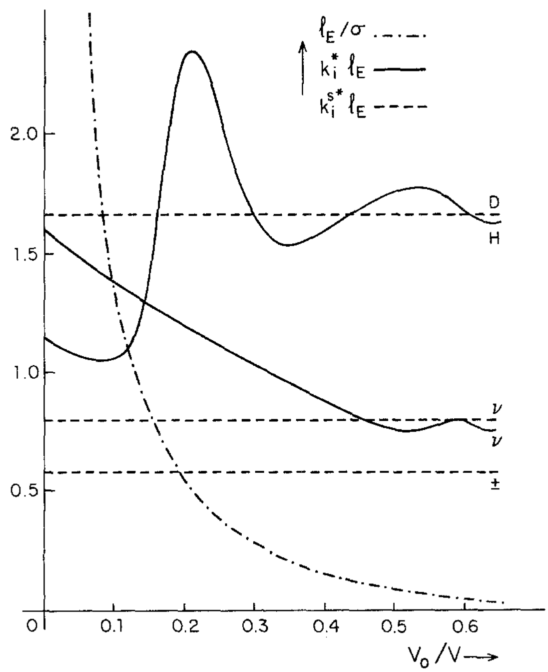

Fig. 3. Limit wave vectors k_i^*(—) and k_i^{s*} (---) up to which the modes $i = H, \nu$ of $\bar{L}(\mathbf{k})$ and $i = D, \nu, \pm$ of $\bar{L}^s(\mathbf{k})$ exist, as functions of the density. The mean free path in units σ, l_E/σ, (-·-) as a function of the density is shown in order to facilitate the conversion of the σ to the l_E scale.

predicted by the hydrodynamical equations. For larger values of k, $|\mathrm{Im}\, z_{\pm}(k)|$ continues almost linearly proportional to ck, which agrees with a similar result obtained by Foch and Ford[2] on the basis of the linearized inhomogeneous Boltzmann equation.

The limit or cutoff wave vectors $k_j^*(j = H, \pm, \nu)$ are determined in the same way as the k_j^{s*} by the implicit equations

$$z_j(k_j^*) = n\chi h_+(k_j^*) \tag{4.2a}$$

for $j = H, \pm$ and

$$z_\nu(k_\nu^*) = n\chi h_-(k_\nu^*) \tag{4.2b}$$

for $j = \nu$.

The results of a numerical solution of these equations for k_j^* as a function of the density are plotted in Fig. 3. For the low density used in Fig. 1, i.e., $V_0/V = 0.055$ one finds $k_H^* = 1.08 l_E^{-1}$, $k_\pm^* = 1.01 l_E^{-1}$, and $k_\nu^* = 1.50 l_E^{-1}$. This means that $k_\pm^* < k_H^* < k_\nu^*$ so that the shear mode extends much further than the heat mode. We remark that for this density $l_E = 2.58\sigma$, so that all the collective modes have disappeared long before k has reached the value $k\sigma \simeq 1$. Therefore, the relations between the eigenvalues $z_j(k)$ $(j = H, \pm, \nu)$ and $z_j^s(k)$ $(j = D, \pm, \nu)$ discussed under point 5 in Section 2 cannot be observed here.

We now turn to a discussion of Fig. 2. Here $z_j^s(k)$ and $z_j(k)$ are plotted as a function of k for a density $V_0/V = 0.625$, where $l_E = 0.052\sigma$ or $\sigma = 19.32 l_E$, so that the value $k\sigma = 1$ is reached for $k = 0.052 l_E^{-1}$.

(1) As noted before, the results for $z_j^s(k)t_E$ $(j = D, \pm, \nu)$ as a function of kl_E are the same as in the low-density case.

(2) The eigenvalues $z_j(k)$ $(j = H, \pm, \nu)$ behave as predicted by hydrodynamics for small k, i.e., $k\sigma \leqslant 1$. However, for larger values of k they are not monotonic functions of k, but instead show a complicated behavior that we will discuss now.

(a) The heat mode eigenvalue $z_H(k)$ softens very appreciably, almost vanishes at $k\sigma \simeq 7$ (i.e., for wavelengths $\lambda = 2\pi/k \approx \sigma$), and then oscillates around the self-diffusion eigenvalue $z_D^s(k)$ up until a limiting value $k_H^* = 31.3\sigma^{-1}$ of k, which is very close to the limiting value $k_D^{s*} = 1.67 l_E^{-1} = 32.2\sigma^{-1}$.

(b) The shear mode eigenvalue $z_\nu(k)$ softens appreciably for $k\sigma \gtrsim 1$ and follows the eigenvalue $z_\nu^s(k)$ up to the limiting k value $k_\nu^* = 15.40\sigma^{-1}$, which is close to $k_\nu^{s*} = 0.8 l_E^{-1} = 15.46\sigma^{-1}$.

(c) The sound mode eigenvalues $z_\pm(k)$ are complex and each other's complex conjugate except for a region $5.5 k\sigma \lesssim 7.5$ around $k\sigma \approx 7$, where both are real. For these values of k the (extended) sound modes are two different strongly damped nonpropagating modes, since $\mathrm{Im}\, z_\pm(k) = 0$ here. For values of k not in this region, the sound modes propagate, although for

$k\sigma \gtrsim 1$ the propagation is very different from that predicted by hydrodynamics, where $\mathrm{Im}\, z_{\pm}(k) = \pm ck$. The real and the imaginary parts of $z_{\pm}(k)$ oscillate around the real and imaginary parts of $z_{\pm}^{s}(k)$, with oscillations much larger and more complicated than those of $z_H(k)$ around $z_D^s(k)$. However, the cutoff vectors for the two modes are close again: $k_{\pm}^{*} = 12.4\sigma^{-1}$ is close to $k_{\pm}^{s*} = 0.585 l_E^{-1} = 11.3\sigma^{-1}$. The limiting values of k satisfy in this case a different inequality than at low densities, viz., $k_{\pm}^{*} < k_{\nu}^{*} < k_H^{*}$. We remark that the limiting value k_H^{*} of the heat mode is much larger than that of the other modes. The possible consequence of this for the negative piece of the velocity autocorrelation function has been pointed out elsewhere.[19]

In addition to the eigenvalues of the collective modes we have also computed the dynamical structure function $S_E(k, \omega)$ and $S_E^s(k, \omega)$ as given by Eqs. (3.36) and (3.39) as well as by Eqs. (3.34) and (3.37), that contain the contributions of the collective modes alone. The latter involves the calculation of $M_j(k)$ and $M_j^s(k)$ from Eqs. (3.35) and (3.38), respectively. As remarked before, explicit expressions for the eigenfunctions are not needed for the calculation of $M_j(k)$ and $M_j^s(k)$.

(1) The results for $M_H(k)$ and $M_D^s(k)$ are shown in Fig. 4 for the density $V_0/V = 0.625$. $M_D^s(k)$ is a smooth monotonically increasing function of k, extending from its value $M_D^s(0) = 1$ for $k = 0$ to a maximum value of $M_D^s(k_D^{s*}) = 1.7$ for $k_D^{s*} = 31.3\sigma^{-1}$. The behavior of $M_H(k)$ with respect to $M_D^s(k)$ is similar to that of $z_H(k)$ with respect to $z_D^s(k)$: for $0 \leqslant k\sigma \leqslant 1$, $M_H(k)$ is close to its hydrodynamic value $M_H(0) = 1 - 1/\gamma = 0.63$ and $M_H(k)$ oscillates for $k\sigma \gtrsim 7$ around $M_D^s(k)$. This is so because, as for the eigenvalues, the heat mode eigenfunctions approach the self-diffusion eigenfunction for $k\sigma \gg 1$.

(2) With $z_H(k)$ and $M_H(k)$ the contribution $S_E^{(H)}(k, \omega)$ of the heat mode alone to $S_E(k, \omega)$ can be computed, using

$$S_E^{(H)}(k, \omega) = \frac{1}{\pi} S(k) M_H(k) \cdot \frac{-z_H(k)}{\omega^2 + [z_H(k)]^2} \tag{4.3}$$

Similarly, with $z_D^s(k)$ and $M_D^s(k)$ the contribution $S_E^{s(D)}(k, \omega)$ of the self-diffusion mode to $S_E^s(k, \omega)$ can be obtained, using

$$S_E^{s(D)}(k, \omega) = \frac{1}{\pi} M_D(k) \cdot \frac{-z_D^s(k)}{\omega^2 + [z_D^s(k)]^2} \tag{4.4}$$

(3) We now compare $S_E(k, \omega)$ with $S_E^{(H)}(k, \omega)$, where $S_E(k, \omega)$ is obtained numerically from Eq. (3.34) and $S_E^{(H)}(k, \omega)$ from Eq. (4.3). For k values $0 \leqslant k\sigma \lesssim 1$, $S_E(k, \omega)$ is described by $S_E^{(H)}(k, \omega)$ as a central or Rayleigh-like line *and* the contributions of the two sound modes or

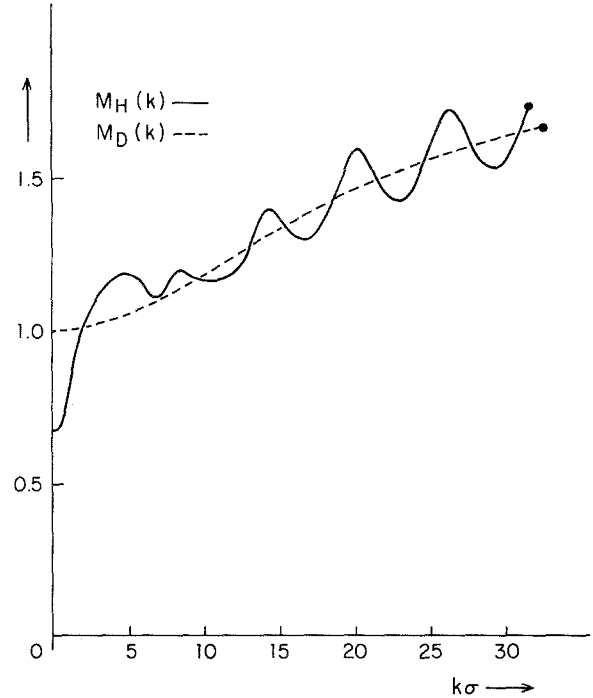

Fig. 4. $M_H(k)$ (—) and $M_D(k)$ (---),, defined in the Eqs. (3.35) and (3.38), respectively, as functions of $k\sigma$ for hard spheres at a density $V_0/V = 0.625$.

Brillouin-like lines, that can be obtained from similar formulas [cf. Eqs. (3.34) and (3.35)]. The sound mode contributions disappear as distinguishable lines in $S_E(k,\omega)$ for $k\sigma \simeq 0.5$. For k values $k\sigma \gtrsim 1$, $S_E(k,\omega)$ has the same form as $S_E^{(H)}(k,\omega)$, i.e., of one line centered around $\omega = 0$. We have compared the values $S_E(k,0)$ and $S_E^{(H)}(k,0)$ for $\omega = 0$ as well as the half-width $\omega_h(k)$ and $\omega_h^{(H)}(k)$ of the two lines where $S_E(k,\omega_h(k)) = (1/2)$ $S_E(k,0)$ and $S_E^{(H)}(k,\omega_h^{(H)}(k)) = (1/2)S_E^{(H)}(k,0)$. From Eq. (4.3) follows directly that

$$S_E^{(H)}(k,0) = \frac{1}{\pi} S(k) \frac{M_H(k)}{\left[-z_H(k)\right]} \tag{4.5}$$

The highly pronounced oscillatory behavior of $S_E^{(H)}(k,0)$ as a function of k is due both to the oscillatory behavior of $z_H(k)$ (cf. Fig. 2), $M_H(k)$ (cf. Fig. 4) and $S(k)$ which enhance each other.

(4) In Fig. 5, $S_E^{(H)}(k,0)/S(k)$ and $S_E(k,0)/S(k)$ are plotted, so that the influence of the oscillations of $S(k)$ alone are suppressed. From Figs. 2

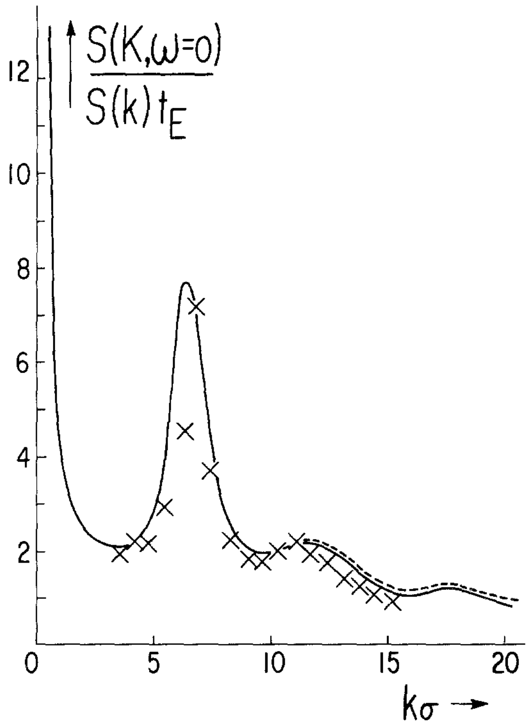

Fig. 5. $S_E(k,0)/S(k)t_E$ (—) and $S_E^{(H)}(k,0)/S(k)t_E$ (---) as functions of $k\sigma$ for hard spheres at a density $V_0/V = 0.625$. The crosses (×) represent $S(k,0)/S(k)t_E$ for liquid argon derived from coherent neutron scattering experiments of Sköld et al., using $\sigma = 3.46$ Å and $t_E = 0.084$ ps. Note that $S_E^{(H)}(k,0)/S(k) = M_H(k)/\pi z_H(k)$, with $M_H(k)$ and $z_H(k)$ plotted in Figs. 3 and 2, respectively.

and 4 it follows then that the still very oscillatory behavior of $S_E^{(H)}(k,0)/S(k)$ mainly reflects that of the heat mode eigenvalue $z_H(k)$, $[S_E^{(H)}(k,0)/S(k) \sim z_H(k)^{-1}]$, the pronounced maximum of $S^{(H)}(k,0)/S(k)$ occurring at $k\sigma = 7$ as it does for $z_H(k)$. We note that up to the limit wave vector k_H^* for the extended heat mode the difference between $S_E(k,0)$ and $S_E^{(H)}(k,0)$ does not exceed a few percent so that $S_E(k,0)$ is very well represented by $S_E^{(H)}(k,0)$ alone. We found no evidence for any singularity in the behavior of $S_E(k,0)$ at $k = k_H^*$, so that it appears that for k near k_H^* the contribution of the heat mode is smoothly taken over by other (noncollective) modes of $\bar{L}(\mathbf{k})$.

