PHYSICAL REVIEW A VOLUME 19, NUMBER 3 MARCH 1979

Statistical mechanics of stationary states. II. Applications to low-density systems

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(Received 7 August 1978)

The singlet distribution function (SDF) and the first two sum rules of the dynamic structure factor in low-density simple fluids are computed using the formalism developed in the first paper in this series. It is shown that the correlation-function expression for the SDF reduces to the Chapman-Enskog and Choh-Uhlenbeck forms in the low-density regime. The leading density dependence of the sum rules in nonequilibrium stationary states (NESS), with and without convection is given, and explicit forms for "Maxwell molecules" are computed. The results clearly show that local-equilibrium theories yield incomplete results for the sum rules in the small-wave-vector regime. The fact that time-reversal symmetry is broken in NESS yields the new result that the first sum rule is nonzero even in the absence of convection. Lastly, the validity of the separation of time-scale assumption used in the formal analysis is examined.

I. INTRODUCTION

The purpose of this article is to implement (and supplement) the formal theory presented in our previous paper[1] (hereafter denoted as I). The implementation includes two topics of considerable experimental importance. The first is the nonequilibrium singlet distribution function and the second is sum rules for the nonequilibrium steady-state (NESS) dynamical structure factor. Furthermore, we supplement the theory presented in I by examining at low densities the separation of time-scales assumption used in the derivations presented in I.

The singlet distribution function (SDF) has been a center of research activity for the last hundred years.[2] The solutions of the Boltzmann equation (or the generalized one) furnish expressions for the SDF in low-density systems. The well-known Chapman-Enskog procedure gives the lowest order in density solution, whereas the first-order correction has been obtained by Choh and Uhlenbeck. A density expansion of the solution to the BBGKY (Bogolyubov, Born, Green, Kirkwood, Yvon) hierarchy of equations was performed by Ernst, Dorfman and Cohen[3] thereby obtaining explicit expressions to various orders of the density.

We show here that the formal theory of I may be used to obtain a time-correlation function expression for the SDF that has no obvious density restrictions. We verify that the low-density form of this general expression is identical to the Chapman-Enskog and Choh-Uhlenbeck expressions.

The singlet velocity distribution function in a simple heat-conducting NESS was measured and reported recently by Baas *et al.*[4] We demonstrate that our theory agrees, in the appropriate density regime, with their experimental results.

The second topic considered here is the lower-order sum rules of the dynamical structure factor,[5] for systems at low density. The sum rules of the dynamical structure factor are measurable in radiation-scattering experiments. We consider them here mainly to demonstrate explicitly the new symmetry properties of the structure factor that were found formally in I. We calculate the explicit forms of the zeroth and first sum rule at low density for molecular systems with a simple repulsive interaction, and obtain an estimate of the new terms in the sum rule. This estimate can be taken as a measure of the importance of the new term in the spectrum of (say) light scattered from the NESS. We find important differences from the prediction of local equilibrium theories. In the small-wave-vector regime we find that the first sum rule, which vanishes in local equilibrium, depends on the wave vector as $1/k^2$, which is an indication of long-range order, as is discussed in detail in the companion paper. This result is valid when k is smaller than the inverse mean free path λ, i.e., $k\lambda \ll 1$, and when k is larger than the wave vector which characterizes the macroscopic gradients in the system.

The analysis of the structure factor at low density has another motivation, in that the very important assumption of the separation of time scales between the quantities $\langle B(\vec{r})C(\vec{r}\,')\underline{I}_T(-\tau)\rangle$ and $\underline{K}^{-1}(\vec{r}_1|\vec{r}_2;\tau)$ that is implied by the transition between Eqs. (2.21) and (2.23) in paper I may be checked. We obtain here an estimate of the relaxation time of $\langle B(\vec{r})C(\vec{r}\,')\underline{I}_T(-\tau)\rangle$ and show what are the conditions that guarantee the needed separation of time scales.

The organization of this paper is as follows: In Sec. II we treat the SDF. We consider it in nonequilibrium states with temperature gradient and velocity field and show in each case how at low densities our theory reduces to previous well-known results. Section III introduces the sum rules of the dynamical structure factor. We discuss the various new contributions to the sum rules and set the stage for their explicit calculation at low densities. In Sec. IV we perform the density expansion of the sum rules. To this end, we introduce a binary-collision expansion of the resolvent operator and resum the resulting series to obtain an explicit result in terms of the linearized Boltzmann collision operator that is valid to lowest order in the density. In Sec. V we work out the resulting classical scattering problem for the case of Maxwell molecules. We find a final result which is extremely simple and fulfills all the formal properties predicted in I. Section VI is devoted to the question of separation of time scales. A slight variation of the density expansion technique is used to obtain the time-domain representation of $\langle N_{\vec{k}\omega} N_{-\vec{k}} \underline{I}_T(-\tau)\rangle$. Section VII contains a summary and concluding remarks.

II. SINGLET DISTRIBUTION FUNCTION

A. Correlation function expression for the SDF

The generic singlet distribution function (SDF) $f(\vec{r},\vec{p};t)$ is defined by[2]

$$f(\vec{r},\vec{p};t)d\vec{r}\,d\vec{p} = \text{Prob}\left[\begin{array}{l}\textit{any}\text{ particle is found}\\ \text{within a volume } d\vec{r} \text{ around}\\ \vec{r} \text{ and } d\vec{p} \text{ around } \vec{p},\ \text{at time } t\end{array}\right]. \tag{2.1}$$

At equilibrium,

$$f_{\text{eq}}(\vec{r},\vec{p}) = \langle N\delta(\vec{r}-\vec{r}_1)\delta(\vec{p}-\vec{p}_1)\rangle\,, \tag{2.2}$$

where the choice of ensemble is unimportant for the SDF. The nonequilibrium SDF is given by the nonequilibrium average of the same quantity,

$$f(\vec{r},\vec{p};t) = \langle N\delta(\vec{r}-\vec{r}_1(t))\,\delta(\vec{p}-\vec{p}_1(t))\rangle_{\text{NE}}\ . \tag{2.3}$$

As was discussed in I Sec. III, the nonequilibrium average can be written as

$$\begin{aligned}\langle N\delta(\vec{r}-\vec{r}_1(t))\,\delta(\vec{p}-\vec{p}_1(t))\rangle_{\text{NE}} &= \langle N\delta(\vec{r}-\vec{r}_1)\delta(\vec{p}-\vec{p}_1)\rangle_L(t)\\ &\quad -\int_0^\infty d\tau\,\langle N\delta(\vec{r}-\vec{r}_1)\delta(\vec{p}-\vec{p}_1)\\ &\qquad\times \underline{I}(\vec{r}\,',-\tau)\rangle_L(t) * \vec{\nabla}\beta\underline{\Phi}(\vec{r}\,',t)\,.\end{aligned} \tag{2.4}$$

As was done in Sec. IV of I [cf. Eq. (4.10)] this expression may be expanded into a functional Taylor series, finally yielding an expression which is a local function of the $\beta\underline{\Phi}(\vec{r},t)$. The result is, to first order in gradients of $\underline{\Phi}$,

$$\begin{aligned}\langle N\delta(\vec{r}-\vec{r}_1(t))\,\delta(\vec{p}-\vec{p}_1(t))\rangle_{\text{NE}} &= \langle N\delta(\vec{r}-\vec{r}_1)\delta(\vec{p}-\vec{p}_1)\rangle_{\text{hom}}(\vec{r},t)\\ &\quad + \langle N\delta(\vec{r}-\vec{r}_1)\delta(\vec{p}-\vec{p}_1)\underline{\hat{A}}(\vec{r}\,')\rangle_{\text{hom}}(\vec{r},t) * (\vec{r}\,'-\vec{r})\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r},t)\\ &\quad - \int_0^\infty d\tau\,\langle N\delta(\vec{r}-\vec{r}_1)\delta(\vec{p}-\vec{p}_1)\underline{I}_T(-\tau)\rangle_{\text{hom}}(\vec{r},t)\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r},t)\,,\end{aligned} \tag{2.5}$$

where the symbol $\langle\ \rangle_{\text{hom}}(\vec{r},t)$ denotes an average in a uniform equilibrium system in which $\beta\underline{\Phi} = \beta\underline{\Phi}(\vec{r},t)$.

It is easy to see that the second term on the right-hand side of Eq. (2.5) vanishes when the A's are hydrodynamic variable densities. Since the average is taken over a uniform system its dependence on $\vec{r}\,'$ is via $|\vec{r}-\vec{r}\,'|$ only. Thus the implicit integral over all $\vec{r}\,'$ yields zero. We can then rewrite Eq. (2.5) as

$$\langle N\delta(\vec{r}-\vec{r}_1(t))\,\delta(\vec{p}-\vec{p}_1(t))\rangle_{\text{NE}} = f_L(\vec{r},\vec{p},t) - \int_0^\infty d\tau\,\langle N\delta(\vec{r}-\vec{r}_1)\delta(\vec{p}-\vec{p}_1)\underline{I}_T(-\tau)\rangle_{\text{hom}}(\vec{r},t)\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r},t)\,, \tag{2.6}$$

where

$$f_L(\vec{r},\vec{p},t) \equiv \rho(\vec{r},t)\phi(\vec{p}-m\vec{v}(\vec{r},t))_{T=T(\vec{r},t)}\,. \tag{2.7}$$

The quantity $f_L(\vec{r},\vec{p},t)$ is the usual local-equilibrium form of the SDF. The singlet momentum distribution function $\phi(\vec{p})$ is given by

$$\phi(\vec{p}) \equiv (2\pi m k_B T)^{-3/2}[\exp(-p^2/2mk_BT)] \tag{2.8}$$

and we have used the fact that

$$\langle N\delta(\vec{r}-\vec{r}_1)\delta(\vec{p}-\vec{p}_1)\rangle_{\vec{v}} = \rho\phi(\vec{p}-m\vec{v})\,, \tag{2.9}$$

where the subscript $\vec{v}$ denotes an average in a system moving with velocity $\vec{v}$.

The second term on the right-hand side of Eq. (2.6) is the subject of the rest of this section. We will examine the contributions which arise in systems which are linearly displaced from equilibrium due to gradients in temperature and velocity.

Thus we drop the notation $\langle\ \rangle_{\mathrm{hom}}(\vec{r}, t)$ from the dissipative correlation function appearing in Eq. (2.6). We shall carry out the calculations for these terms in the canonical ensemble.

B. Dissipative term in the SDF

The integral in the dissipative term in Eq. (2.6) is

$$\underline{D} \equiv N \int_0^\infty \langle \delta(\vec{r} - \vec{r}_1)\delta(\vec{p} - \vec{p}_1)\underline{I}_T(-\tau)\rangle\, d\tau$$

$$= \rho \int_0^\infty \langle \delta(\vec{p} - \vec{p}_1)\underline{I}_T(-\tau)\rangle\, d\tau , \tag{2.10}$$

where the second equality follows from translational invariance.

Introducing the propagator $G_N(t) \equiv e^{iLt}$, where iL is the N-particle Liouville operator, we can rewrite Eq. (2.10) in the form

$$\underline{D} = \rho \int_0^\infty \langle \delta(\vec{p} - \vec{p}_1) G_N(-\tau)\underline{I}_T\rangle\, d\tau$$

$$= \lim_{s\to 0^+} \lim_{\substack{N,V\to\infty \\ N/V \text{ fixed}}} \rho \int_0^\infty \langle \delta(\vec{p} - \vec{p}_1) G_N(-\tau)\underline{I}_T\rangle e^{-s\tau}\, d\tau$$

$$= \lim_{s\to 0^+} \lim_{\substack{N,V\to\infty \\ N/V \text{ fixed}}} \rho\langle \delta(\vec{p} - \vec{p}_1)\tilde{G}_N(s)\underline{I}_T\rangle , \tag{2.11}$$

where we have used the usual method[6] to obtain the resolvent operator

$$\tilde{G}_N(s) \equiv 1/(s + iL) . \tag{2.12}$$

We proceed by using the notation of Hamer and Oppenheim,[7] and rewrite Eq. (2.11) as

$$\underline{D} = \rho \int d\vec{p}_1\, \delta(\vec{p} - \vec{p}_1)\phi(\vec{p}_1)\underline{Y}(\vec{p}_1, \rho) = \rho\phi(\vec{p})\underline{Y}(\vec{p}, \rho) , \tag{2.13}$$

where

$$\underline{Y}(\vec{p}_1, \rho) \equiv \lim_{s\to 0^+} \lim_{\substack{N,V\to\infty \\ N/V \text{ fixed}}} \int d\vec{p}^{\,N-1} \times \prod_{j=2}^{N} \phi(\vec{p}_j) V^N (\vec{0}\,|\,\rho^N \tilde{G}_N(s)\underline{I}_T\,|\,\vec{0}) , \tag{2.14}$$

ρ^N is the N-particle coordinate space distribution function, and

$$(\vec{q}^{\,N}|\,O\,|\vec{q}^{\,\prime N}) \equiv \frac{1}{V^N} \int d\vec{r}^{\,N} e^{-i\vec{q}^{\,N}\cdot\vec{r}^{\,N}} O\, e^{i\vec{q}^{\,\prime N}\cdot\vec{r}^{\,N}} , \tag{2.15}$$

for an arbitrary operator O.