(5) In Fig. 6, the half width $\omega_h(k)$ of $S_E^{(H)}(k,\omega)$ is compared to that of $S_E(k,\omega)$. Again up to the limit wave vector k_H^* the half width of $S_E(k,\omega)$ is

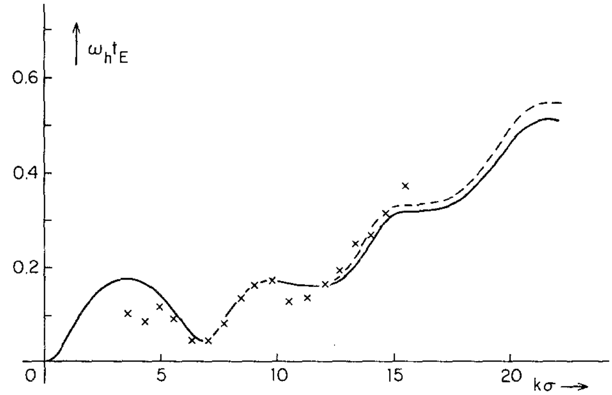

Fig. 6. Half-widths at half-height ω_h (—) of $S_E(k,\omega)$ and $\omega_h^{(H)}$ (---) of $S_E^{(H)}(k,\omega)$ as functions of $k\sigma$ for hard spheres and half-width at half-height of $S(k,\omega)$ for liquid argon ($\times$). V_0/V, σ, and t_E are as in Fig. 5. Note that $-\omega_h^{(H)}$ equals $z_H(k)$ plotted in Fig. 2.

close to that of $S_E^{(H)}(k,\omega)$, i.e., essentially determined by the heat mode alone, since $\omega_h^{(H)}(k) = -z_H(k)$. We note that $\omega_h(k)$ is continuous at $k = k_H^*$, but will be determined exclusively by noncollective modes for $k > k_H^*$. Thus we conclude that the heat mode alone dominates the coherent scattering function $S_E(k,\omega)$ for values of k such that $1 \lesssim k\sigma \lesssim k_H^*\sigma$.

(6) We remark that for any value of $k \neq 0$, the heat mode will not describe correctly the behavior of $S_E(k,\omega)$ for *large* values of ω since the asymptotic behavior of $S_E^{(H)}(k,\omega) \sim 1/\omega^2$ is essentially different from that of $S_E(k,\omega) \sim 1/\omega^4$.[20] This is not due to the model kinetic equation used here but to the representation of $S_E(k,\omega)$ by contributions of a finite number of poles, i.e., by Lorentzian lines alone. We found that $S_E^{(H)}(k,\omega)$ gives for $k\sigma \gtrsim 1$ a correct representation of $S_E(k,\omega)$ only for values of ω up to $|\omega| \approx 3z_H(k)$, at which deviations have grown as large as 10%.

(7) A comparison of $S_E^s(k,\omega)$ obtained numerically from Eq. (3.37) and of $S_E^{s(D)}(k,\omega)$ from Eq. (4.4) leads to similar conclusions. Thus the self-diffusion mode contribution to $S_E^s(k,\omega)$, $S_E^{s(D)}(k,\omega)$ alone, dominates the incoherent scattering $S_E^s(k,\omega)$ for all k up to the limit wave vector $k = k_D^*$ and for $|\omega| \lesssim 3z_D(k)$. The maximum value $S_E^s(k,0)$ at $\omega = 0$ is well described by

$$S_E^{s(D)}(k,0) = \frac{1}{\pi} \frac{M_D(k)}{[-z_D(k)]} \tag{4.6}$$

as shown in Fig. 7. The line width $\omega_h^s(k)$ of $S_E^s(k,\omega)$, defined by $S_E^s(k,\omega_h^s(k)) = (1/2)S_E^s(k,0)$ is well de: ribed by the line width $\omega_h^{s(D)}(k)$

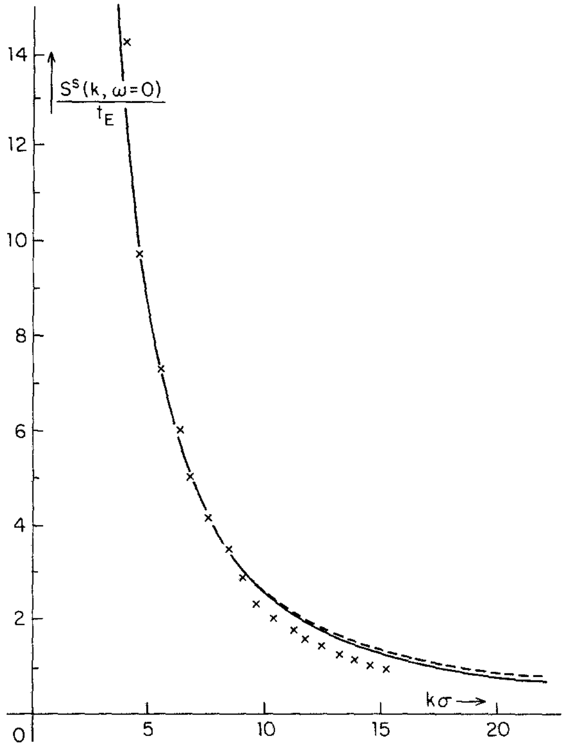

Fig. 7. $S_E^s(k,0)/t_E$ (—) and $S_E^{s(D)}(k,0)/t_E$ (---) as functions of $k\sigma$ for hard spheres. The crosses (×) represent $S^s(k,0)/t_E$ for liquid argon derived from incoherent neutron scattering experiments of Sköld et al. V_0/V, σ, and t_E are as in Fig. 5. Note that $S_E^{s(D)}(k,0) = -M_D(k)/\pi z_D^s(k)$ with $M_D(k)$ and $z_D^s(k)$ plotted in Figs. 3 and 2, respectively.

of $S_E^{s(D)}(k,\omega)$ defined by $S_E^{s(D)}(k,\omega_h^{s(D)}(k)) = (1/2)S_E^{s(D)}(k,0)$, as shown in Fig. 8. Since deviations of $\omega_h^{s(D)}(k)$ from $\omega_h^s(k)$ are small—in fact of the same order as described for the heat mode—the half width of $S_E^s(k,\omega)$ is essentially determined by the self-diffusion mode alone, since $\omega_h^s(k) = -z_D^s(k)$. This implies that the "macroscopic" self-diffusion law as expressed here by $z_D(k) = -Dk^2$ and $M_D(k) = 1$ extends—at least in the generalized Enskog theory—without major modifications to wavelengths as small as a fraction of the size of the molecules.

5. DISCUSSION

In this section we want to make a number of comments on the results obtained in this paper.

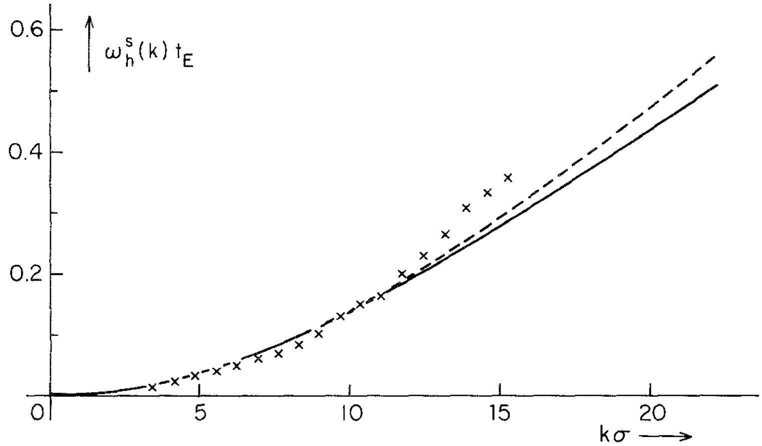

Fig. 8. Half-width at half-height ω_h^s (—) of $S_E^s(k,\omega)$ and $\omega_h^{s(D)}$ (---) of $S_E^{s(D)}(k,\omega)$ as functions of $k\sigma$ for hard spheres and half-width at half-height of $S^s(k,\omega)$ for liquid Ar (×). V_0/V, σ, and t_E are as in Fig. 5. Note that $-\omega_h^{s(D)}$ equals $z_D^s(k)$ plotted in Fig. 2.

(1) The method used here to calculate the contributions of *all* modes to the scattering functions $S(k,\omega)$ and $S^s(k,\omega)$ on the basis of the generalized Enskog theory [cf. Eqs. (3.36) and (3.39)] is similar to that used in the work of Furtado, Mazenko, and Yip.[21] However, since these authors introduced a wave-vector-dependent hard sphere diameter the physical significance of which is unclear, a direct comparison of our and their results cannot be made.

(2) As discussed in Section 4 and in Appendix C below Eq. (C.29), the operator $\bar{L}(\mathbf{k})$ given by Eqs. (3.8)–(3.11) yields a larger value of the sound damping coefficient than that computed from $L(\mathbf{k})$. As a consequence the Brillouin lines in $S(k,\omega)$ calculated with $\bar{L}(\mathbf{k})$ are lower and broader than those calculated with $L(\mathbf{k})$ [cf. Eq. (1.4)]. Therefore, for the region $0 \leqslant k\sigma \lesssim 1$, where the Brillouin lines in $S(k,\omega)$ are distinguishable, we expect the displacement ($\pm ck$) but not the shape of the Brillouin lines to be the same in the two theories. This makes a comparison of our model for $0 \leqslant k\sigma \leqslant 1$ and low densities with experiment not meaningful. However, since γ increases and D_{TE}/Γ_E decreases with increasing density, the Brillouin lines in $S(k,\omega)$ are *less* important for higher densities [cf. Eq. (1.4)]. Therefore, in that case a comparison can be made and we restrict our discussion mainly to high densities and to $k\sigma \gtrsim 1$. Results for a more elaborate model for $L(\mathbf{k})$, containing the correct value of Γ_E [cf. the discussion below Eq. (3.7)] will be published elsewhere. There, also a comparison with low-density experimental scattering data[10,22,23] will be made.

(3) It is clearly interesting to compare our theoretical results with computer data for hard sphere fluids. From the work of Yip, Alley, and Alder[8,24] it appears that our approximation $\bar{L}(\mathbf{k})$ for the Enskog operator $L(\mathbf{k})$, based on Eqs. (3.6) and (3.7) with $M = 5$, is a good one for high densities and $k\sigma \gtrsim 1$. For, these authors calculated the scattering functions $S(k,\omega)$ and $S^s(k,\omega)$ using expressions for $\Lambda_{\mathbf{k}}^{(M)}$ with increasingly larger values of $M \geqslant 5$ and found no significant changes when M increased beyond $M = 5$. Also, from their calculations it appears that the generalized Enskog theory based on the operator $L(\mathbf{k})$ provides a reasonable description of the properties of a real hard sphere fluid. Transport coefficients such as ν_E and D_{TE} obtained on the basis of the generalized Enskog theory deviate for liquid densities typically of the order of 30% from those obtained from computer results for a hard sphere fluid. This might also indicate the order of magnitude of deviations between theory and computer calculations that can be expected in the hydrodynamical regime $0 \leqslant k\sigma \lesssim 1$. Comparisons made by Yip, Alley, and Alder do not indicate any increase of these deviations for larger values of k. At present we do not have sufficient computer data at our disposal to make a meaningful comparison of our theoretical results for the collective modes of a hard sphere fluid with the data of Yip, Alley, and Alder. It is, therefore, difficult to assess whether the heat and diffusion modes play the same dominant roles in the dynamical structure factors of a hard sphere fluid as they do in the generalized Enskog theory.

(4) However, we can compare our results for $S_E(k,\omega)$ and $S_E^s(k,\omega)$ with experimental data for liquid argon.[25] For that, an adaptation of the hard sphere model to argon has to be made by an appropriate choice of the diameter σ of the hard spheres. This can for instance be done by comparing the structure factors $S(k)$ for both liquids.[9] A comparison of the theoretical curves for $S^{(H)}(k,0)$ and $\omega_h^{(H)}(k)$ with the $S(k,0)$ and $\omega_h(k)$ of liquid Ar, respectively, is made in Fig. 5 and 6 for $k\sigma \gtrsim 1$. As will be discussed below, sound modes are unimportant in this region. We feel that the theoretical and experimental curves for $S(k,\omega)$ for argon are sufficiently close to surmise that a collective heat mode is also present in argon and that it dominates its coherent neutron scattering for not too large values of ω. In fact, from the relation $\omega_h(k) = -z_H(k)$ information about the behavior of the (extended) heat mode in Ar as a function of k can be directly deduced.

The behavior of $z_H(k)$ shown in Fig. 2 and deduced from the generalized Enskog theory explains in particular the phenomenon of the De Gennes narrowing,[26] i.e., the narrowing of the central line in $S(k,\omega)$ for wavelengths $\lambda \simeq \sigma$ (i.e., $k\sigma \simeq 7$). Similar results for liquid rubidium have been discussed in a previous publication.[9]

As shown in Figs. 7 and 8, the Enskog theory describes also the overall behavior of the experimental values of $S^s(k,0)$ and $\omega_h^s(k)$ for liquid argon[22] as functions of k, so that the self-diffusion mode seems to dominate the incoherent neutron scattering function $S^s(k,\omega)$ of Ar. However, systematic deviations occur between theory and experiment which are of a wavelike form reminiscent of the behavior of the heat mode (cf. Fig. 2), which suggests an influence of the heat mode on $S^s(k,\omega)$.

In the Enskog theory only *single* collective modes are taken into account and there is no heat mode contribution to $S^s(k,\omega)$. Therefore, we conjecture that corrections to the Enskog theory due to mode coupling effects[6,7] which contain pairs of modes—in particular a heat mode coupled to a diffusion mode—might improve the agreement between theory and experiment. This will be investigated in a future publication.

(5) On the basis of our theory the (extended) sound modes will contribute to $S_E(k,\omega)$ up to the limiting wave vector $k_\pm^* = 11.3\sigma^{-1}$ (cf. Fig. 2). However, the visibility of the sound mode contributions in $S_E(k,\omega)$ depends strongly on k. For $0 \leqslant k \lesssim 0.5\sigma^{-1}$ these contributions manifest themselves as distinct (Brillouin-like) lines, for $0.5\sigma^{-1} \lesssim k \lesssim \sigma^{-1}$ as flat wings in $S_E(k,\omega)$, while for $k \gtrsim \sigma^{-1}$ they rapidly disappear.

Computer simulations suggest that for liquid argon Brillouin lines in $S(k,\omega)$ are visible for values of k such that $k \lesssim \sigma^{-1}$.[27] So far they have not been observed in neutron scattering experiments, but they have been seen in light scattering experiments up to relatively large values of k.[28] Since the thermodynamic and transport properties are appreciably different for a hard sphere (or Enskog) fluid and a real fluid like Ar, a quantitative prediction of the value of k below which two sound modes will be distinguishable in the spectrum is not possible. Qualitatively, the occurrence of sound modes in the "initial" neutron scattering regime should be a general phenomenon.

(6) From the above follows in our view that for not too large values of k and ω neutron scattering of fluids is just like light scattering, i.e., it can be understood on the basis of a Landau–Placzek-like formula, where the thermodynamic quantities are replaced by $S(k)$ and $M_j(k)$ [or $M_j^s(k)$] and the hydrodynamic eigenvalues (or the transport coefficients) by the extended hydrodynamic eigenvalues [cf. Eqs. (1.4), (3.34), and (3.37)].