In Ref. 7, it is shown that $\rho\underline{Y}(\vec{p}_1, \rho)$ can be density expanded to yield

$$\rho\underline{Y}(\vec{p}_1, \rho) = \underline{Y}^{(0)}(\vec{p}_1) + \rho\underline{Y}^{(1)}(\vec{p}_1) + \cdots , \tag{2.16}$$

where, for repulsive forces, $\underline{Y}^{(0)}$ and $\underline{Y}^{(1)}$ are solutions to the appropriate integral equations (depending on $\underline{I}_T$) of the Chapman-Enskog and Choh-Uhlenbeck form, respectively. For attractive potentials, the integral equation for $\underline{Y}^{(0)}$ remains the same and the integral equation for $\underline{Y}^{(1)}$ is modified.[7]

The contributions to the dissipative term in Eq. (2.6) arise from temperature gradients and velocity gradients. In order to make contact with previous work we rewrite this term in the form

$$-\int_0^\infty d\tau \langle N\delta(\vec{r} - \vec{r}_1)\delta(\vec{p} - \vec{p}_1)\underline{I}_T(-\tau)\rangle \cdot \vec{\nabla}\beta\underline{\Phi}(\vec{r}, t)$$

$$= \rho \lim_{s\to 0^+} \lim_{\substack{N,V\to\infty \\ N/V \text{ fixed}}} \{\langle \delta(\vec{p} - \vec{p}_1)\tilde{G}_N(s)\vec{I}_{E,T}\rangle \cdot \nabla\beta(\vec{r}, t) - \langle \delta(\vec{p} - \vec{p}_1)\tilde{G}_N(s)[\overleftrightarrow{\tau} - \tfrac{1}{3}\,\mathrm{Tr}(\overleftrightarrow{\tau})\overleftrightarrow{1}]\rangle : \vec{\nabla}\beta\vec{v}(\vec{r}, t)$$

$$- \left\langle \delta(\vec{p} - \vec{p}_1)\tilde{G}_N(s)\left[\tfrac{1}{3}\,\mathrm{Tr}(\overleftrightarrow{\tau}) - \tfrac{1}{3}\langle \mathrm{Tr}\overleftrightarrow{\tau}\rangle - \left(\frac{\partial p}{\partial \rho}\right)_e \hat{N} + \left(\frac{\partial p}{\partial e}\right)_\rho \hat{E}\right]\right\rangle \vec{\nabla}\cdot\beta\vec{v}(\vec{r}, t)$$

$$= \vec{D}_E \cdot \vec{\nabla}\beta(\vec{r}, t) - \overset{\circ}{\overleftrightarrow{D}}_p : \vec{\nabla}\beta\vec{v}(\vec{r}, t) - \tfrac{1}{3}\,\mathrm{Tr}\overleftrightarrow{D}_p \vec{\nabla}\cdot\beta\vec{v}(\vec{r}, t) , \tag{2.17}$$

where in the second equality we used the explicit form of $\overleftrightarrow{I}_p$ and where the D's are defined by Eq. (2.11). Here $\overset{\circ}{\overleftrightarrow{D}}_p$ is the traceless part of $\overleftrightarrow{D}_p$.

We adopt the conventional notation[2]

$$\vec{Y}_E^{(0)}(\vec{p}) \equiv k_B T \vec{A}^{(0)}(\vec{p}) . \tag{2.18}$$

It was shown in Ref. 7, Eq. (2.3), that

$$\mathfrak{L}\vec{A}^{(0)} = -\left(\frac{p^2}{2mk_BT} - \frac{5}{2}\right)\frac{\vec{p}}{m} , \tag{2.19}$$

where the linearized Boltzmann collision operator is defined by

$$\mathfrak{L}B(\vec{p}_1) \equiv -\int d\vec{p}_2 \int_0^\infty b\, db \int_0^{2\pi} d\psi\, \phi(\vec{p}_2)\, \frac{|\vec{p}_1 - \vec{p}_2|}{m} \times \{B(\vec{p}_1) + B(\vec{p}_2) - B(\vec{p}_1^{\,*}) - B(\vec{p}_2^{\,*})\} , \tag{2.20}$$

where $B(\vec{p})$ is any function of $\vec{p}$, b is the impact parameter, ψ is the azimuthal angle and the superscript $*$ denotes the value of the quantity before the (12) collision which gives final momenta $\vec{p}_1$ and $\vec{p}_2$. Note that the operator $\mathcal{L}$ defined here differs from that in Ref. 7. There is an unimportant difference in sign and in the location of $\phi(\vec{p}_2)$ in the two operators.

Again, we use the conventional notation[2]

$$\overleftrightarrow{Y}_p^{(0)}(\vec{p}) \equiv k_B T \overleftrightarrow{B}^{(0)}(\vec{p}), \tag{2.21}$$

and find from Eq. (2.21) of Ref. 7 that

$$\mathcal{L}\overleftrightarrow{B}^{(0)}(\vec{p}) = -\left(\frac{\vec{p}\,\vec{p}}{mk_BT} - \frac{p^2}{3mk_BT}\overleftrightarrow{1}\right). \tag{2.22}$$

Finally, we find that

$$\mathrm{Tr}\overleftrightarrow{Y}_p^{(0)} = 0 \tag{2.23}$$

(see p. 224 of Ref. 7).

Combining the results of Eqs. (2.2), (2.6), (2.17), (2.21), and (2.23), we find

$$\begin{aligned} f(\vec{r},\vec{p},t) = {} & f_L(\vec{r},\vec{p},t) \\ & + f_{\mathrm{eq}}(\vec{r},\vec{p})\left(\frac{\vec{A}^{(0)}(\vec{p})}{\rho}\cdot\vec{\nabla}\ln T(\vec{r},t)\right. \\ & \left. + \frac{\overleftrightarrow{B}^{(0)}(\vec{p})}{\rho} : \vec{\nabla}\vec{v}(\vec{r},t)\right), \end{aligned} \tag{2.24}$$

which is valid to lowest order in density and to linear order in deviations from equilibrium. The extension to all orders in $\underline{\Phi}$ and linear order in $\vec{\nabla}\beta\underline{\Phi}$ is discussed in Ref. 7. The results are

$$\begin{aligned} f(\vec{r},\vec{p},t) = {} & f_L(\vec{r},\vec{p},t) \\ & \times\left(1 + \frac{\vec{A}^{(0)}(\vec{p}-m\vec{v}(\vec{r},t))\,\vec{\nabla}\ln T(\vec{r},t)}{\rho(\vec{r},t)}\right. \\ & \left. + \frac{\overleftrightarrow{B}^{(0)}(\vec{p}-m\vec{v}(\vec{r},t))}{\rho(\vec{r},t)} : \vec{\nabla}\vec{v}(\vec{r},t)\right), \end{aligned} \tag{2.25}$$

which is valid to lowest order in density and linear order in $\vec{\nabla}\beta\underline{\Phi}$. In this expression, the temperatures which appear in Eqs. (2.19) and (2.22) must be replaced by $T(\vec{r},t)$. Equation (2.25) is the Chapman-Enskog form for $f(\vec{r},\vec{p},t)$.

The extension of Eq. (2.25) to next order in the density is readily carried out using Ref. 7. For repulsive forces, the results are in agreement with Choh and Uhlenbeck. For attractive forces, with bound states, the integral equations for $\vec{Y}^{(1)}$ are given in Ref. 7.

As mentioned in the Introduction, the SDF has been measured recently for a heat-conducting stationary state by Baas *et al.*[4] They report very good agreement with the form of Eq. (2.25) in the absence of a velocity field.

In summary, we have shown in this section that our correlation-function expression for the SDF reduces to the usual kinetic theory expressions at low density. We have demonstrated this explicitly for the Chapman-Enskog solution and indicated how the usual Choh-Uhlenbeck corrections appear. It should be stressed that the correlation-function method is not restricted to the low-density regime and thus our result for the SDF does not have apparent density limitations.

III. DYNAMIC STRUCTURE FACTOR: SUM RULES

We now turn to considerations of the dynamic structure factor in stationary nonequilibrium systems. As was mentioned in the Introduction, this is an experimentally measurable quantity and plays a major role in the scattering of light, neutrons, etc. from fluid systems.[5]

As was shown in I, the dynamic structure factor can be written

$$S_{\vec{k}\omega}(\vec{r}) = S_{\vec{k}\omega}^{\mathrm{hom}}(\vec{r}) + S_{\vec{k}\omega}^{nl}(\vec{r}) + W_{\vec{k}\omega}(\vec{r}), \tag{3.1}$$

where the various terms in the above expression were defined in Eqs. (4.19a)–(4.19c) of paper I. As was discussed in paper I, the first term is just an equilibrium dynamic structure factor in a uniform system where $\beta\underline{\Phi} = \beta\underline{\Phi}(\vec{r})$. The second term is a nonlocality correction to the first term and has the same ω symmetry.

The last term in Eq. (3.1) does not correspond to any equilibrium like phenomenon, and represents a coupling to the dissipative currents present in our system.

Many of the new features embodied in Eq. (3.1) may be found by studying the sum rules, or moments of $S_{\vec{k}\omega}(\vec{r})$. The jth sum rule is defined by[5]

$$S_{\vec{k}}^{(j)}(\mathrm{r}) \equiv \frac{\mathrm{P}}{2\pi}\int_{-\infty}^{\infty} d\omega\,(i\omega)^j S_{\vec{k}\omega}(\vec{r}), \tag{3.2}$$

$$S_{\vec{k}}^{(j)}(r) \equiv (S_{\vec{k}}^{\mathrm{hom}}(\vec{r}))^{(j)} + (S_{\vec{k}}^{nl}(\vec{r}))^{(j)} + W_{\vec{k}}^{(j)}(\vec{r}), \tag{3.3}$$

where the symbol P denotes the Cauchy principal value of the integral and where each of the three terms on the right-hand side of Eq. (3.3) arises from the sum rule associated with the corresponding term in Eq. (3.1).

Use of the definition of the time Fourier transform and Eqs. (4.19) and (4.15) of paper I yields

$$(S_{\vec{k}}^{\mathrm{hom}}(\vec{r}))^{(j)} = \frac{1}{V}\langle N_{\vec{k}}^{(j)} N_{-\vec{k}}\rangle_{\mathrm{hom}}, \tag{3.4a}$$

$$(S_{\vec{k}}^{nl}(\vec{r}))^{(j)} = \frac{i}{2V}\vec{\nabla}_{\vec{k}}\cdot\left(\frac{\partial\langle N_{\vec{k}}^{(j)} N_{-\vec{k}}\rangle_{\mathrm{hom}}}{\partial\beta\underline{\Phi}(\vec{r})}\right)_{\beta\underline{\Phi}=0}\cdot\vec{\nabla}\beta\underline{\Phi}(\vec{r}), \tag{3.4b}$$

and

$$W_{\vec{k}}^{(j)}(\vec{r}) = -\frac{1}{2V}\int_0^\infty d\tau \langle [N_{\vec{k}}^{(j)} N_{-\vec{k}} + (-1)^j N_{\vec{k}} N_{-\vec{k}}^{(j)}] \times \underline{I}_T(-\tau)\rangle \cdot \vec{\nabla}\beta\underline{\Phi}(\vec{r}). \tag{3.4c}$$

In this last expression,

$$N_{\vec{k}}^{(j)} \equiv \left(\frac{d^j}{dt^j} N_{\vec{k}}(t)\right)_{t=0} \tag{3.5}$$

and only linear deviations from equilibrium are considered.

To this order

$$(S_{\vec{k}}^{\mathrm{hom}}(\vec{r}))^{(j)} = \frac{1}{V}\langle N_{\vec{k}}^{(j)} N_{-\vec{k}}\rangle + \frac{1}{V}\langle N_{\vec{k}}^{(j)} N_{-\vec{k}} \underline{\hat{A}}_T\rangle \cdot \beta\underline{\Phi}(\vec{r}). \tag{3.6}$$

Using equilibrium time-reversal symmetry, it may be directly verified that for even j $(S_{\vec{k}}^{\mathrm{hom}}(\vec{r}))^{(j)}$ is, to linear order, equal to the same equilibrium moment in a system which is uniform, at rest, and has chemical potential and temperature equal to those of the system at point $\vec{r}$. For odd j the first term on the right-hand side of Eq. (3.6) vanishes and only couplings to momentum survive in the second. In fact

$$(S_{\vec{k}}^{\mathrm{hom}}(\vec{r}))^{(2j+1)} = \frac{1}{V}\langle N_{\vec{k}}^{(2j+1)} N_{-\vec{k}} \vec{P}_T\rangle \cdot \beta\vec{v}(\vec{r}). \tag{3.7}$$

In particular, for $j=0$

$$(S_{\vec{k}}^{\mathrm{hom}}(\vec{r}))^{(1)} = \frac{1}{V}\langle N_{\vec{k}} N_{-\vec{k}}\rangle i\vec{k}\cdot\vec{v}(\vec{r}). \tag{3.8}$$

Of course these odd moments vanish in the absence of flow, and are responsible for the Doppler shifts associated with light scattering from moving systems.