(7) The disappearance of the two sound modes as propagating modes and the bifurcation of the sound damping at high density ($V_0/V = 0.625$) was also seen by Foch and Ford using the Navier–Stokes equations for a *low* density gas at large values of k. This was the more surprising since their kinetic model, like ours, did not show any such behavior at these low densities. Whether this is a fluke of the Navier–Stokes equations or the kinetic models used is not clear at present.

(8) That all collective modes disappear for all densities when $kl_E \approx 1$ (cf. Fig. 3) and that for high densities these modes change their behavior drastically when $k\sigma \approx 7$ (i.e., $\lambda \approx \sigma$) can physically be understood as follows. There are three lengths in the problem: l_E, σ, and the wavelength λ, characteristic for a small disturbance in the fluid. For low densities $\sigma \ll l_E$ (cf. Fig. 3) and as long as $\lambda > l_E$, at least some collisions will take place between the many particles in λ, before the disturbance has decayed to zero, since the decay time $[z_j(k)]^{-1} > t_E$. Thus, the local number, momentum, and energy density are approximately conserved and an approximate local equilibrium obtains. As a consequence, the behavior of the disturbance can be described in terms of hydrodynamic modes. For high densities $l_E \ll \sigma$, but as long as λ is such that $\lambda > \sigma \gg l_E$, many particles are included in a wavelength and the local number, momentum, and energy density will still be approximately conserved. Therefore, the collective modes will again exhibit typical hydrodynamical, i.e., Landau–Placzek-like, behavior. However, when $\lambda \approx \sigma$ essentially only a single particle is included in a wavelength and only the local number density will be conserved. Then the extended heat mode degenerates into a self-diffusion-like mode and the evolution of a small disturbance will be described by a self-diffusion-like mode alone. Now the coefficient of self-diffusion $D \ll D_T$ because D is a transport coefficient that does not contain any collisional transfer contributions present in D_T and which dominate D_T for high densities. Therefore, when $\lambda \approx \sigma$, the heat mode will go from a behavior $\sim -D_T k^2$ to one like $\sim -Dk^2$, i.e., it will soften very appreciably and continue as a self-diffusion-like mode till it ceases to exist when $\lambda \approx l_E$. This will be so since for $\lambda \leqslant l_E$ no (approximate) conservation laws apply any more and one enters a regime in which free streaming begins to dominate.

(9) The transversal current–current correlation function $\tau(\mathbf{k}, t)$ is defined by

$$\tau(\mathbf{k}, t) = \frac{\beta m}{N} \left\langle \sum_{j=1}^{N} \mathbf{v}_j \cdot \hat{\mathbf{k}}_\perp \exp(-i\mathbf{k} \cdot \mathbf{r}_j) \sum_{l=1}^{N} \mathbf{v}_l(t) \cdot \hat{\mathbf{k}}_\perp \exp\left[i\mathbf{k} \cdot \mathbf{r}_l(t) \right] \right\rangle_0$$

where $\hat{\mathbf{k}}_\perp$ is a unit vector orthogonal to $\mathbf{k}$. For small k, the behavior of $\tau(\mathbf{k}, t)$ is determined by linearized hydrodynamics, so that $\tau(\mathbf{k}, t) \simeq e^{-\nu k^2 t}$. In the generalized Enskog theory, this function is given by $\tau_E(\mathbf{k}, t) = \langle \varphi_4 \exp[L(\mathbf{k})t] \varphi_4 \rangle$ and will behave for small k as $\tau_E(\mathbf{k}, t) = \exp(-\nu_E k^2 t)$. One would expect that for larger values of k, $\tau_E(\mathbf{k}, t)$ is dominated by the extended shear modes, just as $F_E(k, t)$ is dominated by the extended heat mode. This would imply that information about the behavior of $z_\nu(k)$ could be obtained from the half width $\omega_h^{(\nu)}$ of the Fourier transform of $\tau_E(\mathbf{k}, t)$ since $\omega_h^\nu(k) = -z_\nu(k)$. Using this equality, computer data obtained for $\tau(\mathbf{k}, t)$ at high densities indicate indeed a softening of the viscous mode consistent with the behavior of $z_\nu(k)$ in Fig. 2.[24] It would also be interesting to verify whether the relation $z_\nu(k) \cong z_\nu^s(k)$ for $k\sigma \gtrsim 7$ holds, which is the analog of the relation $z_H(k) \cong z_D^s(k)$ for $k\sigma \gtrsim 7$ discussed above.

(10) Wavelength and frequency-dependent transport coefficients, such as $\nu(k,\omega)$, the wavelength–frequency-dependent kinematic viscosity, can be computed on the basis of the generalized Enskog theory in the same fashion as $S(k,\omega)$ here. It would be interesting to see whether these quantities are also dominated by collective modes for not too large values of k and ω and how they compare with Ansätze made about them in the literature.[29,30]

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APPENDIX A

We derive properties of the collision operator $\Lambda_{\mathbf{k}}$ defined in Eq. (2.7) which are needed in the main text. We write $\Lambda_{\mathbf{k}}$ as a sum of real and imaginary parts

$$\Lambda_{\mathbf{k}} = \Lambda_{\mathbf{k}}^R + i\Lambda_{\mathbf{k}}^I \tag{A.1}$$

so that

$$\Lambda_{\mathbf{k}}^R = -\sigma^2 \int d\hat{\boldsymbol{\sigma}} \int d\mathbf{v}_2 \phi(v_2) |\mathbf{v}_{12}\cdot\hat{\boldsymbol{\sigma}}|\, Q_{\hat{\sigma}} \{1 + \cos(\mathbf{k}\cdot\boldsymbol{\sigma}) P_{12}\} \tag{A.2a}$$

$$\Lambda_{\mathbf{k}}^I = \sigma^2 \int d\hat{\boldsymbol{\sigma}} \int d\mathbf{v}_2\, \phi(v_2)(\mathbf{v}_{12}\cdot\hat{\boldsymbol{\sigma}}) Q_{\hat{\sigma}} \sin(\mathbf{k}\cdot\boldsymbol{\sigma}) P_{12} \tag{A.2b}$$

Here $\Lambda_{\mathbf{k}}$ acts on functions of $\mathbf{v}_1$, $\hat{\boldsymbol{\sigma}}$ is a unit vector, $\boldsymbol{\sigma} = \sigma\hat{\boldsymbol{\sigma}}$, P_{12} interchanges $\mathbf{v}_1$ and $\mathbf{v}_2$ in functions of $\mathbf{v}_1$ and $\mathbf{v}_2$ and the operator $Q_{\hat{\sigma}}$ acts on a function $h(\mathbf{v}_1, \mathbf{v}_2)$ as

$$Q_{\hat{\sigma}} h(\mathbf{v}_1,\mathbf{v}_2) = \tfrac{1}{2}\{h(\mathbf{v}_1,\mathbf{v}_2) - h(\mathbf{v}_1^*,\mathbf{v}_2^*)\} \tag{A.3}$$

with the restituting collisional velocities $\mathbf{v}_1^*$ and $\mathbf{v}_2^*$ given by $\mathbf{v}_1^* = \mathbf{v}_1 - (\mathbf{v}_{12}\cdot\hat{\boldsymbol{\sigma}})\hat{\boldsymbol{\sigma}}$ and $\mathbf{v}_2^* = \mathbf{v}_2 + (\mathbf{v}_{12}\cdot\hat{\boldsymbol{\sigma}})\hat{\boldsymbol{\sigma}}$, similarly as below Eq. (2.8).

The relations (A.2) follow from Eq. (2.7) by adding to (2.7) a similar expression in which $\hat{\sigma}$ is replaced by $-\hat{\sigma}$, dividing by 2, and taking the real and imaginary parts. As a result the condition $\mathbf{g}\cdot\hat{\boldsymbol{\sigma}} > 0$ on the $\mathbf{v}'$ integral in (2.7) may be omitted in (A.2) and replaced by a factor $1/2$ in (A.3).

For $Q_{\hat{\sigma}}$ we need the following properties, which follow immediately from Eq. (A.3).

(i) If the function $h(\mathbf{v}_1, \mathbf{v}_2)$ in (A.3) is symmetric (or antisymmetric) under the interchange of $\mathbf{v}_1$ and $\mathbf{v}_2$, the result $Q_{\hat{\sigma}} h(\mathbf{v}_1, \mathbf{v}_2)$ is symmetric (or antisymmetric) under the same operation.

(ii) If $\mathbf{v}_1' = (-v_{1x}, v_{1y}, v_{1z})$ and $\mathbf{v}_2' = (-v_{2x}, v_{2y}, v_{2z})$ and the function $\tilde{h}$ is related to the function h by $\tilde{h}(\mathbf{v}_1', \mathbf{v}_2') = h(\mathbf{v}_1, \mathbf{v}_2)$ then $Q_{\hat{\sigma}'} \tilde{h}(\mathbf{v}_1', \mathbf{v}_2') = Q_{\hat{\sigma}} h(\mathbf{v}_1, \mathbf{v}_2)$, where $\hat{\boldsymbol{\sigma}}' = (-\sigma_x, \sigma_y, \sigma_z)$. A similar property holds for the y and z directions.

(iii) $Q_{\hat{\sigma}}$ is Hermitian with respect to the inner product $\langle\langle \cdots \rangle_1\rangle_2$ where the brackets labeled 1 and 2 denote velocity averages over $\mathbf{v}_1$ and $\mathbf{v}_2$ with weight functions $\phi(v_1)$ and $\phi(v_2)$, respectively.

(iv) $Q_{\hat{\sigma}}$ is a projection operator, i.e., $Q_{\hat{\sigma}}^2 = Q_{\hat{\sigma}}$.

(v) $Q_{\hat{\sigma}} 1 = 0$ and $Q_{\hat{\sigma}}$ commutes with any function of the center of mass velocity $\mathbf{V} \equiv \frac{1}{2}(\mathbf{v}_1 + \mathbf{v}_2)$ and with any function of $\mathbf{v}_{12} - (\mathbf{v}_{12} \cdot \hat{\boldsymbol{\sigma}})\hat{\boldsymbol{\sigma}}$, i.e., any function of the components of that part of the relative velocity $\mathbf{v}_{12}$ which is orthogonal to $\hat{\boldsymbol{\sigma}}$. Also, $Q_{\hat{\sigma}}$ commutes with any function of $|\mathbf{v}_{12} \cdot \hat{\boldsymbol{\sigma}}|$, in particular with $(\mathbf{v}_{12} \cdot \hat{\boldsymbol{\sigma}})^l$ when l is even. For odd values of l one has

$$Q_{\hat{\sigma}} (\mathbf{v}_{12} \cdot \hat{\boldsymbol{\sigma}})^l h(\mathbf{v}_1, \mathbf{v}_2) = (\mathbf{v}_{12} \cdot \hat{\boldsymbol{\sigma}})^l (1 - Q_{\hat{\sigma}}) h(\mathbf{v}_1, \mathbf{v}_2) \qquad (l \text{ is odd}) \quad \text{(A.4)}$$

Next we discuss the properties of $\Lambda_{\mathbf{k}}$.

(1) The first property of $\Lambda_{\mathbf{k}}$ we need, reads

$$\begin{aligned} \Lambda_{\mathbf{k}}^R: &\quad H(\mu_1 \mu_2 \mu_3) \to H(\mu_1 \mu_2 \mu_3) \qquad (\mu_i = \pm) \\ \Lambda_{\mathbf{k}}^I: &\quad H(\mu_1 \mu_2 \mu_3) \to H(\mu_1 \mu_2 - \mu_3) \qquad (\mu_i = \pm) \end{aligned} \quad \text{(A.5)}$$

where $H(+++)$ stands for all functions of $\mathbf{v}_1$ which are even in v_{1x}, v_{1y}, and v_{1z}; $H(-++)$ stands for all functions which are odd in v_{1x} and even in v_{1y} and v_{1z} and so on. We take $\mathbf{k}$ in the z direction. The relation (A.5) follows from (A.2) and the property (ii) for $Q_{\hat{\sigma}}$ given above. Furthermore, it follows from the defining equations (A.2) and (A.3) that $\Lambda_{\mathbf{k}}^R$ and $\Lambda_{\mathbf{k}}^I$ are invariant under the interchange of the x and y components of $\mathbf{v}_1$.

(2) For any two functions $f(\mathbf{v}_1)$ and $g(\mathbf{v}_1)$ one has

$$\begin{aligned} &\langle f(\mathbf{v}_1) \Lambda_{\mathbf{k}}^R g(\mathbf{v}_1) \rangle_1 \\ &\quad = -\frac{1}{4}\sigma^2 \int d\hat{\boldsymbol{\sigma}} \big[(1 + \cos \mathbf{k} \cdot \boldsymbol{\sigma}) \langle\langle \{ Q_{\hat{\sigma}} (f(\mathbf{v}_1) + f(\mathbf{v}_2)) \} \\ &\qquad\qquad \times |\mathbf{v}_{12} \cdot \hat{\boldsymbol{\sigma}}| \{ Q_{\hat{\sigma}} (g(\mathbf{v}_1) + g(\mathbf{v}_2)) \} \rangle_1 \rangle_2 \\ &\qquad + (1 - \cos \mathbf{k} \cdot \boldsymbol{\sigma}) \langle\langle \{ Q_{\hat{\sigma}} (f(\mathbf{v}_1) - f(\mathbf{v}_2)) \} \\ &\qquad\qquad \times |\mathbf{v}_{12} \cdot \hat{\boldsymbol{\sigma}}| \{ Q_{\hat{\sigma}} (g(\mathbf{v}_1) - g(\mathbf{v}_2)) \} \rangle_1 \rangle_2 \big] \end{aligned} \quad \text{(A.6)}$$

where the action of $Q_{\hat{\sigma}}$ is restricted to the brackets $\{\cdots\}$ in which it occurs. The result (A.6) follows from Eq. (A.2) and the properties (i), (iii), and (iv) for $Q_{\hat{\sigma}}$. The relation (A.6) implies that $\Lambda_{\mathbf{k}}^{R}$ is Hermitian, i.e.,

$$\Lambda_{\mathbf{k}}^{R\dagger} = \Lambda_{\mathbf{k}}^{R} \tag{A.7}$$

and that $\Lambda_{\mathbf{k}}^{R}$ is seminegative definite, i.e.,

$$\left\langle f(\mathbf{v}_1)\Lambda_{\mathbf{k}}^{R} f(\mathbf{v}_1)\right\rangle_1 \leqslant 0 \tag{A.8}$$

for any real function $f(\mathbf{v}_1)$, since in (A.6) $1 \pm \cos \mathbf{k}\cdot\boldsymbol{\sigma} \geqslant 0$. For $k=0$ the equality sign in (A.8) holds if $f(\mathbf{v}_1)$ is a collisional invariant, i.e., $Q_{\hat{\sigma}}(f(\mathbf{v}_1) + f(\mathbf{v}_2)) = 0$, i.e., $f(\mathbf{v}_1)$ is a linear combination of 1, $\mathbf{v}_1$ and $\mathbf{v}_1^2$. For $k \neq 0$ the equality sign in (A.8) holds if one has in addition that $Q_{\hat{\sigma}}(f(\mathbf{v}_1) - f(\mathbf{v}_2)) = 0$, which means that $f(\mathbf{v}_1)$ is a constant. In fact the unit function, φ_1, is a zero eigenfunction of $\Lambda_{\mathbf{k}}$ for all $\mathbf{k}$, i.e.,

$$\Lambda_{\mathbf{k}}\varphi_1 = 0 \tag{A.9}$$

while for $k=0$ one has

$$\Lambda_0\varphi_j = \Lambda_0^R\varphi_j = 0 \qquad (j = 1, \ldots, 5) \tag{A.10}$$

where φ_j denote the linear combinations of the collisional invariants given in (2.24)–(2.28).