From Eq. (3.4b) it follows that

$$\begin{aligned}(S_{\vec{k}}^{nl}(\vec{r}))^{(j)} = \frac{i}{2V}\vec{\nabla}_{\vec{k}} \cdot \Bigg[&\left(\frac{\partial S_{\vec{k},\mathrm{eq}}^{(j)}}{\partial\beta\mu}\right)_{\beta,V} \vec{\nabla}\beta\Phi_N(\vec{r}) \\ &- \left(\frac{\partial S_{\vec{k},\mathrm{eq}}^{(j)}}{\partial\beta}\right)_{\beta\mu,V} \vec{\nabla}\beta\Phi_E(\vec{r}) \\ &+ \langle N_{\vec{k}}^{(j)} N_{-\vec{k}} \vec{P}_T\rangle \cdot \beta\vec{v}(\vec{r})\overleftarrow{\nabla}\Bigg],\end{aligned} \tag{3.9}$$

where $S_{\vec{k},\mathrm{eq}}^{(j)}$ is the equilibrium jth sum rule. The first two terms in Eq. (3.9) vanish for odd j whereas the last is zero for even j. When $j=1$ this last expression becomes

$$\begin{aligned}(S_{\vec{k}}^{nl}(\vec{r}))^{(1)} &= -\frac{1}{2V}\vec{\nabla}_{\vec{k}} \cdot \left(\frac{\vec{k}}{m}\cdot\langle \vec{P}_{\vec{k}} N_{-\vec{k}} \vec{P}_T\rangle \cdot \beta\vec{v}(\vec{r})\overleftarrow{\nabla}\right) \\ &= -\frac{1}{2V}\vec{\nabla}_{\vec{k}} \cdot [\langle N_{\vec{k}} N_{-\vec{k}}\rangle \vec{\nabla}_r(\vec{k}\cdot\vec{v}(\vec{r}))].\end{aligned} \tag{3.10}$$

Noting that $\vec{\nabla}\cdot\vec{v}(\vec{r}) = 0$ in the steady state, and that

$$\frac{1}{V}\langle N_{\vec{k}} N_{-\vec{k}}\rangle = \int d\vec{r}_{12} \exp[i\vec{k}\cdot\vec{r}_{12}]\{\rho^{(2)}(r_{12}) - \rho^2\} + \rho, \quad \vec{k} \neq 0, \tag{3.11}$$

where $\rho^{(2)}(\vec{r})$ is the equilibrium pair distribution function. Equation (3.10) becomes

$$(S_{\vec{k}}^{nl}(\vec{r}))^{(1)} = -\vec{\nabla}(\vec{k}\cdot\vec{v})\cdot\vec{\nabla}_{\vec{k}} \frac{\langle N_{\vec{k}} N_{-\vec{k}}\rangle}{2V}$$

$$(S_{\vec{k}}^{nl}(\vec{r}))^{(1)} = -i\vec{\nabla}\tfrac{1}{2}[\vec{k}\cdot\vec{v}(\vec{r})]\cdot\int d\vec{r}_{12}\exp[i\vec{k}\cdot\vec{r}_{12}] \times \vec{r}_{12}\{\rho^{(2)}(\vec{r}_{12}) - \rho^2\}. \tag{3.12}$$

Since $\rho^{(2)}(\vec{r}_{12}) - \rho^2$ vanishes for $\vec{r}_{12}$ larger than some microscopic correlation length λ_c, we see that the contribution of Eq. (3.12) to the first sum rule is of order $k\lambda_c\rho^2$ and is thus negligible. One may proceed in a manner analogous to that used above to verify that all the contributions of Eq. (3.9) to the lower-order sum rules will be at least of order $\rho^2 k\lambda_c$ and may therefore be neglected. The physical reason for this is that the low moments are characteristics of short-time phenomena and therefore probe only small distances. Thus the effects of the gradients are not felt.

The analysis of the $W_{\vec{k}}^{(j)}(\vec{r})$ does not proceed in the above manner, since they do not correspond to any of the usually studied correlation functions. However, they can be density expanded and this is the subject of Sec. IV.

We may, however, again use symmetry under inversion to show that the contributions of (3.4c) to the various sum rules are the following: when j is even, coupling only to $\vec{I}_E$ need be considered. When j is odd, only the correlations involving $\vec{I}_p$ survive. Thus the analysis of the contributions of Eq. (3.4c) separate naturally to the cases with and without a velocity field. In the next sections we evaluate the contributions to the low sum rules that arise from Eq. (3.4c) for systems at low density.

IV. DENSITY EXPANSION OF $W_{\vec{k}}^{(j)}(\vec{r})$

In this section, we evaluate the moments $W_{\vec{k}}^{(j)}(\vec{r})$ at low density. Since they involve equilibrium time-correlation functions, any of the standard techniques for generating the density expansion may be used. We will use the resummation technique first developed by Zwanzig[6] for the density expansion of the self-diffusion constant.

In what follows, many of the technical details are similar to those appearing in Kawasaki and Oppenheim's[9,12] treatment of the shear viscosity. As will soom become apparent, calculation of all the moments is beyond the scope of this work and thus we restrict ourselves to the first two.

A. Temperature-gradient term

From Eq. (3.4c) we find that

$$W^{(j)}_{\vec{k},E} \equiv \frac{1}{2V}\int_0^\infty d\tau \langle [N^{(j)}_{\vec{k}} N_{-\vec{k}} + (-1)^j N_{\vec{k}} N^{(j)}_{-\vec{k}}] \times \vec{I}_E(-\tau)\rangle \cdot \vec{\nabla}\beta(\vec{r}) . \tag{4.1}$$

For even j this term vanishes by symmetry (cf. Sec. IV of I). Since it contains the equilibrium average of a vector, the term is odd in $\vec{k}$ under inversion. On the other hand, by inspection, it is even in $\vec{k}$ when j is even, and thus must vanish. The contribution to the first sum rule does not vanish. As before we write it in the form

$$\begin{aligned} W^{(1)}_{\vec{k},E}(\vec{r}) &= \frac{i\vec{k}}{Vm} \cdot \int_0^\infty d\tau \langle \vec{P}_{\vec{k}} N_{-\vec{k}} G_N(-\tau)\vec{I}_{T,E}\rangle \cdot \vec{\nabla}\beta(\vec{r}) \\ &= \lim_{s\to 0^+} \frac{i\vec{k}}{mV} \cdot \langle \vec{P}_{\vec{k}} N_{-\vec{k}} \tilde{G}_N(s)\vec{I}_{T,E}\rangle \cdot \vec{\nabla}\beta(\vec{r}) , \end{aligned} \tag{4.2}$$

where again $\tilde{G}_N(s)$ is the resolvent operator defined in Eq. (2.12).

It is to be understood that in Eq. (4.2) and succeeding equations, the thermodynamic limit ($N\to\infty$, $V\to\infty$, N/V fixed) is to be taken before the limit as $s\to 0^+$. Using the fact that the particles are identical, and the definitions of $N_{\vec{k}}$ and $\vec{P}_{\vec{k}}$ gives

$$\begin{aligned} W^{(1)}_{\vec{k},E}(\vec{r}) = \lim_{s\to 0^+} \frac{i\vec{k}}{mV} \cdot [&\langle N\vec{p}_1 \tilde{G}_N(s)\vec{I}_{T,E}\rangle \\ &+ \langle N(N-1)\,\vec{p}_1 e^{i\vec{k}\cdot\vec{r}_{12}} \tilde{G}_N(s)\vec{I}_{T,E}\rangle] \cdot \vec{\nabla}\beta(\vec{r}) . \end{aligned} \tag{4.3}$$

The first term in the last expression vanishes because $N\vec{p}_1$ is equivalent to $\vec{P}_T$ in the average and this is both conserved and orthogonal to $\vec{I}_E$. For $\vec{k}\neq 0$ we may replace the grand canonical average by a canonical one. This gives

$$\begin{aligned} W^{(1)}_{\vec{k},E}(\vec{r}) = \lim_{s\to 0^+} &\frac{i\vec{k}}{m}\rho(N-1) \cdot \int d\vec{r}^N d\vec{p}^N \rho^N(\vec{r}^N) \\ &\times \prod_{j=1}^{N} \phi(\vec{p}_j)[\vec{p}_1 e^{i\vec{k}\cdot\vec{r}_{12}} \tilde{G}_N(s)\vec{I}_{T,E}] \cdot \vec{\nabla}\beta(\vec{r}) , \end{aligned} \tag{4.4}$$

where

$$\rho^N(\vec{r}^N) \equiv e^{-\beta U(\vec{r}^N)} \Big/ \int d\vec{r}^N e^{-\beta U(\vec{r}^N)} . \tag{4.5}$$

In addition, to leading order in the density we may take

$$\vec{I}_{T,E} = \sum_{j=1}^{N} \vec{p}_j/m[p_j^2/m - \tfrac{5}{2}k_B T] . \tag{4.6}$$

As is usually the case the explicit potential terms appear only in the first density correction. Noting that

$$\rho^N(\vec{r}^N) = V^{-N} \sum_{q^N} e^{-i\vec{q}^N\cdot\vec{r}^N} \tilde{\rho}^N(\vec{q}^N) , \tag{4.7}$$

where

$$\begin{gathered} \tilde{\rho}^N(\vec{q}^N) \equiv \int d\vec{r}^N e^{i\vec{q}^N\cdot\vec{r}^N} \rho^N(\vec{r}^N) , \\ \vec{q}_1 + \vec{q}_2 + \cdots + \vec{q}_N = \vec{0} , \end{gathered} \tag{4.8}$$

we find, by using (4.4), that

$$\begin{aligned} W^{(1)}_{\vec{k},E}(\vec{r}) = \lim_{s\to 0^+} &\frac{i\vec{k}\rho(N-1)}{m} \cdot \sum_{q^N} \int d\vec{p}^N \tilde{\rho}^N(\vec{q}^N) \\ &\times \prod_{j=1}^{N} \phi(\vec{p}_j)\vec{p}_1(\vec{q}_1 - \vec{k}, \vec{q}_2 + \vec{k}, \vec{q}^{N-2} | \tilde{G}_N(s) | \vec{0}^N) \\ &\times (1 + \mathcal{P}_{12} + (N-2)\mathcal{P}_{13}) \\ &\times \left[\frac{\vec{p}_1}{m}\left(\frac{p_1^2}{2m} - \tfrac{5}{2}k_B T\right)\right] \cdot \vec{\nabla}\beta(\vec{r}) , \end{aligned} \tag{4.9}$$

where we have used the notation of Eq. (2.15) and introduced the particle exchange operator, $\mathcal{P}_{ij}$ which replaces $\vec{p}_i$ by $\vec{p}_j$.

For convenience we define the operator $\mathcal{G}(s)$, an operator on the momentum space of particle 1, by

$$\begin{aligned} \mathcal{G}(s) \equiv (N-1) &\sum_{\vec{q}^N} \int d\vec{p}^{N-1} \tilde{\rho}^N(\vec{q}^N) \\ &\times \prod_{j=2}^{N} \phi(\vec{p}_j)(\vec{q}_1 - \vec{k}, \vec{q}_2 + \vec{k}, \vec{q}^{N-2} | \tilde{G}_N(s) | \vec{0}^N) \\ &\times [1 + \mathcal{P}_{12} + (N-2)(\mathcal{P}_{13})] , \end{aligned} \tag{4.10}$$

which allows us to rewrite Eq. (4.9) as

$$\begin{aligned} W^{(1)}_{\vec{k},E}(\vec{r}) = \lim_{s\to 0^+} &\frac{\rho i\vec{k}}{m} \cdot \int d\vec{p}_1\, \phi(\vec{p}_1)\vec{p}_1 \mathcal{G}(s) \\ &\times \left[\frac{\vec{p}_1}{m}\left(\frac{p_1^2}{2m} - \frac{5k_B T}{2}\right)\right] \cdot \vec{\nabla}\beta(\vec{r}) . \end{aligned} \tag{4.11}$$

At this point the binary-collision expansion for the resolvent is introduced,[6] that is,

$$\tilde{G}_N(s) = G_0(s) - \sum_{\alpha} G_0 T_\alpha G_0 + \sum_{\alpha,\gamma}{}' G_0 T_\alpha G_0 T_\gamma G_0 - \cdots , \tag{4.12}$$

where the sums are over all possible pairs of particles with the proviso that consecutive identical pairs are forbidden. The reader is referred to Zwanzig[6] for a discussion of the properties of the binary-collision operator and of $G_0(s)$, the free-particle resolvent operator. The important properties of these two operators are as follows:

(i) Any matrix element of T_α, i.e., $(\vec{q}^N | T_\alpha | \vec{q}'^N)$ is proportional to V^{-1} in the thermodynamic limit.

(ii) $(\vec{q}^N|T_{ij}|\vec{q}'^N) \sim \Delta(\vec{q}^{N-2} - \vec{q}'^{N-2})\Delta(\vec{q}_i + \vec{q}_j - \vec{q}_i' - \vec{q}_j')$, where Δ is a multidimensional Kronecker δ function,

(iii) $(\vec{q}^N|G_0|\vec{q}'^N) = g(\vec{q}^N)\Delta(\vec{q}^N - \vec{q}'^N)$, where

$$g(\vec{q}^N) \equiv (s + i\vec{q}^N \cdot \vec{p}^N/m)^{-1}. \tag{4.13}$$

(iv) The following equation holds

$$\mathfrak{L} = -\lim_{s\to 0^+} \int d\vec{p}_3\, \phi(\vec{p}_3)(\vec{0}\,|VT_{13}|\,\vec{0})(1 + \mathcal{P}_{13}), \tag{4.14}$$

where $\mathfrak{L}$ is the linearized Boltzmann collision operator defined in Eq. (2.25).

(v) The matrix elements $(\vec{q}^N|T_{ij}|\vec{q}'^N)$ are operators on the momentum space of particles (ij). They give zero when they act on any quantity conserved in an (ij) collision.

(vi) The following equation holds:

$$T_{ij} = -\theta_{ij} + \theta_{ij}G_0T_{ij} = -\theta_{ij} + T_{ij}G_0\theta_{ij} \tag{4.15a}$$

where

$$\theta_{ij} \equiv -\frac{\partial U(\vec{r}_i - \vec{r}_j)}{\partial(\vec{r}_i - \vec{r}_j)} \cdot \left(\frac{\partial}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_j}\right). \tag{4.15b}$$

Note that property (vi) imples (v). As a final remark, we note that for systems interacting via short-range forces, the leading density dependence of $W^{(1)}_{\vec{k},E}(\mathbf{r})$ can be found by neglecting all statistical correlations. That is,

$$\rho^N(\vec{r}^N) = V^{-N}, \tag{4.16a}$$

or

$$\tilde{\rho}^N(\vec{q}^N) = \Delta(\vec{q}^N). \tag{4.16b}$$

Substituting Eqs. (4.12) and (4.16b) into (4.10) allows us to rewrite the latter as

$$\begin{aligned}\mathcal{G}(s) = \frac{(N-1)}{s} \int d\vec{p}^{N-1} \prod_{j=2}^{N} \phi(\vec{p}_j)\Big(&-(-\vec{k},\vec{k}\,|G_0T_{12}|\,\vec{0})(1+\mathcal{P}_{12}) + (N-2)[(-\vec{k},\vec{k}\,|G_0T_{12}|\,\vec{0})\frac{1}{s}(\vec{0}\,|T_{13}|\,\vec{0})(1+\mathcal{P}_{13})\\ &+(-\vec{k},\vec{k}\,|G_0T_{12}|\,\vec{0})\frac{1}{s}(\vec{0}\,|T_{23}|\,\vec{0})(\mathcal{P}_{12}+\mathcal{P}_{13})\\ &+(-\vec{k},\vec{k},\vec{0}\,|G_0T_{13}|-\vec{k},\vec{k},\vec{0})(-\vec{k},\vec{k}\,|G_0T_{12}|\,\vec{0})(1+\mathcal{P}_{12})\\ &+(-\vec{k},\vec{k},\vec{0}\,|G_0T_{13}|\,\vec{0},\vec{k},-\vec{k})(\vec{0},\vec{k},-\vec{k}\,|G_0T_{23}|\,\vec{0})(\mathcal{P}_{13}+\mathcal{P}_{12})\\ &+(-\vec{k},\vec{k},\vec{0}\,|G_0T_{23}|-\vec{k},\vec{k},\vec{0})(-\vec{k},\vec{k}\,|G_0T_{12}|\,\vec{0})(1+\mathcal{P}_{12})\\ &+(-\vec{k},\vec{k},\vec{0}\,|G_0T_{23}|-\vec{k},\vec{0},\vec{k})(-\vec{k},\vec{0},\vec{k}\,|G_0T_{13}|\,\vec{0})(1+\mathcal{P}_{13}) - \cdots\Big),\end{aligned} \tag{4.17}$$

where we have not written out any of the terms containing more than two T operators or three particles. In obtaining this expression use was made of the conservation rules associated with the T and G_0 operators [cf. properties (ii)–(iii) above] and the fact that the right-most T must involve particles 1, 2, or 3 [this follows from Eqs. (4.15)].

Examining Eq. (4.17) we see that each term diverges as $s \to 0^+$. Further, property (i) shows that a term containing n particles is of order ρ^{n-1} in our expansion of $\mathcal{G}(s)$, in the thermodynamic limit. Special attention must be given to the last four terms appearing in Eq. (4.16). For example, using property (iii) gives

$$\begin{aligned}&\rho^2(-\vec{k},\vec{k},\vec{0}\,|VG_0T_{13}|-\vec{k},\vec{k},\vec{0})\\ &\quad\times(-\vec{k},\vec{k},\,|G_0VT_{12}|\,\vec{0})(1+\mathcal{P}_{12})\\ &\qquad=\rho^2 g_{12}(-\vec{k})(\vec{0}\,|VT_{13}|\,\vec{0})\\ &\qquad\quad\times g_{12}(-\vec{k})(\vec{0}\,|VT_{12}|\,\vec{0})(1+\mathcal{P}_{12}),\end{aligned} \tag{4.18}$$

where for $ka \ll 1$ (a is the range of the potential) we may neglect the k dependence of the T matrix elements and

$$g_{ij}(\vec{k}) \equiv (s + i\vec{k} \cdot (\vec{p}_i - \vec{p}_j)/m)^{-1}. \tag{4.19}$$

Equation (4.18) and (4.19) show that, as $s \to 0^+$, the fourth term in the expansion of $\mathcal{G}(s)$ is roughly speaking $O(\rho^2/sk^2)$. For high k, this is a weaker divergence than the other s^{-1} term in Eq. (4.17). On the other hand, as $k \to 0$ the "strength" of this term increases, and it may be larger than the terms with the same s dependence. In this work we are interested in both the high- and low-k regimes and thus we are forced to keep all the terms which appear in Eq. (4.17).

Let us examine some of the other terms which occur in the binary-collision expansion of $\mathcal{G}(s)$. One of the three T terms is

$$\begin{aligned}\frac{-\rho^2}{s}&(-\vec{\mathrm{k}},\vec{\mathrm{k}}\,|\,VG_0T_{12}G_0VT_{13}G_0T_{12}\,|\,\vec{0})\\ &=-\frac{\rho^2}{s}\,g_{12}(-\vec{\mathrm{k}})\sum_q\frac{1}{V}\,(\vec{0}\,|\,VT_{12}\,|\,\vec{0})g_{12}(\vec{\mathrm{q}}-\vec{\mathrm{k}})\\ &\quad\times(\vec{0}\,|\,VT_{13}\,|\,\vec{0})g_{12}(\vec{\mathrm{q}}-\vec{\mathrm{k}})(\vec{0}\,|\,VT_{12}\,|\,\vec{0})\\ &\sim O(\rho^2/sk),\ \text{as}\ s\to 0^+.\end{aligned}\tag{4.20}$$

This is an example of a correlated collision term. The sum over $\vec{\mathrm{q}}$ "protects" the $g_{12}(\vec{\mathrm{q}}-\vec{\mathrm{k}})$ and a weaker divergence results (see Refs. 6 and 12 for a more detailed discussion). To leading order in density we may thus neglect the correlated collision terms (i.e., terms containing sums over intermediate wave vectors).

A second class of terms is that beginning with a T_{ij} not involving either particle 1 or 2. Using property (iv) and the fact that the kinetic energy is conserved in a completed collision, it follows that these terms have a weaker s divergence than those which begin with 1 or 2 and thus do not contribute to leading order in density.

The remaining terms in the binary-collision expansion of $\mathcal{G}(s)$ contain no intermediate wave-vector sums and begin with a T involving 1 or 2. A given term will factorize into two parts. There will be a series of G_0T matrix elements in which the wave vector $\vec{\mathrm{k}}$ appears on both sides, such as in $(-\vec{\mathrm{k}},\vec{\mathrm{k}},\vec{0}\,|\,G_0T_{13}\,|\,-\vec{\mathrm{k}},\vec{\mathrm{k}},\vec{0})$. Then there will be a factor $(\ldots,\vec{\mathrm{k}},\ldots-\vec{\mathrm{k}}\,|\,G_0T_\alpha\,|\,\vec{0})$ followed by factors involving only $(\vec{0}\,|\,T_{\alpha'}\,|\,\vec{0})$. As was discussed above, for small k, all of these terms are non-negligible. The terms involving k matrix elements are known as "ring collision terms" and have been extensively studied[12] within the context of the long time tails and the logarithmic terms in the density expansion of transport coefficients. The methods used there to resum these terms may be used here. In what will follow we use the method outlined by Kawasaki and Oppenheim.[12]

By introducing the operators $\Lambda_l(i),\Lambda_d(i)$, defined as

$$\Lambda_l(i)A\equiv\int d\vec{\mathrm{p}}_3\,\phi(\vec{\mathrm{p}}_3)VG_0T_{i3}A\tag{4.21}$$

and

$$\Lambda_d(i)A\equiv\int d\vec{\mathrm{p}}_3\,\phi(\vec{\mathrm{p}}_3)VG_0T_{i3}\mathcal{P}_{i3}A\,,\quad i=1,2\,,\tag{4.22}$$

one can show[12] that any term in Eq. (4.17) is equivalent to a term of the form

$$\begin{aligned}\int d\vec{\mathrm{p}}_2\,\phi(\vec{\mathrm{p}}_2)\,&\frac{(-\rho)^{n+n'+1}}{s^{n'+1}}\,(-\vec{\mathrm{k}},\vec{\mathrm{k}}\,|\,\Lambda_{u_1}(\alpha_1)\cdots\\ &\times\Lambda_{u_n}(\alpha_n)VG_0T_{12}\,|\,\vec{0})(1+\mathcal{P}_{12})\\ &\times(\vec{0}\,|\,\Lambda_{v_1}(1)\cdots\Lambda_{v_{n'}}(1)\,|\,\vec{0})\,,\end{aligned}\tag{4.23}$$

where

$u_i, v_i=l$ or d, $i=1,\ldots,n,$ or $1,\ldots,n'$,

$\alpha_i=1$ or 2,

and where the terms with n or $n'=0$ are included (i.e., those without Λ's in either factor). Summing over all possible values of n, n', $\{u\}$, $\{v\}$, and $\{\alpha\}$ gives

$$\begin{aligned}\mathcal{G}(s)=-\rho\int d\vec{\mathrm{p}}_2\,\phi(\vec{\mathrm{p}}_2)&(-\vec{\mathrm{k}},\vec{\mathrm{k}}\,|\,[1+\rho G_0(\Lambda_l(1)+\Lambda_d(1)+\Lambda_l(2)+\Lambda_d(2))]^{-1}VG_0T_{12}\,|\,\vec{0})\\ &\times(1+\mathcal{P}_{12})(\vec{0}\,|\,[s+\rho s(\Lambda_l(1)+\Lambda_d(1))]^{-1}\,|\,\vec{0})\,.\end{aligned}\tag{4.24}$$

Defining a Boltzmann collision operator for particle i by

$$\mathcal{L}_i\equiv\lim_{s\to0^+}-\int d\vec{\mathrm{p}}_3\,\phi(\vec{\mathrm{p}}_3)(\vec{0}\,|\,VT_{i3}\,|\,\vec{0})(1+\mathcal{P}_{i3})\,,\tag{4.25}$$

neglecting the k dependence of the T matrix elements appearing in Eq. (4.24), and using Eqs. (4.21), (4.22), and (4.19) shows that

$$\begin{aligned}\mathcal{G}(s)=-\rho\int d\vec{\mathrm{p}}_2\,\phi(\vec{\mathrm{p}}_2)&\,\frac{1}{s-i\vec{\mathrm{k}}\cdot(\vec{\mathrm{p}}_1-\vec{\mathrm{p}}_2)/m-\rho\mathcal{L}_1-\rho\mathcal{L}_2}\\ &\times(\vec{0}\,|\,VT_{12}\,|\,\vec{0})(1+\mathcal{P}_{12})\frac{1}{s-\rho\mathcal{L}_1}\,.\end{aligned}\tag{4.26}$$

In arriving at this last result, we have used the fact that to leading order in ρ the s dependence of the T matrix elements may be neglected. This corresponds to dropping partially completed collisions, a higher-density correction.

The physical significance of the operator $(s-i\vec{\mathrm{k}}\cdot(\vec{\mathrm{p}}_1-\vec{\mathrm{p}}_2)/m-\rho\mathcal{L}_1+\rho\mathcal{L}_2)^{-1}$ is clear. It is simply a free-particle propagator for particles (1, 2) which is modified by collisions with other fluid particles. As we shall demonstrate below, the appearance of the $\rho\mathcal{L}_1+\rho\mathcal{L}_2$ in this operator accounts for the collisional damping associated with a collective motion of wave vector $\vec{\mathrm{k}}$. For small wave vectors this can be quite important. On the other hand for large k, that is, k greater than the inverse mean free path, the collision terms are unimportant and Eq. (4.26) becomes

$$\mathcal{G}(s)=-\rho\int d\vec{p}_2\,\frac{\phi(\vec{p}_2)}{s-i\vec{k}\cdot(\vec{p}_1-\vec{p}_2)/m}\times(\vec{0}\,|VT_{12}|\,\vec{0})(1+\mathcal{P}_{12})\,\frac{1}{s-\rho\mathcal{L}_1}\,,\qquad k\gg\rho a^2 \tag{4.27}$$

where the correction introduced by neglecting the bath collisions is of higher order in density.