(3) For any two functions $f(\mathbf{v}_1)$ and $g(\mathbf{v}_1)$ one has from (A.2)

$$\left\langle f(\mathbf{v}_1)\Lambda_{\mathbf{k}}^{I} g(\mathbf{v}_1)\right\rangle_1 = \sigma^2 \int d\hat{\boldsymbol{\sigma}} \sin \mathbf{k}\cdot\boldsymbol{\sigma} \left\langle\left\langle f(\mathbf{v}_1)(\mathbf{v}_{12}\cdot\hat{\boldsymbol{\sigma}}) Q_{\hat{\sigma}} g(\mathbf{v}_2)\right\rangle_1\right\rangle_2 \tag{A.11}$$

If on the right-hand side we let $Q_{\hat{\sigma}}$ act to the left, use (iii), apply the relation (A.4) with $l = 1$, and interchange $\mathbf{v}_1$ and $\mathbf{v}_2$, the result can be written as

$$\begin{aligned}\left\langle g(\mathbf{v}_1)\Lambda_{\mathbf{k}}^{I\dagger} f(\mathbf{v}_1)\right\rangle_1 &= \left\langle g(\mathbf{v}_1)\Lambda_{\mathbf{k}}^{I} f(\mathbf{v}_1)\right\rangle_1 \\ &\quad - \sigma^2 \int d\hat{\boldsymbol{\sigma}} \sin \mathbf{k}\cdot\boldsymbol{\sigma} \left\langle\left\langle g(\mathbf{v}_1)(\mathbf{v}_{12}\cdot\hat{\boldsymbol{\sigma}}) f(\mathbf{v}_2)\right\rangle_1\right\rangle_2\end{aligned} \tag{A.12}$$

Here the left-hand side of (A.12) is equal to the left-hand side of Eq. (A.11) by the definition of $\Lambda_{\mathbf{k}}^{I\dagger}$. In the second term of (A.12) and in the following, integrals over the unit vector $\hat{\boldsymbol{\sigma}}$ of the following form occur:

$$\int d\hat{\boldsymbol{\sigma}} \cos \mathbf{k}\cdot\boldsymbol{\sigma} = 4\pi j_0(k\sigma) \tag{A.13}$$

$$\int d\hat{\boldsymbol{\sigma}}\, \hat{\sigma}_\alpha \sin \mathbf{k}\cdot\boldsymbol{\sigma} = 4\pi \hat{k}_\alpha j_1(k\sigma) \tag{A.14}$$

$$\int d\hat{\boldsymbol{\sigma}}\, \hat{\sigma}_\alpha \hat{\sigma}_\beta \cos \mathbf{k}\cdot\boldsymbol{\sigma} = 4\pi\delta_{\alpha\beta} j_1(k\sigma)/k\sigma - 4\pi\hat{k}_\alpha\hat{k}_\beta j_2(k\sigma) \tag{A.15}$$

$$\begin{aligned}\int d\hat{\boldsymbol{\sigma}}\, \hat{\sigma}_\alpha \hat{\sigma}_\beta \hat{\sigma}_\gamma \sin \mathbf{k}\cdot\boldsymbol{\sigma} &= 4\pi\left\{\hat{k}_\alpha\delta_{\beta\gamma} + \hat{k}_\beta\delta_{\alpha\gamma} + \hat{k}_\gamma\delta_{\alpha\beta}\right\} j_2(k\sigma)/k\sigma \\ &\quad - 4\pi\hat{k}_\alpha\hat{k}_\beta\hat{k}_\gamma j_3(k\sigma)\end{aligned} \tag{A.16}$$

where $\hat{\sigma}_\alpha$ and $\hat{k}_\alpha$ denote the components of the unit vectors $\hat{\boldsymbol{\sigma}}$ and $\hat{k}$, respectively, and $j_l(x)$ are spherical Bessel functions.[11] The relations (A.14)–(A.16) follow from (A.13) by taking partial derivatives with respect to the components of **k**.

Using Eq. (A.14) in the second term on the right-hand side of eq. (A.12) yields

$$\Lambda_{\mathbf{k}}^{I\dagger} = \Lambda_{\mathbf{k}}^{I} - \frac{4\pi\sigma^2}{(\beta m)^{1/2}} j_1(k\sigma)\{|\varphi_2\rangle_1\langle\varphi_1| - |\varphi_1\rangle_1\langle\varphi_2|\} \qquad \text{(A.17)}$$

where $\varphi_1(\mathbf{v}_1)$ and $\varphi_2(\mathbf{v}_1)$ are given by (2.24) and (2.25), respectively, and $|\rangle_1, \langle|$ are defined with respect to the inner product $\langle \cdots \rangle_1$, similarly as in (2.31).

(4) $\Lambda_{\mathbf{k}}^{I}$ acting on $\mathbf{v}_1$ and $\mathbf{v}_1^2$ yields

$$\begin{aligned}
\Lambda_{\mathbf{k}}^{I}\mathbf{v}_1 &= -\frac{1}{2}\sigma^2\int d\hat{\boldsymbol{\sigma}} \sin \mathbf{k}\cdot\boldsymbol{\sigma}\int d\mathbf{v}_2\,\phi(v_2)(\mathbf{v}_{12}\cdot\hat{\boldsymbol{\sigma}})^2\hat{\boldsymbol{\sigma}} \\
\Lambda_{\mathbf{k}}^{I}\mathbf{v}_1^2 &= -\frac{1}{2}\sigma^2\int d\hat{\boldsymbol{\sigma}} \sin \mathbf{k}\cdot\boldsymbol{\sigma}\int d\mathbf{v}_2\,\phi(v_2)(\mathbf{v}_{12}\cdot\hat{\boldsymbol{\sigma}})^2(\mathbf{v}_1+\mathbf{v}_2)\cdot\hat{\boldsymbol{\sigma}}
\end{aligned} \qquad \text{(A.18)}$$

as follows from Eqs. (A.2b) and (A.3). Carrying out the integrals over $\hat{\boldsymbol{\sigma}}$ as well as the integrals over $\mathbf{v}_2$, using (A.16), yields

$$\begin{aligned}
\Lambda_{\mathbf{k}}^{I}\mathbf{v}_1 &= -\frac{2\pi\sigma^2}{5\beta m}\left\{j_1(k\sigma)(5+\beta m\mathbf{v}_1^2) + j_3(k\sigma)\beta m\left[\mathbf{v}_1^2 - 5(\mathbf{v}_1\cdot\mathbf{k})^2\right]\right\}\hat{\mathbf{k}} \\
&\quad - \frac{4\pi\sigma^2}{5}\{j_1(k\sigma)+j_3(k\sigma)\}(\mathbf{v}_1\cdot\hat{\mathbf{k}})\mathbf{v}_1 \\
\Lambda_{\mathbf{k}}^{I}\mathbf{v}_1^2 &= \frac{2\pi\sigma^2}{5\beta m} j_1(k\sigma)(\mathbf{v}_1\cdot\hat{\mathbf{k}})\{5-3\beta m\mathbf{v}_1^2\} \\
&\quad + \frac{2\pi\sigma^2}{5} j_3(k\sigma)(\mathbf{v}_1\cdot\hat{\mathbf{k}})\{5(\mathbf{v}_1\cdot\hat{\mathbf{k}})^2 - 3\mathbf{v}_1^2\}
\end{aligned} \qquad \text{(A.19)}$$

From this result one can derive how $\Lambda_{\mathbf{k}}^{I}$ acts on the functions $\varphi_2, \ldots, \varphi_5$ defined in (2.25)–(2.28). The result can be written as

$$\begin{aligned}
\Lambda_{\mathbf{k}}^{I}\varphi_2 &= -\frac{\sqrt{\pi}}{nt_0} j_1(k\sigma)\left[\varphi_1 + \frac{\sqrt{6}}{6}\varphi_3 - \frac{2}{15}\sqrt{3}\,\varphi_8\right] - \frac{(3\pi)^{1/2}}{5nt_0} j_3(k\sigma)\varphi_8 \\
\Lambda_{\mathbf{k}}^{I}\varphi_3 &= -\frac{\sqrt{\pi}}{nt_0} j_1(k\sigma)\left[\frac{\sqrt{6}}{6}\varphi_2 + \frac{\sqrt{15}}{10}\varphi_7\right] - \frac{(10\pi)^{1/2}}{10nt_0} j_3(k\sigma)\varphi_{10} \\
\Lambda_{\mathbf{k}}^{I}\varphi_4 &= -\frac{\sqrt{\pi}}{5nt_0}\left[j_1(k\sigma)+j_3(k\sigma)\right]\varphi_6 \\
\Lambda_{\mathbf{k}}^{I}\varphi_5 &= -\frac{\sqrt{\pi}}{5nt_0}\left[j_1(k\sigma)+j_3(k\sigma)\right]\varphi_9
\end{aligned} \qquad \text{(A.20)}$$

where $(nt_0)^{-1} = 4\sigma^2(\pi/\beta m)^{1/2}$, according to the discussion in point 5 of Section 2, and where we introduced the polynomials

$$\begin{aligned}
\varphi_6(\mathbf{v}_1) &= \beta m v_{1x} v_{1z} \\
\varphi_7(\mathbf{v}_1) &= \left(\frac{\beta m}{10}\right)^{1/2} v_{1z}\left(\beta m \mathbf{v}_1^2 - 5\right) \\
\varphi_8(\mathbf{v}_1) &= \tfrac{1}{2}\sqrt{3}\,\beta m\left(v_{1x}^2 + v_{1y}^2 - \tfrac{2}{3}\mathbf{v}_1^2\right) \\
\varphi_9(\mathbf{v}_1) &= \beta m v_{1y} v_{1z} \\
\varphi_{10}(\mathbf{v}_1) &= \beta m\left(\frac{3\beta m}{20}\right)^{1/2} v_{1z}\left(\mathbf{v}_1^2 - \frac{5}{3} v_{1z}^2\right)
\end{aligned} \tag{A.21}$$

which are such that $\langle \varphi_j \varphi_l \rangle_1 = \delta_{jl}$, with $j, l \leqslant 10$. Using in Eq. (A.20) that for small k, $j_1(k\sigma) = k\sigma/3$ and $j_3(k\sigma) \sim k^3$ we find

$$\begin{aligned}
P_\perp n\chi\Lambda_\mathbf{k}^I \varphi_2 &= \frac{2(3\pi)^{1/2}\sigma}{45 t_E} k\varphi_8 + O(k^3) \\
P_\perp n\chi\Lambda_\mathbf{k}^I \varphi_3 &= -\frac{(15\pi)^{1/2}\sigma}{30 t_E} k\varphi_7 + O(k^3) \\
P_\perp n\chi\Lambda_\mathbf{k}^I \varphi_4 &= -\frac{\sqrt{\pi}\,\sigma}{15 t_E} k\varphi_6 + O(k^3)
\end{aligned} \tag{A.22}$$

where $t_E = t_0/\chi$ and where $P_\perp$ projects orthogonal to $\varphi_1, \ldots, \varphi_5$. We also need a relation similar to (A.22) for the free streaming term $-i\mathbf{k}\cdot\mathbf{v}$ in (2.5), i.e.,

$$\begin{aligned}
P_\perp i\mathbf{k}\cdot\mathbf{v}_1\varphi_2(\mathbf{v}_1) &= -\frac{2}{3}\sqrt{3}\,\frac{i}{(\beta m)^{1/2}} k\varphi_8 \\
P_\perp i\mathbf{k}\cdot\mathbf{v}_1\varphi_3(\mathbf{v}_1) &= \frac{1}{3}\sqrt{15}\,\frac{i}{(\beta m)^{1/2}} k\varphi_7 \\
P_\perp i\mathbf{k}\cdot\mathbf{v}_1\varphi_4(\mathbf{v}_1) &= \frac{i}{(\beta m)^{1/2}} k\varphi_6
\end{aligned} \tag{A.23}$$

which follows from the definitions of $P_\perp$ and φ_j.

(5) Finally, we consider the matrix elements which appear in the matrix representation (3.5), i.e.,

$$\Omega_{j,l}(k\sigma) = \langle \varphi_j \Lambda_\mathbf{k} \varphi_l \rangle_1 \tag{A.24}$$

The first ten orthonormal polynomials φ_j are given in (2.24)–(2.28) and (A.21). A complete set of orthonormal polynomials can be obtained by supplementing the set $\varphi_1, \ldots, \varphi_{10}$ with an infinite number of Hermite polynomials of increasing order in v_{1x}, v_{1y}, and v_{1z}.

As a consequence each function φ_j, with $j = 1, \ldots, \infty$, is an element of one of the subspaces $H(\mu_1, \mu_2, \mu_3)$ introduced in (A.5), i.e., each φ_j is either even or odd in v_{1x}, v_{1y}, and v_{1z}. We remark that closed expressions for all elements $\Omega_{j,l}$ in (A.24) can be derived using the generating functions for the Hermite polynomials. However, since these expressions are rather involved[24] we restrict ourselves here to a few general properties of the matrix $\Omega_{j,l}$ and only give the elements which are needed in the main text.