Combining Eqs. (4.26) and (4.11) yields

$$W^{(1)}_{\vec{k},E}=+\frac{\rho i\vec{k}}{m}\cdot\int d\vec{p}_1\,d\vec{p}_2\,\vec{p}_1\phi(\vec{p}_1)\phi(\vec{p}_2)\times\frac{1}{0^+-i\vec{k}\cdot(\vec{p}_1-\vec{p}_2)/m-\rho\mathcal{L}_1-\rho\mathcal{L}_2}\times F_E(\vec{p}_1,\vec{p}_2)\,, \tag{4.28}$$

with

$$F_E(\vec{p}_1,\vec{p}_2)\equiv-\rho(\vec{0}\,|VT_{12}|\,\vec{0})(1+\mathcal{P}_{12})\times\frac{1}{0^+-\rho\mathcal{L}_1}\,\frac{\vec{p}_1}{m}\left(\frac{\vec{p}_1^{\,2}}{2m}-\tfrac{5}{2}k_BT\right)\cdot\vec{\nabla}\beta(\vec{r}) \tag{4.29}$$

and where the $s\to0^+$ limit has been taken. Note that $\vec{I}_E$ is orthogonal to the conserved variables (collisional invariants), and thus $\mathcal{L}_1^{-1}\vec{I}_E$ is well defined. Proceeding in the manner[6,12] used to show Eq. (4.14) one may easily verify that

$$-(\vec{0}\,|VT_{12}|\,\vec{0})(1+\mathcal{P}_{12})f(\vec{p}_1)=-\frac{|\vec{p}_1-\vec{p}_2|}{m}\int_0^\infty b\,db\int_0^{2\pi}d\psi\,[f(\vec{p}_1)+f(\vec{p}_2)-f(\vec{p}_1^{\,*})-f(\vec{p}_2^{\,*})]\,, \tag{4.30}$$

where $f(\vec{p}_1)$ is any function of $\vec{p}_1$ and the notation is as in Eq. (2.25). Using this fact and Eq. (2.19) shows that

$$F_E(\vec{p}_1,\vec{p}_2)=-\left|\frac{\vec{p}_1-\vec{p}_2}{m}\right|k_BT\int_0^\infty b\,db\times\int_0^{2\pi}d\psi\,[\vec{A}^{(0)}(\vec{p}_1)+\vec{A}^{(0)}(\vec{p}_2)-\vec{A}^{(0)}(\vec{p}_1^{\,*})-\vec{A}^{(0)})\,\vec{p}_2^{\,*})]\cdot\vec{\nabla}\beta(\vec{r})\,, \tag{4.31}$$

where $\vec{A}^{(0)}(\vec{p})$ appears in the correction to the SDF in the presence of a termperature gradient. For a given molecular interaction, the functions $\vec{A}^{(0)}(\vec{p})$ can be computed using a variety of techniques. In Sec. V we shall carry this out for Maxwell molecules.

In order to compute the integral appearing in Eq. (4.28) we introduce an auxiliary function, $Q_E(\vec{p}_1,\vec{p}_2)$, which satisfies

$$\left[0^+-i\vec{k}\cdot\left(\frac{\vec{p}_1-\vec{p}_2}{m}\right)-\rho\mathcal{L}_1-\rho\mathcal{L}_2\right]Q_E(\vec{p}_1,\vec{p}_2)=F_E(\vec{p}_1,\vec{p}_2) \tag{4.32}$$

where Q_E also depends on ρ and $\vec{k}$. Postponing the actual solution of Eq. (4.32) for a moment we see that

$$W^{(1)}_{\vec{k},E}=\frac{\rho i\vec{k}}{m}\cdot\int d\vec{p}_1\,d\vec{p}_2\,\phi(\vec{p}_1)\phi(\vec{p}_2)\vec{p}_1Q_E(\vec{p}_1,\vec{p}_2)\,, \tag{4.33}$$

where Eq. (4.28) was used. This shows that once the solution to Eq. (4.32) is known the calculation of the first sum rule in the presence of a temperature gradient reduces to evaluating an integral. Before turning to Eq. (4.32) we analyze the velocity terms.

B. Velocity-gradient terms

The analysis of the $\vec{v}$ terms proceeds along the same lines as the $\vec{\nabla}T$ ones. As was discussed in the preceding section, only even moments arise from the velocity gradients. The contribution to the zeroth sum rule is nontrivial and may be written

$$\begin{aligned}W^{(0)}_{\vec{k},\vec{p}}(\vec{r})&=-\frac{1}{V}\int_0^\infty d\tau\,\langle N_{\vec{k}}N_{-\vec{k}}\overleftrightarrow{I}_{T,\vec{p}}(-\tau)\rangle:(\beta\vec{v}(\vec{r}))\\&=-\rho\lim_{s\to0^+}(N-1)\langle e^{i\vec{k}\cdot\vec{r}_{12}}\tilde{G}_N(s)\overleftrightarrow{I}_{T,\vec{p}}\rangle:\vec{\nabla}\beta\vec{v}(\vec{r})\,,\end{aligned}$$

where we have used particle identity in obtaining the last equality.

As was shown in Sec. II, we may take

$$\overleftrightarrow{I}_{T,\vec{p}}=\sum_j\left(\frac{\vec{p}_j\vec{p}_j}{m}-\frac{p_j^2\overleftrightarrow{1}}{3m}\right) \tag{4.34}$$

at low densities. Proceeding as in the case of the temperature gradient, we find

$$W^{(0)}_{\vec{k},\vec{p}}(\vec{r})=-\rho\lim_{s\to0^+}\int d\vec{p}_1\,\phi(\vec{p}_1)\mathcal{G}(s)\times\left[\frac{\vec{p}_1\vec{p}_1}{m}-\frac{p_1^2\overleftrightarrow{1}}{3m}\right]:\vec{\nabla}\beta\vec{v}(\vec{r})\,. \tag{4.35}$$

Using Eq. (4.27) for $\mathcal{G}(s)$ allows us to rewrite Eq. (4.35) as:

$$W^{(0)}_{\vec{k},\vec{p}}(\vec{r})=-\rho\int d\vec{p}_1\,d\vec{p}_2\,\phi(\vec{p}_1)\phi(\vec{p}_2)\times[0^+-i\vec{k}\cdot(\vec{p}_1-\vec{p}_2)/m-\rho\mathcal{L}_1-\rho\mathcal{L}_2]^{-1}\times F_{\vec{p}}(\vec{p}_1,\vec{p}_2)\,, \tag{4.36}$$

where

$$F_{\vec{P}}(\vec{p}_1,\vec{p}_2)\equiv-\rho(\vec{0}\,|\,T_{12}V\,|\,\vec{0})(1+\mathcal{P}_{12})\frac{1}{0^+-\rho\mathcal{L}_1}\times\left(\frac{\vec{p}_1\vec{p}_1}{m}-\frac{p_1^2}{3m}\overleftrightarrow{1}\right):\vec{\nabla}\beta\vec{v}(\vec{r}) \tag{4.37}$$

$$=-\left|\frac{\vec{p}_1-\vec{p}_2}{m}\right|\int_0^\infty b\,db\times\int_0^\pi d\psi[\overleftrightarrow{B}^{(0)}(\vec{p}_1)+\overleftrightarrow{B}^{(0)}(\vec{p}_2)-\overleftrightarrow{B}^{(0)}(\vec{p}_1^{\,*})-\overleftrightarrow{B}^{(0)}(\vec{p}_2^{\,*})]:\vec{\nabla}\vec{v}(\vec{r}). \tag{4.38}$$

The last equality follows from Eqs. (2.22) and (4.30). Introducing the function $Q_{\vec{P}}(\vec{p}_1,\vec{p}_2)$, defined by

$$(0^+-i\vec{k}\cdot(\vec{p}_1-\vec{p}_2)/m-\rho\mathcal{L}_1-\rho\mathcal{L}_2)Q_{\vec{P}}(\vec{p}_1,\vec{p}_2)=F_{\vec{P}}(\vec{p}_1,\vec{p}_2), \tag{4.39}$$

allows Eq. (4.36) to be reexpressed as

$$W^{(0)}_{\vec{k},\vec{P}}(\vec{r})=-\rho\int d\vec{p}_1\,d\vec{p}_2\,\phi(\vec{p}_1)\phi(\vec{p}_2)Q_{\vec{P}}(\vec{p}_1,\vec{p}_2). \tag{4.40}$$

Again, $Q_{\vec{P}}$ depends on ρ and $\vec{k}$. Thus, as was seen in the case of a temperature gradient, the contribution of the velocity gradient to the zeroth sum rule involves the solution of an inhomogeneous integral equation, Eq. (4.39). Once this is accomplished, the evaluation of the sum rule reduces to performing some integrations.

The remainder of this section is devoted to solving Eqs. (4.32) and (4.39).

C. Functions $Q_\alpha(\vec{p}_1,\vec{p}_2)$

The remaining nontrivial step in obtaining the sum rules is to solve Eqs. (4.32) and (4.39). That is,

$$(s-i\vec{k}\cdot(\vec{p}_1-\vec{p}_2)/m-\rho\mathcal{L}_1-\rho\mathcal{L}_2)Q_\alpha(\vec{p}_1,\vec{p}_2)=F_\alpha(\vec{p}_1,\vec{p}_2),\quad \alpha=E,\vec{P}\ , \tag{4.41}$$

where for a later application, the Laplace transform variable s has been reintroduced. In any of the sum rules, the limit $s\to 0^+$ is to be taken once Eq. (4.41) is solved.

The exact solution of Eq. (4.41) for any k, s, and interaction potential is, if possible, an extremely difficult task. Fortunately, approximate solutions, valid for the high-and low-k regimes, are not too difficult to find. By high- and low-k regimes, we mean those where the streaming or collision terms on the left-hand side of Eq. (4.41) are more important. Roughly speaking, the parameter which determines the regime is $k(k_BT/m)^{1/2}/\rho\lambda$, where λ is one of the nonzero eigenvalues of the linearized Boltzmann collision operator. When k is larger than the inverse mean free path, $k(k_BT/m)^{1/2}/\rho\lambda\gg 1$ and the effect of collisions is small (in fact it is the same size as the higher-density corrections to the sum rules). On the other hand, for k's typically found in light scattering, this parameter is small.

As we shall now show, the size of k determines whether a hydrodynamic (small-k) or kinetic (large-k) behavior is found.

When k is large, the collision terms in Eq. (4.41) can be omitted, and the resulting equation is then trivially solved:

$$Q_\alpha(\vec{p}_1,\vec{p}_2)=(s-i\vec{k}\cdot(\vec{p}_1-\vec{p}_2)/m)^{-1}F_\alpha(\vec{p}_1,\vec{p}_2), \tag{4.42}$$

[cf. Eq. (4.27)]. For a given interaction potential, $F_\alpha(\vec{p}_1,\vec{p}_2)$ can be found [cf. Eqs. (4.31) and (4.39)] and the sum rules computed using Eqs. (4.33), (4.40), and (4.42). This procedure is carried out in Sec. V for Maxwell molecules.

When k is small a different approach is used. We consider the eigenvalue problem.

$$(\tfrac{1}{2}s-i\vec{k}\cdot\vec{p}_1/m-\rho\mathcal{L}_1)\Psi_j(\vec{p}_1)=(\tfrac{1}{2}s+\omega_j)\Psi_j(\vec{p}_1). \tag{4.43}$$

In Appendix A, we show some of the formal properties of the operator $\frac{1}{2}s-i\vec{k}\cdot\vec{p}_1/m-\rho\mathcal{L}_1$. The most important property is that the eigenfunctions $\{\Psi_\alpha\}$ are orthonormal in the sense that

$$\int d\vec{p}_1\,\phi(\vec{p}_1)\Psi_j^*(\vec{p}_1)\Psi_l(\vec{p}_1)=\Delta_{jl}, \tag{4.44}$$

where the symbol $*$ denotes complex conjugation (not to be confused with the value before a collision).

Writing

$$Q_\alpha(\vec{p}_1,\vec{p}_2)=\sum_{j,l}Q_\alpha(j,l)\Psi_j(\vec{p}_1)\Psi_l^*(\vec{p}_2), \tag{4.45}$$

and using Eqs. (4.41), (4.43), (A2), and (4.44) gives

$$(s+\omega_j+\omega_l^*)Q_\alpha(j,l)=\int d\vec{p}_1\,d\vec{p}_2\,\phi(\vec{p}_1)\phi(\vec{p}_2)\times\Psi_j^*(\vec{p}_1)\Psi_l(\vec{p}_2)F_\alpha(\vec{p}_1,\vec{p}_2)\equiv F_\alpha(j,l). \tag{4.46}$$

Thus solving (4.46) for $Q_\alpha(j,l)$ and using Eq. (4.45) yields

$$Q_\alpha(\vec{p}_1,\vec{p}_2)=\sum_{j,l}\frac{F_\alpha(j,l)}{s+\omega_j+\omega_l^*}\Psi_j(\vec{p}_1)\Psi_l^*(\vec{p}_2) \tag{4.47}$$

which may be used in either of Eqs. (4.33) or (4.40) to compute the appropriate contribution to the sum rules.