Owing to Eq. (A.5), $\Omega_{j,l}$ is real when $\varphi_j \in H(\mu_1 \mu_2 \mu_3)$ and $\varphi_l \in H(\mu_1 \mu_2 \mu_3)$; $\Omega_{j,l}$ is purely imaginary when $\varphi_j \in H(\mu_1 \mu_2 \mu_3)$ and $\varphi_l \in H(\mu_1 \mu_2 - \mu_3)$ and $\Omega_{j,l}$ is zero otherwise. In particular the diagonal elements $\Omega_{j,j}$ are real and

$$\Omega_{j,j}(k\sigma) \leqslant 0 \tag{A.25}$$

as follows from Eq. (A.8). The equality sign in (A.25) holds for all k if $j = 1$, and for $k = 0$ if $j = 1, \ldots, 5$, as is discussed below Eq. (A.8). Because of Eqs. (A.7) and (A.17) one has that

$$\Omega_{l,j}(k\sigma) = \Omega_{j,l}(k\sigma) - i\frac{4\pi\sigma^2}{(\beta m)^{1/2}}\, j_1(k\sigma)\{\delta_{l,1}\delta_{j,2} - \delta_{l,2}\delta_{j,1}\} \tag{A.26}$$

which means that $\Omega_{l,j}$ is a symmetric matrix except that $\Omega_{1,2} \neq \Omega_{2,1}$. Owing to (A.9) all elements $\Omega_{j,1}(k\sigma)$ vanish. Using these properties for $\Omega_{j,l}(k\sigma)$ we can determine them explicitly. Firstly, for $j, l \leqslant 5$ one finds

$$\Omega_{2,2}(x) = -\frac{2}{3}\frac{1}{nt_0}\left[1 - j_0(x) + 2j_2(x)\right]$$

$$\Omega_{3,3}(x) = -\frac{2}{3}\frac{1}{nt_0}\left[1 - j_0(x)\right]$$

$$\Omega_{4,4}(x) = \Omega_{5,5}(x) = -\frac{2}{3}\frac{1}{nt_0}\left[1 - j_0(x) - j_2(x)\right]$$

$$\Omega_{1,2}(x) = -i\sqrt{\pi}\,\frac{1}{nt_0}\, j_1(x)$$

$$\Omega_{2,3}(x) = \Omega_{3,2}(x) = -\left(\frac{\pi}{6}\right)^{1/2}\frac{1}{nt_0}\, i\, j_1(x)$$

while

$$\Omega_{j,l}(x) = 0 \qquad \text{otherwise for } j, l \leqslant 5 \tag{A.27}$$

We remark that the off-diagonal elements in this list can be read off from the results (A.20) by taking inner products with φ_j on both sides of the equations and using that $\{\varphi_j\}$ is an orthonormal set. The diagonal matrix elements in the list (A.27) are obtained after a lengthy calculation starting from Eqs. (A.6) and (A.3) where we introduced in Eq. (A.6) center of mass and relative velocities in order to perform the integrals over $\mathbf{v}_1$ and $\mathbf{v}_2$ and where the relations (A.13)–(A.16) were used in order to perform the integral over $\hat{\boldsymbol{\sigma}}$.

The matrix elements $\Omega_{j,l}$ outside the 5×5 block given in (A.27) and which are needed in the main text are

$$
\begin{aligned}
\Omega_{6,6}(x) &= \Omega_{9,9}(x) = \frac{1}{nt_0}\left\{-\frac{16}{15} + \frac{4}{15}j_0(x) - \frac{4}{21}j_2(x) - \frac{16}{35}j_4(x)\right\} \\
\Omega_{7,7}(x) &= \frac{1}{nt_0}\left\{-\frac{59}{60} + \frac{9}{20}j_0(x) - \frac{9}{10}j_2(x)\right\} \\
\Omega_{8,8}(x) &= \frac{1}{nt_0}\left\{-\frac{16}{15} + \frac{4}{15}j_0(x) - \frac{8}{21}j_2(x) + \frac{24}{35}j_4(x)\right\} \\
\Omega_{4,6}(x) &= \Omega_{5,9}(x) = -\frac{1}{5}\frac{\sqrt{\pi}}{nt_0}i\left[j_1(x) + j_3(x)\right] \\
\Omega_{3,7}(x) &= -\frac{\sqrt{15\pi}}{10nt_0}i\,j_1(x) \\
\Omega_{2,8}(x) &= \frac{\sqrt{3\pi}}{15nt_0}i\left[2j_1(x) - 3j_3(x)\right]
\end{aligned}
\tag{A.28}
$$

The off-diagonal elements in this list are obtained from Eq. (A.20) and the diagonal elements from Eqs. (A.3) and (A.6) in a similar way as discussed below Eq. (A.27). We remark that the limiting values $\Omega_{j,l}(0)$ and $\Omega_{j,l}(\infty)$ can be read off from Eqs. (A.27) and (A.28), using that $j_l(\infty) = 0$ for $l = 0, 1, \ldots, \infty$, that $j_0(0) = 1$, and that $j_l(0) = 0$ for $l = 1, \ldots, \infty$.

APPENDIX B

We derive four properties of the operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$ defined in Eqs. (2.5) and (2.6). We show that these are sufficient to prove the spectral relations of $L(\mathbf{k})$ and $L^s(\mathbf{k})$ mentioned in Section 2 [i.e., eqs. (2.50)–(2.56)]. It is also shown that the set of operators $L^{(M)}(\mathbf{k})$ and $L^{s(M)}(\mathbf{k})$ introduced in Section 3 and in particular $\bar{L}(\mathbf{k})$ and $\bar{L}^s(\mathbf{k})$ have the same four properties and therefore obey similar spectral relations.

We need the following properties of $L(\mathbf{k})$ and $L^s(\mathbf{k})$.

(1) The real and imaginary parts of $L(\mathbf{k})$ and $L^s(\mathbf{k})$ satisfy

$$
\begin{aligned}
&\mathrm{Re}\,L(\mathbf{k}),\ \mathrm{Re}\,L^s(\mathbf{k})\colon H(\mu_1\mu_2\mu_3) \to H(\mu_1\mu_2\mu_3) \\
&\mathrm{Im}\,L(\mathbf{k}),\ \mathrm{Im}\,L^s(\mathbf{k})\colon H(\mu_1\mu_2\mu_3) \to H(\mu_1\mu_2 - \mu_3)
\end{aligned}
\tag{B.1}
$$

where the function spaces $H(\mu_1\mu_2\mu_3)$ with $\mu_i = \pm$ introduced in (A.5). This property follows from Eqs. (2.5), (2.6), (3.4), and (A.5) and using that $\Lambda^s = \Lambda^R_\infty = \Lambda_\infty$ [cf.(2.16)]. Also, the operators $L(\mathbf{k})$ and $L^s(\mathbf{k})$ are invariant under the interchange of the x and y components of the velocity $\mathbf{v}$ (with $\mathbf{k}$

in the z direction as in the main text and in Appendix A), since $\Lambda_{\mathbf{k}}$, Λ^s, $i\mathbf{k}\cdot\mathbf{v}$ and $A_{\mathbf{k}}$ are invariant under this interchange. This has been used under point 3 of Section 2.

(2) $L(\mathbf{k})$ and $L^s(\mathbf{k})$ act on the unit function, φ_1, as

$$L(\mathbf{k})\varphi_1 = L^s(\mathbf{k})\varphi_1 = \frac{-ik}{(\beta m)^{1/2}}\varphi_2 \tag{B.2}$$

with φ_2 given in Eq. (2.25). This property follows from Eqs. (2.5), (2.6), (3.4) and (A.9).

(3) The Hermitian conjugates of $L(\mathbf{k})$ and $L^s(\mathbf{k})$ read

$$\begin{aligned} L^\dagger(\mathbf{k}) &= L^*(\mathbf{k}) + \frac{ik}{(\beta m)^{1/2}}\frac{S(k)-1}{S(k)}\{|\varphi_1\rangle\langle\varphi_2| - |\varphi_2\rangle\langle\varphi_1|\} \\ L^{s\dagger}(\mathbf{k}) &= L^{s*}(\mathbf{k}) \end{aligned} \tag{B.3}$$

This follows from Eqs. (2.5), (2.6), (2.10), (3.4), (A.7), and (A.17). We remark that in Eqs. (2.5) and (2.6), $\mathbf{k}\cdot\mathbf{v}$ and Λ^s are Hermitian operators but that $\Lambda_{\mathbf{k}}$ and $A_{\mathbf{k}}$ are not Hermitian. The relation (B.3) implies that the real parts of $L(\mathbf{k})$ and $L^s(\mathbf{k})$ are Hermitian operators.

(4) The real part of $L(\mathbf{k})$ is semi-negative-definite, i.e.,

$$\langle\Phi^*(\mathbf{v})\{\operatorname{Re} L(\mathbf{k})\}\Phi(\mathbf{v})\rangle \leqslant 0 \tag{B.4}$$

for any complex function $\Phi(\mathbf{v})$. This follows from (A.7) and (A.8) since $\operatorname{Re} L(\mathbf{k}) = n\chi\Lambda_{\mathbf{k}}^R$, according to (2.5) and since $A_{\mathbf{k}}$ is a purely imaginary operator. The equality sign in (B.4) holds for $k \neq 0$ if and only if Φ is a multiple of the unit function and for $k=0$ if Φ is a linear combination of 1, $\mathbf{v}$ and $\mathbf{v}^2$ [cf. the discussion below Eq. (A.8)]. The relation (B.4) also applies to the real part of $L^s(\mathbf{k})$ since $\operatorname{Re} L^s(\mathbf{k}) = \operatorname{Re} L(\infty)$.

From these four properties we derive the spectral relations mentioned in Section 2. We start with the relation (2.52). Let, for a certain for value of k, $L(\mathbf{k})$ have an eigenfunction $\Psi(\mathbf{k},\mathbf{v})$ with eigenvalue $z(k)$, i.e.,

$$L(\mathbf{k})\Psi(\mathbf{k},\mathbf{v}) = z(k)\Psi(\mathbf{k},\mathbf{v}) \tag{B.5}$$

Then, according to (B.3), the operator $L^{\dagger *}(\mathbf{k})$ acts on this function as

$$\begin{aligned} L^{\dagger *}(\mathbf{k})\Psi(\mathbf{k},\mathbf{v}) &= z(k)\Psi(\mathbf{k},\mathbf{v}) \\ &\quad - \frac{ik}{(\beta m)^{1/2}}\frac{S(k)-1}{S(k)}\{\langle\Psi\varphi_2\rangle\varphi_1 - \langle\Psi\varphi_1\rangle\varphi_2\} \end{aligned} \tag{B.6}$$

Furthermore, $L^{\dagger *}(\mathbf{k})$ acts on the unit function, φ_1, as

$$L^{\dagger *}(\mathbf{k})\varphi_1 = -\frac{ik}{(\beta m)^{1/2}S(k)}\varphi_2 \tag{B.7}$$

as follows from (B.2) and (B.3). Therefore, if we define $\Phi(\mathbf{k}, \mathbf{v})$ by

$$\Phi(\mathbf{k}, \mathbf{v}) = A^*\left[\Psi^*(\mathbf{k}, \mathbf{v}) + \left[S(k) - 1\right]\langle\Psi^*\varphi_1\rangle\varphi_1\right] \tag{B.8}$$

with A^* an arbitrary constant, then $L^{\dagger *}$ acts on the complex conjugate of Φ as

$$L^{\dagger *}(\mathbf{k})\Phi^*(\mathbf{k}, \mathbf{v}) = A\left\{z(k)\Psi(\mathbf{k}, \mathbf{v}) - \frac{ik}{(\beta m)^{1/2}} \frac{S(k) - 1}{S(k)} \langle\Psi\varphi_2\rangle\right\} \tag{B.9}$$

For the second term on the right-hand side we use the relation

$$\frac{-ik}{(\beta m)^{1/2} S(k)} \langle\Psi\varphi_2\rangle = z(k)\langle\Psi\varphi_1\rangle \tag{B.10}$$

which follows from Eq. (B.5) by taking the inner product of both sides of the equation with φ_1 and by letting $L(\mathbf{k})$ act to the left, using (B.3). Substitution of (B.10) into (B.9), using (B.8) and taking the complex conjugate of the resulting equation yields

$$L^{\dagger}(\mathbf{k})\Phi(\mathbf{k}, \mathbf{v}) = z^*(k)\Phi(\mathbf{k}, \mathbf{v}) \tag{B.11}$$

Thus, the function Φ given by (B.8) is the left eigenfunction of $L(\mathbf{k})$ which corresponds to the right eigenfunction Ψ in (B.5). The constant A in (B.8) is determined by the normalization condition (2.36), i.e., $\langle\Phi^*\Psi\rangle = 1$, so that

$$A = \left\{\langle\Psi^2\rangle + \left[S(k) - 1\right]\langle\Psi\rangle^2\right\}^{-1} \tag{B.12}$$

and therefore Eq. (2.52) follows from Eqs. (B.8) and (B.12). The relation (2.53) can be derived in a similar way, in particular, by setting $S(k)$ equal to 1 everywhere in the proof given above, but we omit the details.

Next we prove the relation (2.50). We start from

$$\operatorname{Re} z(k) = \frac{1}{2\langle\Psi\Phi\rangle} \langle\Phi\{L(\mathbf{k}) + L^*(\mathbf{k})\}\Psi\rangle \tag{B.13}$$

which follows from Eqs. (B.5) and (B.11) if one lets $L^*(\mathbf{k})$ in (B.13) act to the left. Therefore

$$\operatorname{Re} z(k) = \frac{1}{\langle\Psi\Phi\rangle} \langle\Psi\{\operatorname{Re} L(\mathbf{k})\}\Phi\rangle \tag{B.14}$$

where we used that $\operatorname{Re} L(\mathbf{k})$ is an Hermitian operator. Substitution of (B.8) for Φ and using that, according to (B.2), $\operatorname{Re} L(\mathbf{k})\varphi_1 = 0$ yields

$$\operatorname{Re} z(k) = \frac{\langle\Psi\{\operatorname{Re} L(\mathbf{k})\}\Psi^*\rangle}{\langle\Psi\Psi^*\rangle + \left[S(k) - 1\right]|\langle\Psi\varphi_1\rangle|^2} \tag{B.15}$$

We first observe that the unit function, φ_1, is *not* an eigenfunction of $L(\mathbf{k})$ for $k \neq 0$ due to (B.2), so that $\Psi \neq \varphi_1$. Therefore, owing to Schwartz's inequality, $|\langle\Psi\varphi_1\rangle|^2$ is strictly smaller than $\langle\Psi\Psi^*\rangle$. Secondly, the static structure factor $S(k)$ obeys $S(k) \geqslant 0$. This is a consequence of the fact that the intermediate scattering function $F(k, t)$ defined in Eq. (1.2), is for $t = 0$ an average over a non-negative function and equal to $S(k)$. Hence, the numerator of the expression on the right-hand side of Eq. (B.15) is for $k \neq 0$ strictly positive. Furthermore, since $\Psi \neq \varphi_1$, the denominator in (B.15) is strictly negative for $k \neq 0$ as discussed below Eq. (B.4). Therefore,

$$\operatorname{Re} z(k) < 0 \qquad (k \neq 0) \tag{B.16}$$

which is the relation (2.50). The relation (2.51) is proved similarly by setting $S(k)$ equal to 1.

Next we prove the relation (2.55). The eigenfunction $\Psi(\mathbf{k}, \mathbf{v})$ in (B.5) can be written as

$$\Psi(\mathbf{k}, \mathbf{v}) = \Psi_+(\mathbf{k}, \mathbf{v}) + \Psi_-(\mathbf{k}, \mathbf{v}) \tag{B.17}$$

with

$$\Psi_\pm(\mathbf{k}, \mathbf{v}) = \tfrac{1}{2}\left[\Psi(\mathbf{k}, v_x, v_y, v_z) \pm \Psi(\mathbf{k}, v_x, v_y - v_z)\right] \tag{B.18}$$

so that Ψ_+ is even and Ψ_- is odd in v_z. Substitution of (B.17) into (B.5), writing $L(\mathbf{k})$ as a sum of a real and an imaginary part and using the relation (B.1) yields two equations: one equates the functions in (B.5) which are even in v_z, and the other equates the functions which are odd in v_z, i.e.,

$$\begin{aligned} \{\operatorname{Re} L(\mathbf{k})\}\psi_+ + i\{\operatorname{Im} L(\mathbf{k})\}\psi_- &= z(k)\psi_+ \\ \{\operatorname{Re} L(\mathbf{k})\}\psi_- + i\{\operatorname{Im} L(\mathbf{k})\}\psi_+ &= z(k)\psi_- \end{aligned} \tag{B.19}$$

Subtracting both equations and taking the complex conjugate yields

$$L(\mathbf{k})(\Psi_+^* - \Psi_-^*) = z^*(k)(\Psi_+^* - \Psi_-^*) \tag{B.20}$$

Thus $\Psi_+^* - \Psi_-^*$ is an eigenfunction of $L(\mathbf{k})$ with eigenvlaue $z^*(k)$. This and Eqs. (B.17) and (B.18) lead to the relation (2.55). The relation (2.56) follows in a completely similar manner.