While being an exact result, Eq. (4.47) is not useful unless the eigenfunctions and eigenvalues are known. Since we now consider the small-k regime, the term proportional to k in Eq. (4.43) can be handled using perturbation theory. That is, the eigenfunctions and eigenvalues are expanded in a series in k:

$$\omega_j = \omega_j^{(0)} + k\omega_j^{(1)} + k^2\omega_j^{(2)} + \cdots \tag{4.48a}$$

and

$$\Psi_j(\vec{p}_1) = \Psi_j^{(0)}(\vec{p}_1) + k\Psi_j^{(1)}(\vec{p}_1) + \cdots . \tag{4.48b}$$

The lowest-order terms satisfy

$$\rho\mathcal{L}_1\Psi_j^{(0)}(\vec{p}_1) = -\omega_j^{(0)}\Psi_j^{(0)}, \tag{4.49}$$

which shows that to leading order the $\{\Psi_j^{(0)}(\vec{p}_1)\}$ are eigenfunctions of the linearized Boltzmann collision operator, or

$$\Psi_j^{(0)}(\vec{p}_1) \equiv S_j(\vec{p}_1), \quad \omega_j^{(0)} = -\rho\lambda_j ; \tag{4.50a}$$

where

$$\mathcal{L}S_j(\vec{p}_1) = \lambda_j S_j(\vec{p}_1). \tag{4.50b}$$

The eigenvalues λ_j of the linearized Boltzmann collision operator have the property that they are real and nonpositive. In fact, unless $S_j(\vec{p}_1)$ is a collisional invariant they are strictly negative. For the collisional invariants, $\lambda_j = 0$. This is an extremely important point, since it means that the terms in Eq. (4.47) where both j and l correspond to collisional invariants go at least like k^{-1} as $k \to 0$ ($s \to 0^+$ having already been taken) and should thus dominate in the small-k regime. As we shall show below, the most divergent terms are proportional to k^{-2} and give a nonvanishing contribution to the sum rules.

The various corrections terms in Eqs. (4.48) are found by expanding

$$\Psi_j^{(l)} = \sum_{n=0}^{\infty} S_n(\vec{p}_1) C_n^{(l)}(j), \tag{4.51}$$

where it should be remembered that the zero-order eigenfunctions $\{S_j\}$ satisfy the orthogonality requirement, Eq. (4.44). Using Eqs. (4.51), (4.48), and (4.44) in (4.43) gives, on equating the coefficients of each order in k:

$$(\omega_j^{(0)} + \rho\lambda_n)C_n^{(l)}(j) + \sum_{l_1=1}^{l} \omega_j^{(l_1)} C_n^{(l-l_1)}(j) + \sum_{n_1=0}^{\infty} U_{n,n_1} C_{n_1}^{(l-1)}(j) = 0, \tag{4.52}$$

where $C_n^{(l)}(j) \equiv 0$ for $l < 0$ and

$$U_{n,n_1} \equiv \frac{i\vec{k}}{mk} \cdot \int d\vec{p}_1\, \phi(\vec{p}_1) S_n^*(\vec{p}_1)\vec{p}_1 S_{n_1}(\vec{p}_1). \tag{4.53}$$

This is completely analogous to perturbation theory of degenerate states in quantum mechanics.

As was mentioned above we require only the corrections to the collisional invariants since this yields the most divergent part of Q_α. In fact, in order to find the leading k dependence, it is sufficient to compute ω to second order and only the $C_n^{(0)}(j)$.

The collisional invariants are chosen in the usual fashion:

$$S_0(\vec{p}_1) \equiv 1 \tag{4.54a}$$

$$S_1(\vec{p}_1) \equiv \frac{(p_1^2/2m - \frac{3}{2}k_BT)}{(\frac{3}{2})^{1/2}k_BT}, \tag{4.54b}$$

and

$$S_{2,3,4}(\vec{p}_1) \equiv \vec{p}_1/(mk_BT)^{1/2}. \tag{4.54c}$$

In addition, the x axis is chosen to lie along k. Using Eq. (4.52) for the collisional invariants yields

$$\omega_j^{(0)} = 0, \quad C_n^{(0)}(j) = 0, \quad n > 4, \; j \leqslant 4,$$

and

$$\omega_j^{(1)} C_n^{(0)}(j) - \sum_{n_1=0}^{4} U_{n,n_1} C_{n_1}^{(0)}(j) = 0, \quad n \leqslant 4. \tag{4.55}$$

Equation (4.55) is an eigenvalue problem. Using Eqs. (4.55), (4.54), and (4.53) gives for the five solutions of Eq. (4.55)

$$\omega_0^{(1)} = 0, \quad \vec{C}^{(0)}(0) = [0, 0, 0, 1, 0], \tag{4.56a}$$

$$\omega_1^{(1)} = 0, \quad \vec{C}^{(0)}(1) = [0, 0, 0, 0, 1], \tag{4.56b}$$

$$\omega_2^{(1)} = 0, \underline{C}^{(0)}(2) = (\tfrac{3}{5})^{1/2}[-(\tfrac{2}{3})^{1/2}, 1, 0, 0, 0], \tag{4.56c}$$

and

$$\omega_{3,4}^{(1)} = \pm ic_0, \underline{C}^{(0)}(3,4) = \frac{1}{\sqrt{2}}\,[(\tfrac{3}{5})^{1/2}, (\tfrac{2}{5})^{1/2}, \pm 1, 0, 0], \tag{4.56d}$$

with

$$c_0 \equiv (\tfrac{5}{3}\,k_BT/m)^{1/2}. \tag{4.57}$$

Note that Eq. (4.57) is the low-density form of the adiabatic sound speed, and that the eigenfunctions given by Eq. (4.56) are orthonormal. The first two are just the transverse velocity modes, the third the heat mode, and the last two the longitudinal sound modes as are found in the hydrodynamics of simple fluids, at low density.

By examining Eq. (4.52) for $l = 2$ one may easily show that

$$\omega_j^{(2)} = \sum_{n_1=0}^{4}\sum_{n_2=5}^{\infty}\sum_{n_3=0}^{4} C_{n_1}^{(0)}(j) U_{n_1,n_2} \frac{1}{\rho\lambda_{n_2}} U_{n_2,n_3} C_{n_3}^{(0)}(j), \quad j \leqslant 4 \tag{4.58}$$

where the zero-order coefficients are given by Eqs. (4.56). Returning to Eqs. (4.47) we see that the leading k dependence is found by taking

$$\Psi_j(\vec{p}_1) = \sum_{n=0}^{4} C_n^{(0)}(j) S_j(\vec{p}_1) \tag{4.59}$$

and using Eqs. (4.58) and (4.56) for ω_j. This gives

$$Q_\alpha(\vec{p}_1,\vec{p}_2)=\sum_{j,l=0}^{4}(s+\omega_j+\omega_l^*)^{-1}\times\int d\vec{p}_1'\,d\vec{p}_2'\,\phi(\vec{p}_1')\phi(\vec{p}_2')F_\alpha(\vec{p}_1',\vec{p}_2')\times\sum_{n_1=0}^{4}\sum_{n_2=0}^{4}C_{n_1}^{(0)}(j)C_{n_2}^{(0)}(j)S_{n_1}(\vec{p}_1')S_{n_2}(\vec{p}_1)\times\sum_{n_3=0}^{4}\sum_{n_4=0}^{4}C_{n_3}^{(0)}(l)C_{n_4}^{(0)}(l)S_{n_3}(\vec{p}_2')S_{n_3}(\vec{p}_2)\,. \tag{4.60}$$

Using Eq. (4.60) in Eqs. (4.33) and (4.40) gives

$$W_{\vec{k},E}^{(1)}=\frac{\rho i\vec{k}}{m}\sum_{j,l=0}^{4}(\omega_j+\omega_l^*)^{-1}\sum_{n_1,n_2=0}^{4}(mk_BT)^{1/2}\times\int d\vec{p}_1\,d\vec{p}_2\;\phi(\vec{p}_1)\phi(\vec{p}_2)F_E(\vec{p}_1,\vec{p}_2)\times S_{n_1}(\vec{p}_1)S_{n_2}(\vec{p}_2)C_{n_1}^{(0)}(j)C_{n_2}^{(0)}(l)\times C_2^{(0)}(j)C_0^{(0)}(l)\,, \tag{4.61a}$$

and

$$W_{\vec{k},\vec{P}}^{(0)}=-\sum_{j,l=0}^{4}(\omega_j+\omega_l^*)^{-1}\times\sum_{n_1,n_2=0}^{4}\int d\vec{p}_1\,d\vec{p}_2\;\phi(\vec{p}_1)\phi(\vec{p}_2)F_{\vec{P}}(\vec{p}_1,\vec{p}_2)\times S_{n_1}(\vec{p}_1)S_{n_2}(\vec{p}_2)\times C_{n_1}^{(0)}(j)C_{n_2}^{(0)}(l)C_0^{(0)}(j)C_0^{(0)}(l)\,, \tag{4.61b}$$

where we have again used the orthonormality properties of the $S_j(\vec{p})$. This form is valid for small k. Alternatively for large k Eq. (4.42) is used in Eqs. (4.33) and (4.40), thereby obtaining

$$W_{\vec{k},E}^{(1)}=\rho i\vec{k}\cdot\int d\vec{p}_1\,d\vec{p}_2\;\frac{\vec{p}_1\phi(\vec{p}_1)\phi(\vec{p}_2)}{0^+-i\vec{k}\cdot(\vec{p}_1-\vec{p}_2)}\;F_E(\vec{p}_1,\vec{p}_2) \tag{4.62a}$$

and

$$W_{\vec{k},\vec{P}}^{(0)}=-\rho m\int d\vec{p}_1\,d\vec{p}_2\;\frac{\phi(\vec{p}_1)\phi(\vec{p}_2)F_{\vec{P}}(\vec{p}_1,\vec{p}_2)}{0^+-i\vec{k}\cdot(\vec{p}_1-\vec{p}_2)}\,. \tag{4.62b}$$

Equations (4.61) and (4.62) depend only on the fact that the density is low, and that the interaction potential is short range. Unfortunately, one still needs to consider the details of the scattering problem and the spectrum of the collision operator for each choice of interparticle potential. In Sec. V we carry out this task for Maxwell molecules.

V. SUM RULES FOR MAXWELL MOLECULES

In this section we shall compute the value of the sum rules at low densities. We choose a particular form for the interparticle potential[2]:

$$U(r_{ij})\equiv\epsilon/r_{ij}^4\,,\quad \epsilon>0\,, \tag{5.1}$$

which is often referred to in the literature as a Maxwell molecule potential.[2(b)] This choice is motivated by the simple solutions of the linearized Boltzmann equation which result for this potential. The qualitative features of the low-density properties of molecules which interact via other potentials are known to be similar.[2]

The main advantage of Maxwell molecules lies in the fact that the eigenfunctions of the linearized Boltzmann collision operator have a very simple form. In fact, they are given in terms of Sonine polynomials.[2] Further, the eigenvalues are known exactly. For our purposes we require only the collisional invariants and the eigenfunctions corresponding to two other eigenvalues:

$$\left(\tfrac{2}{5}\right)^{1/2}\frac{\vec{p}}{(mk_BT)^{1/2}}\left(\frac{p^2}{2mk_BT}-\frac{5}{2}\right), \tag{5.2a}$$

with eigenvalue $\lambda_{1,1}$, and

$$(mk_BT)^{-2}\begin{pmatrix}p_xp_y,\,p_xp_z,\,p_yp_z\\ \left(\tfrac{3}{4}\right)^{1/2}\left(p_z^2-\tfrac{1}{3}p^2\right),\,\tfrac{1}{2}\left(p_x^{\,2}-p_y^{\,2}\right)\end{pmatrix} \tag{5.2b}$$

with eigenvalue $\lambda_{0,2}$. The eigenvalues $\lambda_{1,1}$ and $\lambda_{0,2}$ are

$$\lambda_{1,1}=-4\pi A^{(2)}(4)(\epsilon/m)^{1/2} \tag{5.3a}$$

and

$$\lambda_{0,2}=-6\pi A^{(2)}(4)(\epsilon/m)^{1/2}\,. \tag{5.3b}$$

The quantity $A^{(2)}(4)$ is given in Refs. 2(a)–2(c) and equals 0.308. Note that the eigenfunctions given in Eqs. (5.2) are orthonormal, both to themselves and to the collisional invariants.

Since the tensor $(\vec{p}\vec{p}-\frac{1}{3}p^2\overleftrightarrow{1})$ is a linear combination of the eigenfunctions in Eq. (5.2b), it is a simple matter to use Eqs. (5.2) to solve (2.19) and (2.22) with the result

$$\vec{A}^{(0)}(\vec{p}_1)=-\frac{1}{k_BT\lambda_{1,1}}\left(\frac{p_1^2}{2m}-\frac{5k_BT}{2}\right)\frac{\vec{p}_1}{m} \tag{5.4a}$$

and

$$\overleftrightarrow{B}^{(0)}(\vec{p}_1)=-\frac{1}{k_BT\lambda_{0,2}}\left(\frac{\vec{p}_1\vec{p}_1}{m}-\frac{1}{3}\,\frac{p_1^2}{m}\,\overleftrightarrow{1}\right). \tag{5.4b}$$

Using this last result, we show in Appendix B, that

$$F_E(\vec{p}_1,\vec{p}_2)=-(3\vec{p}_{\rm c.m}/m^2)\cdot(\vec{p}_{12}\vec{p}_{12}-\tfrac{1}{3}p_{12}^2\overleftrightarrow{1})\cdot\vec{\nabla}\beta \tag{5.5a}$$

and

$$F_{\vec{P}}(\vec{p}_1,\vec{p}_2)=-(4/m)(\vec{p}_{12}\vec{p}_{12}-\tfrac{1}{3}\overleftrightarrow{1}p_{12}^2):\vec{\nabla}\beta\vec{v}\,, \tag{5.5b}$$

where the (1, 2) center of mass and relative momenta are defined by

$$\vec{p}_{\rm c.m.}\equiv\vec{p}_1+\vec{p}_2\,,\quad \vec{p}_{12}\equiv\tfrac{1}{2}(\vec{p}_1-\vec{p}_2)\,. \tag{5.6}$$

As a final preliminary remark, we note that $p_x S_n(x)$, $n \leqslant 4$ can be written as a linear combination of the eigenfunctions given in Eqs. (4.54) and (5.2). This allows the matrix elements $U_{n,n'}$, where n or $n' \leqslant 4$, to be evaluated in a straightforward fashion using orthonormality and Eq. (4.53). Combining this with Eqs. (4.56) and (4.58) yields

$$\omega_j^{(2)} = -\frac{k_B T}{m\rho}\begin{cases} 1/\lambda_{0,2}, & j=0 \\ 1/\lambda_{0,2}, & j=1 \\ 1/\lambda_{1,1}, & j=2 \\ \frac{1}{3}\lambda_{1,1}+\frac{2}{3}\lambda_{0,2}, & j=3,4 \end{cases} . \tag{5.7}$$

Noting that the shear viscosity η and thermal conductivity κ for a low-density Maxwell molecule gas are given by[2]

$$\eta = -\frac{k_B T}{\lambda_{0,2}}, \quad \kappa = -\frac{k_B T}{m\lambda_{1,1}} \frac{5k_B}{2}, \tag{5.8}$$

and the low-density forms of the heat capacities at constant pressure and volume per particle ($\bar{C}_p$ and $\bar{C}_V$, respectively) gives

$$-\frac{k_B T}{m\rho\lambda_{0,2}} = \frac{\eta}{m\rho}, \tag{5.9a}$$

$$-\frac{k_B T}{m\rho\lambda_{1,1}} = \frac{\kappa}{\rho\bar{C}_p} \equiv \Gamma_T, \tag{5.9b}$$

and

$$-\frac{k_B T}{m\rho}\left(\frac{1}{3\lambda_{1,1}}+\frac{2}{3\lambda_{0,2}}\right) = \frac{1}{2}\left[\left(\frac{C_p}{\bar{C}_V}-1\right)\frac{\kappa}{\rho\bar{C}_p}+\frac{4}{3}\frac{\eta}{m\rho}\right] \equiv \Gamma_s, \tag{5.9c}$$

where the sound and heat damping constants, Γ_s and Γ_T, are the same as are found in the hydrodynamics of simple fluids. Equations (5.9) show that the small-k collisional damping times are hydrodynamic as was expected.

With these results the calculation of the sum rules can now be completed.

A. Small-wave-vector regime

When the wave vector is small $W^{(1)}_{\vec{k},E}$ and $W^{(0)}_{\vec{k},\vec{P}}$ are computed from Eqs. (4.61). The calculation is straightforward, although tedious, and we omit many of the details.

For the $\vec{\nabla} T$ terms, using Eqs. (4.61a) and (4.56), we see that only terms with $j, l = 2, 3, 4$ in Eq. (4.61a) are nonzero. Of these terms, the most divergent ones are those where $j = l = 3, 4$ [cf. Eqs. (4.48a), (4.65), and (5.7)]. Lastly, note that ($n_1, n_2 = 0, 1, 2$)

$$\int d\vec{p}_1\, d\vec{p}_2\, \phi(\vec{p}_1)\phi(\vec{p}_2)S_{n_1}(\vec{p}_1)S_{n_2}(\vec{p}_2)F_E(\vec{p}_1,\vec{p}_2) = \begin{cases} \left(\frac{2mk_B T}{3}\right)^{3/2} \frac{15}{4m^2} \frac{\partial\beta}{\partial x}, & (n_1,n_2)=(1,2) \text{ or } (2,1) \\ 0, & \text{otherwise} \end{cases} \tag{5.10}$$

which follows directly from Eqs. (5.5a) and (4.54). Combining Eqs. (5.10), (5.7), (4.61a), and (4.56) yields

$$W^{(1)}_{\vec{k},E}(\vec{r}) = \frac{\rho(k_B T)^2}{2\Gamma_s k^2} \frac{ik}{m} \frac{\partial\beta(r)}{\partial x} + O(1) \tag{5.11a}$$

$$= + \frac{\rho k_B T}{2\Gamma_s k^2} \frac{i\vec{k}\cdot\vec{\nabla}\ln\beta(\vec{r})}{m}, \tag{5.11b}$$

where we have used Eq. (5.9c) and where the second equality is valid to linear order in displacements from equilibrium. Thus using Eqs. (3.8), (3.11), and (5.11) in (3.3) gives for the low-k low-density form of the first sum rule

$$S^{(1)}_{\vec{k}}(\vec{r}) = \rho i\vec{k}\cdot\left(\vec{v}(\vec{r}) + \frac{k_B T}{2\Gamma_s k^2 m}\vec{\nabla}\ln\beta(\vec{r})\right). \tag{5.12}$$

We postpone the discussion of this result until the end of this work.

The calculation of $W^{(0)}_{\vec{k},\vec{P}}(\vec{r})$ proceeds exactly as above except for the fact that now Eq. (4.61b) is used. Using Eq. (5.5b) we find ($n_1, n_2 = 0, 1, 2$)

$$\int d\vec{p}_1\, d\vec{p}_2\, \phi(\vec{p}_1)\phi(\vec{p}_2)S_{n_1}(\vec{p}_1)S_{n_2}(\vec{p}_2)F_{\vec{P}}(\vec{p}_1,\vec{p}_2) = \begin{cases} \frac{2\partial v^x}{\partial x} - \frac{2}{3}\vec{\nabla}\cdot\vec{v}, & n_1=n_2=2 \\ 0, & \text{otherwise} \end{cases} . \tag{5.13}$$

As was done in the first sum rule, Eq. (5.13) is used in conjunction with Eqs. (4.56) and (4.61b) to give

$$W^{(0)}_{\vec{k},\vec{P}}(\vec{r}) = -\frac{\rho}{2\Gamma_s k^2}\left(\frac{3}{5}\ \frac{\vec{k}\vec{k}}{k^2} : (\vec{\nabla}\vec{v}(\vec{r}) - \tfrac{1}{3}\overleftrightarrow{1}\vec{\nabla}\cdot\vec{v}(\vec{r}))\right) + O(k^{-1}). \tag{5.14}$$

Combining Eqs. (5.14) and (3.11) gives for the zeroth sum rule

$$S^{(0)}_{\vec{k}}(\vec{r}) = \rho(\vec{r})\left(1 - \frac{3}{10\Gamma_s k^4}\ \vec{k}\vec{k} : (\vec{\nabla}\vec{v}(\vec{r}) - \tfrac{1}{3}\vec{\nabla}\cdot\vec{v}(\vec{r})\overleftrightarrow{1})\right). \tag{5.15}$$

The result is valid for small k and ρ and close to equilibrium.

B. Large-wave-vector regime

When k is large, the sum rules are obtained by using Eqs. (5.5) in (4.62). That is,

$$\begin{aligned} W^{(1)}_{\vec{k},E}(\vec{r}) &= -\frac{3\rho i\vec{k}}{m}\cdot\int d\vec{p}_1\, d\vec{p}_2\, \frac{\vec{p}_1\phi(\vec{p}_1)\phi(\vec{p}_2)\vec{p}_{\mathrm{c.m.}}(\vec{p}_{12}\vec{p}_{12} - \vec{p}^{\,2}_{12}\overleftrightarrow{1})\cdot\vec{\nabla}\beta(\vec{r})}{s - 2i\vec{k}\cdot\vec{p}_{12}}\,, \quad s \to 0^+ \\ &= \frac{\rho}{4}\left(\frac{\pi k_B T}{m}\right)^{1/2} \frac{i\vec{k}}{k}\cdot\vec{\nabla}\ln\beta(\vec{r}) \end{aligned} \tag{5.16}$$

Using this last expression and Eqs. (3.8) and (3.11) shows that for large k

$$S^{(1)}_{\vec{k},E}(\vec{r}) = \rho(\vec{r})i\vec{k}\cdot\left[\vec{v}(\vec{r}) + \frac{1}{4}\left(\frac{\pi k_B T}{m}\right)^{1/2} \frac{\vec{\nabla}\ln\beta(\vec{r})}{k}\right]. \tag{5.17}$$

As was discussed above, this result is valid when $ka \ll 1$ but still in the kinetic regime.

Proceeding in a similar manner, shows [cf. Eqs. (5.5b) and (4.62b)]

$$\begin{aligned} W^{(0)}_{\vec{k},\vec{P}}(\vec{r}) &= 4\rho\int d\vec{p}_1\, d\vec{p}_2\, \frac{\phi(\vec{p}_1)\phi(\vec{p}_2)(\vec{p}_{12}\vec{p}_{12} - \frac{1}{3}\overleftrightarrow{1}p^2_{12})}{s - 2i\vec{k}\cdot\vec{p}_{12}} : \vec{\nabla}\beta\vec{v}(\vec{r}), \quad s \to 0^+ \\ &= -\rho\left(\frac{\pi m}{k_B T}\right)^{1/2} \frac{(\vec{k}\vec{k} - \frac{1}{3})k^2\overleftrightarrow{1}}{k^3} : \vec{\nabla}\vec{v}(\vec{r}). \end{aligned} \tag{5.18}$$

This in turn gives

$$S^{(0)}_{\vec{k}}(\vec{r}) = \rho(\vec{r})\left[1 - \left(\frac{\pi m}{k_B T}\right)^{1/2} \frac{\vec{k}\vec{k}}{k^3} : (\vec{\nabla}\vec{v}(\vec{r}) - \tfrac{1}{3}\vec{\nabla}\cdot\vec{v}(\vec{r})\overleftrightarrow{1})\right]. \tag{5.19}$$

The new contributions to the sum rules have some common features [cf. Eqs. (5.19), (5.17), (5.15), and (5.12)] in that they are proportional either to $\vec{\nabla}\ln\beta(\vec{r})/k$ or $k^{-3}\vec{k}\vec{k} : (\vec{\nabla}\vec{v}(\vec{r}) - \frac{1}{3}\vec{\nabla}\cdot\vec{v}(\vec{r})\overleftrightarrow{1})$. Aside from this, the similarity between the high- and low-k results ends. The significance of this difference is discussed in Sec. VII. As a last comment we note that for systems in NESS, $\vec{\nabla}\cdot\vec{v}(\vec{r}) = 0$, thereby simplifying the results somewhat.

VI. ASSUMPTION OF SEPARATION OF TIME SCALES

The formal analysis of I depended strongly on the separation of the time-scale assumption. As was discussed there, this means that the correlation function

$$\langle \underline{A}_{\vec{k}}\underline{A}_{-\vec{k}}\underline{I}_T(-\tau)\rangle \tag{6.1}$$

decays on a time scale which is short compared to the macroscopic time scale. By macroscopic time scale, we mean the time scale of fluctuations whose characteristic length equals that of the macroscopic nonequilibrium phenomena. To be more specific, we want Eq. (6.1) to decay faster than $\langle \underline{A}_{\vec{k}'}(\tau)\underline{A}_{-\vec{k}'}\rangle$ where $\vec{k}'$ is of the order of the inverse macroscopic length scale.

Using the density expansion technique, we can investigate the separation of time scale assumption for low-density systems and thereby determine its range of validity. In this section we do this for Maxwell molecules. For concreteness we shall examine the correlation function.

$$\overleftrightarrow{\Omega}(\vec{k},\tau) \equiv \frac{1}{V}\langle N_{\vec{k}}N_{-\vec{k}}\overleftrightarrow{I}_{\vec{P}}(-\tau)\rangle. \tag{6.2}$$

Its Laplace transform is defined as

$$\overleftrightarrow{\Omega}(\vec{k}, s) \equiv \int_0^\infty d\tau\, e^{-s\tau}\, \frac{1}{V}\, \langle N_{\vec{k}} N_{-\vec{k}} \overleftrightarrow{I}_{\vec{p}}(-\tau)\rangle\,. \tag{6.3}$$

We can again introduce the resolvent operator (cf. Sec. IV) to obtain the leading order in density.

$$\overleftrightarrow{\Omega}(\vec{k}, s) = \rho \int d\vec{p}_1\, \phi(\vec{p}_1) \mathcal{G}(s) \left(\frac{\vec{p}_1\vec{p}_1}{m} - \frac{p_1^2}{3m}\, \overleftrightarrow{1}\right), \tag{6.4}$$

where $\mathcal{G}(s)$ is given in Eq. (4.10). Using the low-density form for $\mathcal{G}(s)$, Eq. (4.26), allows Eq. (6.4) to be rewritten as

$$\begin{aligned}\overleftrightarrow{\Omega}(\vec{k}, s) = -\rho^2 \int d\vec{p}_1\, d\vec{p}_2\, \phi(\vec{p}_1)\phi(\vec{p}_2) \\ \times \frac{1}{s - i\vec{k}\cdot(\vec{p}_1 - \vec{p}_2)/m - \rho\mathcal{L}_1 - \rho\mathcal{L}_2} \\ \times(\vec{0}\,|\,VT_{12}\,|\,\vec{0})(1 + \mathcal{P}_{12}) \\ \times \frac{1}{s - \rho\mathcal{L}_1}\left(\frac{\vec{p}_1\vec{p}_1}{m} - \frac{1}{3m}\, \overleftrightarrow{1} p_1^2\right).\end{aligned} \tag{6.5}$$

For Maxwell molecules, as was discussed in Sec. V, $[\vec{p}_1\vec{p}_1 - \frac{1}{3}\overleftrightarrow{1} p_1^2]$ is an exact eigenfunction of $\mathcal{L}_1$ with eigenvalue $\lambda_{0,2}$ [cf. Eq. (5.2b)]. Referring to Eq. (4.37) we see that

$$\begin{aligned}\overleftrightarrow{\Omega}(\vec{k}, s) = \frac{-\lambda_{0,2}\rho^2}{s - \rho\lambda_{0,2}} \int d\vec{p}_1\, d\vec{p}_2\, \phi(\vec{p}_1)\phi(\vec{p}_2) \\ \times \frac{1}{s - i\vec{k}\cdot(\vec{p}_1 - \vec{p}_2)/m - \rho\mathcal{L}_1 - \rho\mathcal{L}_2} \\ \times F'_{\vec{p}}(\vec{p}_1, \vec{p}_2)\end{aligned} \tag{6.6}$$

where the prime implies that the $\vec{\nabla}\beta\vec{v}(\vec{r})$ factor of the right-hand side of Eq. (4.37) should be omitted. For high k the s dependence of the integral appearing in Eq. (6.6) may be omitted (it is of the same importance as the higher-density corrections) and thus

$$\Omega(\vec{k}, t) \sim \exp(-\rho\lambda_{0,2} t)\,. \tag{6.7}$$

The decay given by Eq. (6.7) is on the kinetic time scale. On the other hand, the time scale of the correlation function $\langle A_{\vec{k}'}(t) A_{-\vec{k}'}\rangle$ is hydrodynamic and thus an excellent separation of the time scales exists.