Finally, we discuss the general properties of the set of operators $L^{(M)}(\mathbf{k})$ with $M \geqslant 5$ defined by Eqs. (3.1) and (3.6). This includes in particular the operator $\bar{L}(\mathbf{k})$ introduced in Section 3 above Eq. (3.8) for $M = 5$. In fact we restrict ourselves to the operator $\bar{L}(\mathbf{k})$, since the generalizations to $L^{(M)}(\mathbf{k})$ are rather obvious.

Using Eqs. (3.1), (3.5), and (3.6), the operator $\bar{L}(\mathbf{k})$ can be written as

$$\begin{aligned} \bar{L}(\mathbf{k}) = &-i\mathbf{k}\cdot\mathbf{v} + n\chi P_H \Lambda_{\mathbf{k}} P_H + nA_{\mathbf{k}} \\ &+ \left[n\chi\, g_+(k)(\varphi_2 - P_H\varphi_2 P_H) + n\chi h_+(k)(1 - P_H)\right]P_+ \\ &+ \left[n\chi\, g_-(k)(\varphi_2 - P_H\varphi_2 P_H) + n\chi h_-(k)(1 - P_H)\right]P \end{aligned} \tag{B.21}$$

where P_H projects on the five functions $\varphi_1, \ldots, \varphi_5$, i.e.,

$$P_H = \sum_{j=1}^{5} |\varphi_j\rangle\langle\varphi_j| \tag{B.22}$$

where the $g_\pm(k)$, given by Eq. (3.7), are purely imaginary and vanishing for $k = 0$ and $k = \infty$, and where the $h_\pm(k)$, given by Eq. (3.7), are real and strictly negative for all k.

We mention the following four properties of $\bar{L}(\mathbf{k})$, which are the analogs of the four properties of $L(\mathbf{k})$ give above:

(1) The real and imaginary parts of $\bar{L}(\mathbf{k})$ satisfy

$$\begin{aligned} &\operatorname{Re}\bar{L}(\mathbf{k}): H(\mu_1\mu_2\mu_3) \to H(\mu_1\mu_2\mu_3) \\ &\operatorname{Im}\bar{L}(\mathbf{k}): H(\mu_1\mu_2\mu_3) \to H(\mu_1\mu_2 - \mu_3) \end{aligned} \tag{B.23}$$

similarly as in (B.1), and $\bar{L}(\mathbf{k})$ is invariant under the interchange of v_x and v_y. To prove this property from Eq. (B.21) one needs the properties of $\mathbf{k}\cdot\mathbf{v} \sim \varphi_2$, $\Lambda_\mathbf{k}$ and $A_\mathbf{k}$ that were also needed in order to prove Eq. (B.1). In addition one needs that P_H, P_+, and P_- map functions from $H(\mu_1\mu_2\mu_3)$ into $H(\mu_1\mu_2\mu_3)$ and that P_H, P_+, and P_- are invariant under the interchange of v_x and v_y.

(2) $\bar{L}(\mathbf{k})$ acts on the unit function, φ_1, as

$$\bar{L}(\mathbf{k})\varphi_1 = \frac{-ik}{(\beta m)^{1/2}}\varphi_2 \tag{B.24}$$

similarly as in (B.2). This follows from Eqs. (B.21), (B.22), (A.9), and (3.4), using that $P_+\varphi_1 = \varphi_1$ and $P_-\varphi_1 = 0$.

(3) The Hermitian conjugate of $\bar{L}(\mathbf{k})$ satisfies

$$\bar{L}^\dagger(\mathbf{k}) = \bar{L}^*(\mathbf{k}) + \frac{ik}{(\beta m)^{1/2}}\frac{S(k)-1}{S(k)}\{|\varphi_1\rangle\langle\varphi_2| - |\varphi_2\rangle\langle\varphi_1|\} \tag{B.25}$$

similarly as in (B.3). This follows from the equations (B.21) and (3.4) since the operators P_H, P_+, P_-, $\varphi_2 \sim \mathbf{k}\cdot\mathbf{v}$ are Hermitian; P_+ and P_- commute with φ_2 and with P_H and $\Lambda_\mathbf{k}$ obeys Eqs. (A.7) and (A.17).

(4) The real part of $L(\mathbf{k})$ satisfies

$$\left\langle \Phi^* \left\{ \operatorname{Re}\bar{L}(\mathbf{k}) \right\} \Phi \right\rangle \leqslant 0 \tag{B.26}$$

for any complex function Φ and the equality sign holds if and only if Φ is a linear combination of $\varphi_1, \ldots, \varphi_5$ (when $k = 0$) or if Φ is a multiple of φ_1 (when $k \neq 0$). In order to prove Eq. (B.26) one needs: that $\operatorname{Re}\bar{L}(\mathbf{k})$ is Hermitian, as follows from (B.25); Eq. (A.8) for $\Lambda_\mathbf{k}$ in (B.21); the fact that the $h_\pm(k)$ are strictly negative for all k and that $-i\mathbf{k}\cdot\mathbf{v}$, $A_\mathbf{k}$, and $g_\pm(k)$ in

(B.21) are purely imaginary and therefore do not contribute to $\mathrm{Re}\,\bar{L}(\mathbf{k})$.

We remark that the operator $\bar{L}^s(\mathbf{k})$ introduced in Section 3 above Eq. (3.8) obeys the four properties mentioned in (B.1)–(B.4) for $L^s(\mathbf{k})$. This is a consequence of the definition of $\bar{L}^s(\mathbf{k})$ given by Eqs. (3.2), (3.3), (3.6), and (3.7), i.e., $\mathrm{Re}\,\bar{L}^s(\mathbf{k}) = \bar{L}(\infty)$ and $\mathrm{Im}\,\bar{L}^s(\mathbf{k}) = -\mathbf{k}\cdot\mathbf{v}$, but we omit the details of the proof.

As a consequence of the four properties (B.23)–(B.26) of $\bar{L}(\mathbf{k})$ and the four similar properties of $\bar{L}^s(\mathbf{k})$, the spectral relations (2.50)–(2.56) mentioned in Section 2 apply both to the spectral decompositions of $\bar{L}(\mathbf{k})$ and $\bar{L}^s(\mathbf{k})$. Also, the statement made in Section 3 below Eq. (3.7) about the spectral decompositions of $L^{(M)}(\mathbf{k})$ and $L^{s(M)}(\mathbf{k})$ with $M \geqslant 5$ follows in a completely similar manner.

APPENDIX C

We determine the hydrodynamic modes of $L(\mathbf{k})$ and $L^s(\mathbf{k})$ which appear in Eqs. (2.29) and (2.30) for small values of k, using perturbation theory. The results are compared at the end with the hydrodynamic modes of the operators $\bar{L}(\mathbf{k})$ and $\bar{L}^s(\mathbf{k})$, introduced in Section 3.

We start with the five hydrodynamic modes of $L(\mathbf{k})$ which are defined by Eq. (2.32), i.e.,

$$L(\mathbf{k})\Psi_j(\mathbf{k},\mathbf{v}) = z_j(k)\Psi_j(\mathbf{k},\mathbf{v}) \qquad (j = H, \pm, \nu_1, \nu_2) \tag{C.1}$$

where for $k \to 0$, the functions $\Psi_j(\mathbf{k},\mathbf{v})$ tend to linear combinations of the conserved quantities $\varphi_1, \ldots, \varphi_5$ of $L(0)$ [cf. (2.22)] and the $z_j(k)$ tend to zero.

We expand the quantities in (C.1) in powers of k,

$$L(\mathbf{k}) = L(0) + ikL^{(1)} + k^2 L^{(2)} + \cdots \tag{C.2a}$$

$$\Psi_j(\mathbf{k},\mathbf{v}) = \Psi_j(0,\mathbf{v}) + ik\Psi_j^{(1)}(\mathbf{v}) + k^2\Psi_j^{(2)}(\mathbf{v}) + \cdots \tag{C.2b}$$

$$z_j(k) = ikz_j^{(1)} + k^2 z_j^{(2)} + \cdots \tag{C.2c}$$

and equate the terms in (C.1) with equal powers in k. Thus

$$L(0)\Psi_j(0,\mathbf{v}) = 0 \tag{C.3a}$$

$$\left(L^{(1)} - z_j^{(1)}\right)\Psi_j(0,\mathbf{v}) + L(0)\Psi_j^{(1)}(\mathbf{v}) = 0 \tag{C.3b}$$

$$\left(L^{(2)} - z_j^{(2)}\right)\Psi_j(0,\mathbf{v}) - \left(L^{(1)} - z_j^{(1)}\right)\Psi_j^{(1)}(\mathbf{v}) + L(0)\Psi_j^{(2)}(\mathbf{v}) = 0 \tag{C.3c}$$

The first equation, (C.3a), is satisfied, as discussed above. In Eq. (C.3b) we let the projection operator P_H defined in (B.22) and subsequently its orthogonal complement $P_\perp = 1 - P_H$ act on both sides of the equation, yielding two equations which read

$$P_H\left(L^{(1)} - z_j^{(1)}\right)P_H\Psi_j(0,\mathbf{v}) = 0 \tag{C.4a}$$

$$P_\perp L^{(1)}\Psi_j(0,\mathbf{v}) + P_\perp L(0)\Psi_j^{(1)}(\mathbf{v}) = 0 \tag{C.4b}$$

where we used that $\Psi_j(0,\mathbf{v}) = P_H\Psi_j(0,\mathbf{v})$ and $P_H L(0) = L(0)P_H = 0$ as follows from (2.22) and (B.22). Using the representation (B.22) for P_H, Eq. (C.4a) reduces to a 5×5 matrix eigenvalue problem for the matrix representation of $L^{(1)}$, i.e., for the matrix with elements

$$L_{j,l}^{(1)} \equiv \langle \varphi_j L^{(1)} \varphi_l \rangle \qquad (j, l \leqslant 5) \tag{C.5}$$

These can be obtained from (C.2a) and Eq. (2.5), using for $j, l \leqslant 5$

$$\langle \varphi_j(-i\mathbf{k}\cdot\mathbf{v})\varphi_l \rangle = \frac{-ik}{(\beta m)^{1/2}}\left\{\delta_{j,1}\delta_{l,2} + \delta_{j,2}\delta_{l,1} + \frac{1}{3}\sqrt{6}\left(\delta_{j,3}\delta_{l,2} + \delta_{j,2}\delta_{l,3}\right)\right\} \tag{C.6}$$

the result (A.27) for the averages of $\Lambda_\mathbf{k}$ in Eq. (2.5) and the expression (3.4) for $A_\mathbf{k}$. Thus one finds

$$\begin{aligned} L_{2,1}^{(1)} &= \frac{-1}{(\beta m)^{1/2}} \\ L_{1,2}^{(1)} &= \frac{-1}{(\beta m)^{1/2} S(0)} \\ L_{2,3}^{(1)} &= L_{3,2}^{(1)} = -\frac{\sqrt{6}}{3(\beta m)^{1/2}}\left(1 + \tfrac{2}{3}\pi n\sigma^3\chi\right) \\ L_{j,l}^{(1)} &= 0 \qquad (\text{otherwise for } j, l \leqslant 5) \end{aligned} \tag{C.7}$$

where in the expression for $L_{2,3}^{(1)}$ the relation for $(nt_0)^{-1}$, given below Eq. (A.20), has been used.

Next we use the following thermodynamic properties of a hard sphere gas. The equation of state is given by $p(n,T) = nk_BT(1 + \frac{2}{3}\pi n\sigma^3\chi)$; $c_v = \frac{3}{2}k_B$; $\gamma = c_p/c_v = 1 + \alpha^2T/nc_v\chi_T = 1 + \frac{2}{3}S(0)(p/nk_BT)^2$; $c = (\gamma/mn\chi_T)^{1/2} = [\gamma/\beta m S(0)]^{1/2}$. Here p is the pressure, c_p and c_v are the specific heats at constant pressure and volume, respectively, $\chi_T = (\partial n/\partial p)_T/n$ is the isothermal compressibility, related to $S(0)$ by the compressibility theorem: $S(0) = nk_BT\chi_T$ and $\alpha = -(\partial n/\partial T)_p/n$ is the expansion coefficient.

Thus, using the equation of state, the matrix element $L_{2,3}^{(1)}$ in Eq. (C.7) can be written as

$$L_{2,3}^{(1)} = -\left(\frac{\gamma - 1}{\gamma}\right)^{1/2} c = -\tilde{c} \tag{C.8}$$

where the quantity $\tilde{c}$ has been introduced in Eq. (2.41). From this result and the relation $\gamma = \beta mc^2 S(0)$ given above, follows straightforwardly that the matrix $L_{j,l}^{(1)}$ has three eigenvalues equal to zero and two eigenvalues equal to $\pm c$ with eigenvectors $\Psi_{\nu_1}, \Psi_{\nu_2}, \Psi_H$, and $\Psi_\pm$, respectively, which are given by Eqs. (2.46), (2.47), (2.39), and (2.43).

The left eigenfunctions $\Phi_j(\mathbf{k}, \mathbf{v})$ corresponding to the right eigenfunctions $\Psi_j(\mathbf{k}, \mathbf{v})$ in Eq. (C.1) are obtained from the relation (2.52) which holds for all values of k. In particular the expressions for the left hydrodynamic modes to lowest order in k, $\Phi_j(0, \mathbf{v})$ with $j = H, \pm, \nu_1, \nu_2$, which are given by Eqs. (2.40) (2.44), (2.46), and (2.47) are a consequence of the relation (2.52). We remark that $\langle \Phi_j(0, \mathbf{v}) \Psi_l(0, \mathbf{v}) \rangle = \delta_{jl}$ and that

$$\langle \Phi_j(0, \mathbf{v}) L^{(1)} \Psi_l(0, \mathbf{v}) \rangle = z_j^{(1)} \delta_{jl} \tag{C.9}$$

which is a consequence of Eq. (C.4a), using that $L^{(1)}$ on the left-hand side of Eq. (C.9) may be replaced by $P_H L^{(1)} P_H$.

Next we consider the equation (C.4b). Since the operator $P_\perp$ commutes with $L(0)$ and projects orthogonal to all five zero eigenfunctions of $L(0)$, the equation (C.4b) determines uniquely the functions $P_\perp \Psi_j^{(1)}(\mathbf{v})$ for $j = H, \pm, \nu_1, \nu_2$, i.e.,

$$P_\perp \Psi_j^{(1)}(\mathbf{v}) = -\frac{1}{L(0)} P_\perp L^{(1)} \Psi_j(0, \mathbf{v}) \tag{C.10}$$

Next we determine the coefficients $z_j^{(2)}$ in the expansion (C.2c). By multiplying Eq. (C.3c) to the left with $\Phi_j(0, \mathbf{v})$ and averaging over all $\mathbf{v}$ one obtains

$$\begin{aligned} z_j^{(2)} = & -\left\langle \Phi_j(0, \mathbf{v}) \left(L^{(1)} - z_j^{(1)} \right) \Psi_j^{(1)}(\mathbf{v}) \right\rangle \\ & + \left\langle \Phi_j(0, \mathbf{v}) L^{(2)} \Psi_j(0, \mathbf{v}) \right\rangle \end{aligned} \tag{C.11}$$

where we have used that $\Phi_j(0, \mathbf{v})$ is a linear combination of conserved quantities and that $L(0)$ is a Hermitian operator.

In the first term on the right-hand side of Eq. (C.11) we write $\Psi_j^{(1)}(\mathbf{v})$ as a sum of $P_H \Psi_j^{(1)}(\mathbf{v})$ and $P_\perp \Psi_j^{(1)}(\mathbf{v})$. The contribution of $P_H \Psi_j^{(1)}(\mathbf{v})$ vanishes due to Eq. (C.9) and for $P_\perp \Psi_j^{(1)}(\mathbf{v})$ we substitute the relation (C.10), so that

$$z_j^{(2)} = \left\langle \Phi_j(0, \mathbf{v}) \left\{ L^{(1)} P_\perp \frac{1}{L(0)} P_\perp L^{(1)} + L^{(2)} \right\} \Psi_j(0, \mathbf{v}) \right\rangle \tag{C.12}$$

Expressions for the transport coefficients ν_E, D_{TE}, and Γ_E which appear in Eqs. (2.38), (2.42), and (2.45) follow from this relation using the explicit expressions for $\Psi_j(0,\mathbf{v})$ and $\Phi_j(0,\mathbf{v})$. Firstly, with Eq. (2.46) follows that

$$\nu_E = -\left\langle \varphi_4 \left\{ L^{(1)} P_\perp \frac{1}{L(0)} P_\perp L^{(1)} + L^{(2)} \right\} \varphi_4 \right\rangle \tag{C.13}$$

Secondly, from Eqs. (2.39) and (2.40) one has that

$$D_{\text{TE}} = -\frac{1}{\gamma} \left\langle \varphi_3 \left\{ L^{(1)} P_\perp \frac{1}{L(0)} P_\perp L^{(1)} + L^{(2)} \right\} \varphi_3 \right\rangle \tag{C.14}$$

Here we have used that it follows from Eq. (B.3) that the operator in brackets $\{\cdots\}$ on the right-hand side of Eq. (C.12) is Hermitian, and from Eq. (B.2) that this operator yields zero when acting on the unit function φ_1 either to the right or to the left. Furthermore we used the thermodynamic relation $\gamma = m\beta c^2 S(0)$ which was given above. Finally, from Eqs. (2.43), (2.44), and (C.14) and the thermodynamic properties described above follows that

$$\Gamma_E = \frac{1}{2}(\gamma - 1) D_{\text{TE}} - \frac{1}{2} \left\langle \varphi_2 \left\{ L^{(1)} P_\perp \frac{1}{L(0)} P_\perp L^{(1)} + L^{(2)} \right\} \varphi_2 \right\rangle \tag{C.15}$$

where furthermore is used that the operator in brackets $\{\cdots\}$ in Eq. (C.12) transforms from the function space $H(\mu_1 \mu_2 \mu_3)$ into the function space $H(\mu_1 \mu_2 \mu_3)$, as follows from (B.1), so that cross terms of the form $\langle \varphi_2 \{\cdots\} \varphi_3 \rangle$ vanish. Next we use in the expressions for ν_E, D_{TE}, and Γ_E that

$$P_\perp L^{(1)} \varphi_j(\mathbf{v}) = e_j J_j(\mathbf{v}) \qquad (j = 2, 3, 4) \tag{C.16}$$

where $J_2(\mathbf{v}) = \varphi_8(\mathbf{v})$ denotes the normalized longitudinal current given in Eq. (A.21), $J_3(\mathbf{v}) = \varphi_7(\mathbf{v})$ denotes the heat flow function and $J_4(\mathbf{v}) = \varphi_6(\mathbf{v})$ a shear flow, while the coefficients e_j are given by

$$\begin{aligned}
e_2 &= \frac{2}{(3\beta m)^{1/2}} + \frac{n\chi}{i} \Omega'_{2,8}(0) = \frac{2}{(3\beta m)^{1/2}} \left(1 + \frac{4\pi}{15} n\sigma^3 \chi\right) \\
e_3 &= -\left(\frac{5}{3\beta m}\right)^{1/2} + \frac{n\chi}{i} \Omega'_{3,7}(0) = -\left(\frac{5}{3\beta m}\right)^{1/2} \left(1 + \frac{2\pi}{5} n\sigma^3 \chi\right) \\
e_4 &= \frac{-1}{(\beta m)^{1/2}} + \frac{n\chi}{i} \Omega'_{4,6}(0) = \frac{-1}{(\beta m)^{1/2}} \left(1 + \frac{4\pi}{15} n\sigma^3 \chi\right)
\end{aligned} \tag{C.17}$$

where the primes indicate first derivatives with respect to k. The results (C.16) and (C.17) follow from the definition (C.2a) for $L^{(1)}$, the expression (2.5) for $L(\mathbf{k})$, the equations (A.22) and (A.23), and the definition (A.24) for $\Omega_{j,l}$.

We remark that the first terms on the right-hand sides of Eq. (C.17) arise from the free streaming term in $L(\mathbf{k})$, the second terms from the linear term in the expansion of the operator $n\chi\Lambda_{\mathbf{k}}$ present in $L(\mathbf{k})$, and that the operator $A_{\mathbf{k}}$ in $L(\mathbf{k})$ does not contribute since $P_{\perp}A_{\mathbf{k}} = 0$ as follows from Eq. (3.4). Furthermore one has

$$\left\langle J_j \frac{1}{L(0)} J_j \right\rangle = \frac{w_j}{\langle J_j L(0) J_j \rangle} \qquad (j = 2, 3, 4) \tag{C.18}$$

where the coefficients w_j are given by[12]

$$\begin{aligned} w_2 &= w_4 = 1.01600 \\ w_3 &= 1.02513 \end{aligned} \tag{C.19}$$

Thus we find from Eqs. (C.14)–(C.19) and (A.24), using that $L(0) = n\chi\Lambda_0$

$$\nu_E = -\frac{w_4 e_4^2}{n\chi\Omega_{6,6}(0)} - \frac{1}{2} n\chi\Omega''_{4,4}(0) \tag{C.20a}$$

$$D_{\mathrm{TE}} = -\frac{w_3 e_3^2}{n\chi\gamma\Omega_{7,7}(0)} - \frac{1}{2\gamma} n\chi\Omega''_{3,3}(0) \tag{C.20b}$$

$$\Gamma_E = \frac{1}{2}(\gamma - 1) D_{\mathrm{TE}} - \frac{w_2 e_2^2}{2n\chi\Omega_{8,8}(0)} - \frac{1}{4} n\chi\Omega''_{2,2}(0) \tag{C.20c}$$

where the double primes denote second derivatives with respect to k. We remark that the transport coefficients are built up from diagonal matrix elements $\Omega_{j,j}(k\sigma)$ with $j = 2, 3, 4$ and $j = 6, 7, 8$ and the off-diagonal matrix elements $\Omega_{2,8}$, $\Omega_{3,7}$, and $\Omega_{4,6}$ which are present in the coefficients e_j [cf. (C.17)]. The explicit values of these matrix elements can be read off from Eqs. (A.27) and (A.28), i.e., $\Omega_{6,6}(0) = \Omega_{8,8}(0) = -\frac{4}{5}(nt_0)^{-1}$; $\Omega_{7,7}(0) = -\frac{8}{15}(nt_0)^{-1}$; $\Omega''_{2,2}(0) = -\frac{2}{5}\sigma^2(nt_0)^{-1}$; $\Omega''_{3,3}(0) = -\frac{2}{9}\sigma^2(nt_0)^{-1}$; and $\Omega''_{4,4}(0) = -\frac{2}{15}\sigma^2(nt_0)^{-1}$. The expression for Γ_E given in Eq. (C.20c) can be written in a form similar to that given below Eq. (1.1), i.e.,

$$\Gamma_E = \tfrac{1}{2}(\gamma - 1) D_{\mathrm{TE}} + \tfrac{2}{3}\nu_E + \tfrac{1}{2}\zeta_E / mn \tag{C.21}$$

with ζ_E, the Enskog value of the bulk viscosity, given by

$$\zeta_E = mn^2\chi\left(\tfrac{2}{3}\Omega''_{4,4}(0) - \tfrac{1}{2}\Omega''_{2,2}(0)\right) = \frac{mn\sigma^2}{9t_E} \tag{C.22}$$

The expressions (C.21) and (C.22) follow from (C.20c) using that $w_2 = w_4$ [cf. (C.19)], $e_2^2 = \frac{4}{3}e_4^2$ [cf. (C.17)] and $\Omega_{6,6}(0) = \Omega_{8,8}(0)$ as discussed below (C.20).

We remark that the Boltzmann values of the transport coefficients are obtained from Eq. (C.20) by omitting the higher density (collisional transfer) corrections $\Omega''_{j,j}(0)$ and replacing the coefficients e_j by their low-density limits, i.e., by the first terms in Eq. (C.17).

Next we consider the hydrodynamic modes of the operator $\bar{L}(\mathbf{k})$ which is introduced in Section 3 above Eq. (3.8) and explicitly given by Eq. (B.21). The modes are determined by the eigenvalue equation

$$\bar{L}(\mathbf{k})\bar{\Psi}_j(\mathbf{k},\mathbf{v}) = \bar{z}_j(k)\bar{\Psi}_j(\mathbf{k},\mathbf{v}) \qquad (j = H, \pm, \nu_1, \nu_2) \tag{C.23}$$

for small k, similarly as in (C.1). We will need the equality

$$\langle \varphi_j L(\mathbf{k})\varphi_l \rangle = \langle \varphi_j \bar{L}(\mathbf{k})\varphi_l \rangle \tag{C.24}$$

which holds for all k and $j, l \leqslant 5$; $j = l = 6$; $j = l = 7$; $j = 3, l = 7$; and $j = 4, l = 6$. This follows from Eqs. (B.21) and (3.7). As a consequence of (C.24) the operator $\bar{L}^{(1)}$, which occurs in the expansion $\bar{L}(\mathbf{k}) = \bar{L}(0) + ik\bar{L}^{(1)} + k^2\bar{L}^{(2)} + \cdots$, has the same matrix representation as $L^{(1)}$ which occurs in Eq. (C.2a), i.e., $\bar{L}^{(1)}_{j,l} = L^{(1)}_{j,l}$, for $j, l \leqslant 5$. Therefore, according to the discussion below Eq. (C.8), the eigenfunctions in (C.23) are for $k = 0$ equal to those in (C.1), i.e., $\bar{\Psi}_j(0,\mathbf{v}) = \Psi_j(0,\mathbf{v})$, while for the eigenvalues one has that $\bar{z}_j(k) = z_j(k)$ up to linear order in k.

Also, a left eigenfunction $\bar{\Phi}_j(\mathbf{k},\mathbf{v})$ of $\bar{L}(\mathbf{k})$ is related to a right eigenfunction $\bar{\Psi}_j(\mathbf{k},\mathbf{v})$ in the same way as $\Phi_j(\mathbf{k},\mathbf{v})$ is related to $\Psi_j(\mathbf{k},\mathbf{v})$ in Eq. (2.52). This has been discussed at the end of Appendix B. Thus $\bar{\Phi}_j(0,\mathbf{v}) = \Phi_j(0,\mathbf{v})$. We define the transport coefficients $\bar{\nu}_E, \bar{D}_{\text{TE}}$, and $\bar{\Gamma}_E$ corresponding to $\bar{L}(\mathbf{k})$ in a similar way as in Eqs. (2.38), (2.42), and (2.45), i.e.,

$$\begin{aligned} \bar{z}_{\nu_1}(k) &= \bar{z}_{\nu_2}(k) = \bar{z}_\nu(k) = -\bar{\nu}_E k^2 + \mathcal{O}(k^4) \\ \bar{z}_H(k) &= -\bar{D}_{\text{TE}}k^2 + \mathcal{O}(k^4) \\ \bar{z}_\pm(k) &= \pm ick - \bar{\Gamma}_E k^2 + \mathcal{O}(k^3) \end{aligned} \tag{C.25}$$

Then it follows straightforwardly that $\bar{\nu}_E, \bar{D}_{\text{TE}}$, and $\bar{\Gamma}_E$ are given by expressions similar to (C.13), (C.14), and (C.15), respectively, in which $L(0), L^{(1)}$, and $L^{(2)}$ are replaced by $\bar{L}(0), \bar{L}^{(1)}$, and $\bar{L}^{(2)}$. Next we write

$$P_\perp \bar{L}^{(1)}\varphi_j(\mathbf{v}) = \bar{e}_j J_j(\mathbf{v}) \tag{C.26}$$

similarly as in Eq. (C.16). From Eqs. (B.21), (A.23) (using that $\varphi_2 \sim i\mathbf{k}\cdot\mathbf{v}$) and (3.7) follows that $\bar{e}_3 = e_3$, $\bar{e}_4 = e_4$, and

$$\bar{e}_2 = \frac{2}{(3\beta m)^{1/2}} - \frac{2\sqrt{5}\,n\chi}{5i}\Omega'_{3,7}(0) = \frac{2}{(3\beta m)^{1/2}}\left(1 + \frac{2\pi}{5}n\sigma^3\chi\right) \tag{C.27}$$

We remark that $\bar{e}_2 \neq e_2$ since the relation (C.24) does not apply to the matrix elements $j=2$, $l=8$ on both sides of the equation. Using furthermore a relation similar to (C.18), i.e.,

$$\left\langle J_j \frac{1}{\bar{L}(0)} J_j \right\rangle = \frac{1}{\langle J_j \bar{L}(0) J_j \rangle} \qquad (j=2,3,4) \tag{C.28}$$

which holds since each function J_j is an eigenfunction of $\bar{L}(0)$ [cf. (B.21)] one finds that

$$\bar{\nu}_E = -\frac{e_4^2}{n\chi\Omega_{6,6}(0)} - \frac{1}{2} n\chi\Omega''_{4,4}(0) \tag{C.29a}$$

$$\bar{D}_{\mathrm{TE}} = -\frac{e_3^2}{n\chi\gamma\Omega_{7,7}(0)} - \frac{1}{2\gamma} n\chi\Omega''_{3,3}(0) \tag{C.29b}$$

$$\bar{\Gamma}_E = \frac{1}{2}(\gamma-1)\bar{D}_{\mathrm{TE}} - \frac{\bar{e}_2^2}{2n\chi\Omega_{7,7}(0)} - \frac{1}{4} n\chi\Omega''_{2,2}(0) \tag{C.29c}$$

Here the equality (C.24) has been used for the diagonal matrix elements $j=l=2$, 3, 4, 6, 7 as well as the relation $\langle J_2\bar{L}(0)J_2\rangle = n\chi\Omega_{7,7}(0)$ which follows from the Eqs. (B.21) and (3.7). We remark that $\bar{\nu}_E$ and $\bar{D}_{\mathrm{TE}}$ in (C.29) are equal to ν_E and D_{TE} in (C.20) in "first Enskog approximation," i.e., with w_4 and w_3 in Eq. (C.20) replaced by 1. The quantity $\bar{\Gamma}_E$ in (C.29c) differs in three respects from Γ_E in (C.20c). Firstly in the appearance of w_2 in (C.20c), furthermore $e_2 \neq \bar{e}_2$ [cf. (C.17) and (C.27)] and $\Omega_{8,8}(0) \neq \Omega_{7,7}(0)$ [cf. the discussion below (C.20)]. The origins of these defects are discussed below Eq. (C.27) and in Section 3 below Eq. (3.7). From Eqs. (C.27) and (C.29) follows that $\bar{\Gamma}_E$ is for all densities about 30% larger than Γ_E.