When k is small, it is the s dependence of the integral in Eq. (6.6) which is important. From our discussion in Sec. IV [cf. Eq. (4.47)] we see that the decay of $\overleftrightarrow{\Omega}$ will be governed by the real parts of the characteristic frequencies ω_j. As was shown in the last section, these decays were also hydrodynamic, having decay constants proportional to $k^2\Gamma_s$, $k^2\Gamma_T$, etc. For small k', $\langle A_{\vec{k}'}(t) A_{-\vec{k}'}\rangle$ evolves on a time scale governed by $k'^2\Gamma_s$, $k'^2\Gamma_T$, etc.[10,11] Thus there will be a separation of time scales as long as $k > k'$, that is, providing one is not interested in NESS fluctuations with macroscopic wave vectors. Since k' is extremely small this requirement is easily satisfied.

A separation of time scales is also expected at high densities although the situation may be somewhat complicated by the presence of long time tails. Should long time tails be important, the standard techniques for circumventing this difficulty may be used.[12]

A more careful analysis of Eq. (6.6) could be used to compute the correction to the light-scattering spectrum due to $\vec{\nabla}\vec{v}(\vec{r})$. We do not offer this consideration here but will present a method for finding the full spectrum in the next paper. This method will not depend on the low-density restriction and/or choice of Maxwell molecules.

VII. DISCUSSION

We have shown in this paper how the formal theory of I, when applied to low-density systems, brings about well-known results as well as new predictions.

We first generated a correlation-function expression for the SDF, and demonstrated that at low densities the classical results of Chapman-Enskog and Choh-Uhlenbeck are recaptured. We stress, however, that our starting expression, Eq. (2.4), has no apparent density limitation.

New predictions were obtained when we considered the sum rules of the dynamic structure factor. Taking the density-density correlation function as a typical example of fluctuations in the NESS Eqs. (5.12), (5.15), (5.17), and (5.19) allow us to draw clear cut conclusions about the validity of local-equilibrium theory for the computation of fluctuations. As long as k is large, the new terms are not important. Taking Eq. (5.17) as an example, we see that the new term is proportional to $(\vec{\nabla}\ln T)/k$. This is the ratio of the microscopic and macroscopic length scales and is negligible for large k. As k becomes smaller, we must use Eq. (5.12) to compute the sum rule. The main difference in the new term at high and low k is the appearance of an additional factor, $(2/\Gamma_s k)(k_B T/\pi m)^{1/2}$, in the latter. This number is typically $O(10^3)$ for light-scattering k's and dramatically increases the size of the new term. As we make k even smaller the new terms can be made arbitrarily large, (as long as $k > k'$, the macroscopic wave vector) the size growing as k^{-2}. A similar analysis holds for the $\vec{\nabla}\vec{v}(\vec{r})$ terms.

Thus it is clear that if one is interested in *short-wavelength phenomena,* the ideas of local equilibrium are sufficient. The coupling between the macroscopic flux and the fluctuations in the local properties is not felt on the short-wavelength scale. If, however, k is small, and thus one is interested in *long-wavelength phenomena,* such as those characterizing hydrodynamic modes and light scattering, the importance of the second term grows, and one cannot in general compute correlation functions with local-equilibrium techniques alone. The difference between the low- and high-wave-vector regimes lies mainly in the appearance of a factor $c_0/\Gamma_s k$ in the low-k expressions. In hydrodynamics, this factor is a measure of the effectiveness of the damping mechanisms in the system. Thus the poorer the damping the larger is the new term in the sum rules.

From the results of Sec. V we see that the presence of a temperature gradient causes the first sum rule to be nonzero even when convection is absent. This is quite different from what is normally found in equilibrium systems and may facilitate an experimental observation of this effect. This point will be amplified in the next paper. (See also paper I.)

As a final remark concerning the fluctuations, we reiterate that aside from the quantitative aspects of the new terms, they have a striking qualitative difference from the equilibrium terms. They have reversed symmetry compared to the corresponding equilibrium terms, and reflect the breaking of time-reversal symmetry that arises from the coupling to the dissipative fluxes.

The analysis presented above allowed us also to examine the separation of time scales embodied in the derivation of Eq. (2.23) in paper I. We have shown in what sense this separation exists and justify the use of Eq. (2.23) (paper I) for the computation of NESS correlation functions.

In the companion paper we evaluate the density-density time-correlation functions for dense systems. We show there that the results obtained here are not particular to Maxwell molecules or to low-density systems. We stress that the new qualitative aspects of the corrections to the local-equilibrium sum rules are not an artifact of the Maxwell molecule potential or of the low density, and are a direct consequence of the underlying properties associated with the NESS. We shall also show that the new features found here are present in other correlation functions, and in fact lead to considerable changes in the light scattering spectrum.

ACKNOWLEDGMENT

This work was supported in part by the NSF.

APPENDIX A

In this Appendix we consider some of the formal properties of the eigenvalue problem

$$(i\vec{k}\cdot\vec{p}_1/m-\rho\mathcal{L}_1)\Psi_j(\vec{p}_1)=\omega_j(\vec{k})\Psi_j(\vec{p}_1)\,. \tag{A1}$$

Taking the complex conjugate of Eq. (A1) shows that

$$\omega_j(\vec{k})=\omega_j^*(-\vec{k})\,. \tag{A2}$$

The inner product of any two functions of $\vec{p}_1$ is defined as

$$((f_1,f_2))\equiv\int d\vec{p}_1\,\phi(\vec{p}_1)f_1^*(\vec{p}_1)f_2(\vec{p}_1) \tag{A3}$$

which is the usual definition employed in studies of the Boltzmann equation. With this choice the collision operator is Hermitian. Using (A3) we see that

$$((\Psi_l,(i\vec{k}\cdot\vec{p}_1/m-\rho\mathcal{L}_1)\Psi_j))$$
$$=(([-i\vec{k}\cdot\vec{p}_1/m-\rho\mathcal{L}_1]\Psi_l,\Psi_j))$$

or from Eqs. (A1) and (A2)

$$(\omega_j(\vec{k})-\omega_l(\vec{k}))((\Psi_l,\Psi_j))=0\,. \tag{A4}$$

Thus unless $\omega_j=\omega_l$ the eigenfunctions are orthogonal. Further even when $\omega_j=\omega_l$ we can choose Ψ_j, Ψ_l to be orthogonal.

APPENDIX B

In this Appendix we prove Eq. (5.5). Before doing this we need to evaluate the following integral:

$$\int_0^\infty b\,db\int_0^{2\pi}d\psi[\vec{p}_{12}\vec{p}_{12}-\vec{p}_{12}^{\,*}\vec{p}_{12}^{\,*}]\,. \tag{B1}$$

Let $\underline{T}$ be the unitary matrix which gives

$$\underline{T}l_3=\vec{p}_{12}/p_{12}\,, \tag{B2}$$

where l_3 is the unit vector in the z direction. Let $2\theta(d,\vec{p}_{12})$ be the scattering angle, i.e., the angle between $\vec{p}_{12}$ and $\vec{p}_{12}^{\,*}$. Then

$$\vec{p}_{12}^{\,*}\vec{p}_{12}^{\,*}-\vec{p}_{12}\vec{p}_{12}=p_{12}^2\underline{T}\cdot\begin{pmatrix}\sin^2 2\theta\cos^2\psi & \sin^2 2\theta\cos\psi\sin\psi & \sin 2\theta\cos 2\theta\cos\psi\\ \sin^2 2\theta\sin\psi\cos\psi & \sin^2 2\theta\sin^2\psi & \sin 2\theta\cos 2\theta\sin\psi\\ \cos 2\theta\sin 2\theta\cos\psi & \sin 2\theta\cos 2\theta\sin\psi & \cos^2 2\theta-1\end{pmatrix}\cdot\underline{T}^{-1}\,. \tag{B3}$$

Substituting in Eq. (B1) we perform the ψ integration and obtain

$$\begin{aligned}\int_0^{2\pi} d\psi\,(\vec{p}_{12}^{\,*}\vec{p}_{12}^{\,*}-\vec{p}_{12}\vec{p}_{12}) &= p_{12}^2\underline{T}\sin^2 2\theta\begin{pmatrix}\pi & 0 & 0\\ 0 & \pi & 0\\ 0 & 0 & -2\pi\end{pmatrix}\underline{T}^{-1}\\ &= -3\pi\sin^2(2\theta(\vec{p}_{12},b))\,[\vec{p}_{12}\vec{p}_{12}-\tfrac{1}{3}\overleftrightarrow{1}p_{12}^2]\,. \qquad \text{(B4)}\end{aligned}$$

The remaining b integration is performed after changing the integration variable to

$$y\equiv(m/16\epsilon)^{1/4}(p_{12}/\mu)^{1/2}b\,, \qquad \text{(B5)}$$

where we are considering only Maxwell molecules [cf. Eq. (5.1)]. Noting[2] that for Maxwell molecules the scattering angle θ depends only on y gives

$$\int_0^\infty b\,db\int_0^{2\pi} d\psi\,[\vec{p}_{12}\vec{p}_{12}-\vec{p}_{12}^{\,*}\vec{p}_{12}^{\,*}] = 12\pi\left(\frac{\epsilon}{m}\right)^{1/2}\left(\frac{\mu}{p_{12}}\right)[\vec{p}_{12}\vec{p}_{12}-\tfrac{1}{3}\overleftrightarrow{1}p_{12}^2]A^{(2)}(4)\,, \qquad \text{(B6)}$$

where

$$A^{(2)}(4)\equiv\int_0^\infty y\,dy[1-\cos^2(2\theta(y))]\,. \qquad \text{(B7)}$$

The quantity $A^{(2)}(4)$ equals 0.308.[2]

Having Eq. (B6), we can proceed with the proof of Eqs. (5.5). Consider first Eq. (5.5a). Using Eqs. (4.31) and (5.4a) shows that

$$F_E(\vec{p}_1,\vec{p}_2)=\frac{p_{12}}{\mu\lambda_{1,1}}\int_0^\infty db\,b\int_0^{2\pi} d\psi[p_1^2\vec{p}_1+p_2^2\vec{p}_2-p_1^{2*}\vec{p}_1^{\,*}-p_2^{2*}\vec{p}_2]\cdot\frac{\vec{\nabla}\beta(\vec{r})}{2m^2}\,. \qquad \text{(B8)}$$

Transforming to center of mass and relative momenta [cf. Eqs. (5.6)] allows us to rewrite Eq. (B8) in the form

$$F_E(\vec{p}_1,\vec{p}_2)=\frac{p_{12}}{\mu\lambda_{1,1}}\int_0^\infty b\,db\times\int_0^\pi d\psi\,\vec{p}_{\text{c.m.}}\cdot[\vec{p}_{12}\vec{p}_{12}-\vec{p}_{12}^{\,*}\vec{p}_{12}^{\,*}]\cdot\frac{\vec{\nabla}\beta(\vec{r})}{m^2} \qquad \text{(B9)}$$

where we have used the facts that $\vec{p}_{\text{c.m.}}$ and p_{12}^2 are conserved in a collision. Finally using Eqs. (B6) and (5.3a) yields

$$F_E(\vec{p}_1,\vec{p}_2)=-\frac{3\vec{p}_{\text{c.m.}}}{m^2}\cdot(\vec{p}_{12}\vec{p}_{12}-\tfrac{1}{3}p_{12}^2\overleftrightarrow{1})\cdot\vec{\nabla}\beta(\vec{r})$$

which is Eq. (5.5a).

The proof of Eq. (5.5b) follows in the same fashion.

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