Next we consider the hydrodynamic modes, i.e., the diffusion mode, of the operator $L^s(\mathbf{k})$ which is defined in Eq. (2.6). The Eq. (2.49) for the right and left diffusion mode eigenfunctions to lowest order in k, is an immediate consequence of Eqs. (2.23) and (2.53). An expression for the self-diffusion coefficient D_E which appears in Eq. (2.48) can be derived in a similar manner as described above for ν_E, D_{TE}, and Γ_E. Here we give only the result, i.e.,

$$D_E = -\frac{1}{\beta m}\left\langle \varphi_2 \frac{1}{L^s(0)} \varphi_2 \right\rangle = -\frac{1}{\beta m} \frac{w_s}{\langle \varphi_2 L^s(0) \varphi_2 \rangle} \tag{C.30}$$

where we applied a relation similar to Eq. (C.18) with the quantity w_s, given by $w_s = 1.01896$.[12] Furthermore using in (C.30) that $L^s(0) = n\chi\Lambda^s = \lim_{k\to\infty} n\chi\Lambda_{\mathbf{k}}$, according to Eq. (2.16), one has that

$$D_E = -\frac{1}{\beta m n\chi} \frac{w_s}{\Omega_{2,2}(\infty)} \tag{C.31}$$

where the value of $\Omega_{2,2}(\infty)$ can be read off from (A.27), i.e., $\Omega_{2,2}(\infty) = -\frac{2}{3}(nt_0)^{-1}$. Thus the self-diffusion coefficient is expressed in the matrix element $\Omega_{2,2}$ of $\Lambda_{\mathbf{k}}$ for $k \to \infty$.

Finally we consider the diffusion mode of the operator $\bar{L}^s(\mathbf{k})$ which is introduced in Section 3 below (3.7). The right and left diffusion mode eigenfunctions are equal to 1 to lowest order in k, similarly as in Eq. (2.49). The result for the self-diffusion coefficient $\bar{D}_E$ corresponding to $\bar{L}^s(k)$ is similar to Eq. (C.30) and reads

$$\bar{D}_E = -\frac{1}{\beta m}\left\langle \varphi_2 \frac{1}{\bar{L}^s(0)} \varphi_2 \right\rangle \tag{C.32}$$

Since φ_2 is an exact eigenfunction of $\bar{L}^s(0)$ with eigenvalue $n\chi\Omega_{2,2}(\infty)$ one has

$$\bar{D}_E = -\frac{1}{\beta m n \chi \Omega_{2,2}(\infty)} \tag{C.33}$$

Thus $\bar{D}_E$ is equal to D_E in first Enskog approximation, i.e., with w_s in Eq. (C.31) replaced by 1.

APPENDIX D

We derive Eq. (3.13) from Eq. (3.12) and a few results related to Eq. (3.13).

The first term on the right-hand side of Eq. (3.12) obeys the equation

$$\begin{aligned}\frac{1}{z - f_+(k,\mathbf{v}) - F_+(k)} &= \frac{1}{z - f_+(k,\mathbf{v})} \\ &\quad \times \left\{ 1 + F_+(k)\left[1 + \frac{1}{z - f_+(k,\mathbf{v}) - F_+(k)} F_+(k)\right] \right. \\ &\quad \left. \times \frac{1}{z - f_+(k,\mathbf{v})} \right\}\end{aligned} \tag{D.1}$$

which holds for any function $f_+(k,\mathbf{v})$ and any operator $F_+(k)$. Next we introduce the 3×3 matrix $\mathsf{B}(k,z)$ with matrix elements $B_{j,l}(k,z)$ defined by

$$B_{j,l}(k,z) = \left\langle \varphi_j \frac{1}{z - \bar{L}(\mathbf{k})} \varphi_l \right\rangle \tag{D.2a}$$

$$= \left\langle \varphi_j \frac{1}{z - f_+(k,\mathbf{v}) - F_+(k)} \varphi_l \right\rangle \qquad (j,l \leqslant 3) \tag{D.2b}$$

where in the second step we used Eq. (3.12) and the fact that $P_- \varphi_j = 0$ for $j = 1,2,3$. Using the representation (3.10a) for the 3×3 matrix operator

$F_+(k)$, the identity (D.1) can be written as

$$\frac{1}{z - f_+(k,\mathbf{v}) - F_+(k)} = \frac{1}{z - f_+(k,\mathbf{v})} \times \left\{ 1 + \sum_{j,l=1}^{3} |\varphi_j\rangle \left[\mathsf{F}(k)\{1 + \mathsf{B}(k,z)\mathsf{F}(k)\} \right]_{j,l} \times \langle \varphi_l | \frac{1}{z - f_+(k,\mathbf{v})} \right\} \tag{D.3}$$

where $\mathsf{F}(k)$ denotes the matrix with elements $F_{j,l}(k)$ given by Eq. (3.11a). The matrix $\mathsf{B}(k,z)$ is related to the matrices $\mathsf{A}(k,z)$ defined in Eq. (3.14) and $\mathsf{F}(k)$ by

$$\mathsf{B}(k,z) = \{1 - \mathsf{A}(k,z)\mathsf{F}(k)\}^{-1}\mathsf{A}(k,z) \tag{D.4}$$

This follows by substituting the operator identity $(a+b)^{-1} = a^{-1} - a^{-1}b(a+b)^{-1}$ with $a = z - f_+(k,\mathbf{v})$ and $b = -F_+(k)$ into Eq. (D.2b) and solving the resulting equation for $\mathsf{B}(k,z)$.

From Eq. (D.4) follows that

$$1 + \mathsf{B}(k,z)\mathsf{F}(k) = \{1 - \mathsf{A}(k,z)\mathsf{F}(k)\}^{-1} \tag{D.5}$$

Using this result in Eq. (D.3) one sees that the first terms on the right-hand sides of Eqs. (3.12) and (3.13) are equal. In a completely similar manner one proves that the second terms on the right-hand sides of Eqs. (3.12) and (3.13) are equal. We remark that for this case the matrices corresponding to $\mathsf{A}(k,z)$, $\mathsf{B}(k,z)$, and $\mathsf{F}(k)$ are diagonal. This is a consequence of Eqs. (3.10b), (B.23) and the symmetry in v_x and v_y of the functions φ_4 and φ_5, cf. (2.27), (2.28). This completes the derivation of Eq. (3.13) from Eq. (3.12).

The coherent scattering function $S_E(k,\omega)$ given by Eq. (3.33a) can be written in view of Eq. (D.2a) as

$$S_E(k,\omega) = \frac{1}{\pi} S(k) \operatorname{Re} B_{1,1}(k, i\omega) \tag{D.6}$$

Therefore, using Eq. (D.4) for $\mathsf{B}(k,z)$ and the definition (3.17) for $\mathsf{H}(k,z)$ and $D(k,z)$ one finds that

$$S_E(k,\omega) = \frac{1}{\pi} S(k) \operatorname{Re} \frac{1}{D(k,i\omega)} \left[\mathsf{H}(k,i\omega)\mathsf{A}(k,i\omega) \right]_{1,1} \tag{D.7}$$

which is the relation (3.36).

The relation (3.34) for the contributions of the collective modes to $S_E(k,\omega)$ is derived as follows. First one substitutes Eq. (3.21) into the relation (2.1) for $F_E(k,t)$ with $L(\mathbf{k})$ replaced by $\bar{L}(\mathbf{k})$. Then for $t \geqslant 0$

$$F_E(k,t) = S(k) \sum_{j=H,\pm} e^{z_j(k)t} M_j(k) \tag{D.8}$$

where with the definition (3.14) for $\mathsf{A}(k,z)$

$$M_j(k) = \left\{ \frac{1}{D'(k,z)} \left[\mathsf{A}(k,z)\mathsf{F}(k)\mathsf{H}(k,z)\mathsf{A}(k,z) \right]_{1,1} \right\}_{z=z_j(k)} \tag{D.9}$$

Since from Eq. (3.17) follows that

$$D(k,z)\mathsf{1} = (\mathsf{1} - \mathsf{A}(k,z)\mathsf{F}(k))\mathsf{H}(k,z) \tag{D.10}$$

and by definition $D(k,z) = 0$ for $z = z_j(k)$ one has $\mathsf{AFH} = \mathsf{H}$ for $z = z_j(k)$ and

$$M_j(k) = \left\{ \frac{1}{D'(k,z)} \left[\mathsf{H}(k,z)\mathsf{A}(k,z) \right]_{1,1} \right\}_{z=z_j(k)} \tag{D.11}$$

The results (3.34) and (3.35) follow from (D.8) and (D.11) and the fact that $F_E(k,t)$ is symmetric in t.

We remark that the coefficients $M_j(k)$ can also be expressed in terms of right and left eigenfunctions of $\bar{L}(k)$ as $M_j(k) = \langle \bar{\Psi}_j(\mathbf{k},\mathbf{v}) \rangle \langle \bar{\Phi}_j^*(\mathbf{k},\mathbf{v}) \rangle$. This follows from Eqs. (2.1), (2.29), and (D.8). For $k \to 0$ one has that $M_H(0) = 1 - 1/\gamma$ and $M_\pm(0) = 1/2\gamma$, from Eqs. (2.39), (2.40), (2.43), and (2.44) and the thermodynamic relation $S(0) = \gamma(\beta mc^2)^{-1}$. These results have been used in Section 3 under Eq. (3.36).

For larger values of k the representation (D.11) for $M_j(k)$ is more convenient since it avoids the diagonalization procedure discussed below Eq. (3.21).

Finally we express the functions $A_{j,l}(k,z)$ with $j, l \leqslant 3$ defined in Eq. (3.14) and the function $A_\nu(k,z)$ defined in Eq. (3.15) in terms of the plasma dispersion function $Z(z)$ defined in Eq. (3.16). From Eqs. (3.14) and (3.15) one has that

$$A_{j,l}(k,z) = \frac{i(\beta m/2)^{1/2}}{k + in\chi(\beta m)^{1/2} g_+(k)} \cdot \frac{-1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} dx \, \frac{e^{-x^2} a_{j,l}(x)}{x - iy(k,z)} \tag{D.12}$$

and

$$A_\nu(k,z) = \frac{i(\beta m/2)^{1/2}}{k + in\chi(\beta m)^{1/2} g_-(k)} \cdot \frac{-1}{\sqrt{\pi}} \int_{\infty}^{\infty} dx \, \frac{e^{-x^2}}{x - iy_\nu(k,z)} \tag{D.13}$$

Here the integration variable $x = (\beta m/2)^{1/2} v_z$ is proportional to $v_z = \mathbf{v} \cdot \hat{\mathbf{k}}$

and

$$y(k,z) = (\beta m/2)^{1/2} \frac{z - n\chi h_+(k)}{k + in\chi(\beta m)^{1/2} g_+(k)} \tag{D.14}$$

$$y_\nu(k,z) = (\beta m/2)^{1/2} \frac{z - n\chi h_-(k)}{k + in\chi(\beta m)^{1/2} g_-(k)} \tag{D.15}$$

are functions of k and z. The quantities $a_{j,l}(x)$ in (D.12) result from the integrations over v_x and v_y in Eq. (3.14). They are, using Eqs. (2.24)–(2.28)

$$\begin{aligned}
a_{1,1}(x) &= 1 \\
a_{1,2}(x) &= a_{2,1}(x) = \sqrt{2}\, x \\
a_{2,2}(x) &= 2x^2 \\
a_{1,3}(x) &= a_{3,1}(x) = \tfrac{1}{6}\sqrt{6}\,(2x^2 - 1) \\
a_{2,3}(x) &= a_{3,2}(x) = \tfrac{1}{3}\sqrt{3}\, x(2x^2 - 1) \\
a_{3,3}(x) &= \tfrac{1}{6}(5 - 4x^2 + 4x^4)
\end{aligned} \tag{D.16}$$

With these expressions and the definition (3.16) for $Z(z)$, one finds the following results

$$A_\nu(k,z) = \frac{-i(\beta m)^{1/2}}{k + in\chi(\beta m)^{1/2} g_-(k)} Z(iy_\nu(k,z)) \tag{D.17}$$

and

$$\begin{aligned}
A_{1,1}(k,z) &= \frac{-i(\beta m/2)^{1/2}}{k + in\chi(\beta m)^{1/2} g_+(k)} Z(iy(k,z)) \\
A_{1,2}(k,z) &= A_{2,1}(k,z) = \frac{-i(\beta m/2)^{1/2}}{k + in\chi(\beta m)^{1/2} g_+(k)} + \sqrt{2}\, iy(k,z) A_{1,1}(k,z) \\
A_{2,2}(k,z) &= i\sqrt{2}\; y(k,z) A_{1,2}(k,z) \\
A_{1,3}(k,z) &= A_{3,1}(k,z) = \tfrac{1}{6}\sqrt{6}\,\{A_{2,2}(k,z) - A_{1,1}(k,z)\} \\
A_{2,3}(k,z) &= A_{3,2}(k,z) = i\sqrt{2}\; y(k,z) A_{1,3}(k,z) \\
A_{3,3}(k,z) &= \tfrac{5}{6} A_{1,1}(k,z) - \tfrac{1}{6} A_{2,2}(k,z) + \tfrac{1}{3}\sqrt{3}\, iy(k,z) A_{2,3}(k,z)
\end{aligned} \tag{D.18}$$

These equations are used in order to calculate the quantities $D(k,z)$ and $\mathsf{H}(k,z)$ in Eq. (3.17).

Expressions for the functions $A_{jl}^{s}(k,z)$ defined in Eq. (3.27a) and $A_{\nu}^{s}(k,z)$ defined in Eq. (3.27b) are obtained from the equations (D.14), (D.15), (D.17), (D.18) when one replaces everywhere $h_+(k)$ by $h_+(\infty)$, $h_-(k)$ by $h_-(\infty)$, and $g_\pm(k)$ by $g_\pm(\infty) = 0$, respectively.

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