Moderately dense gas quantum kinetic theory: Transport coefficient expressions

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Expressions for the transport coefficients of a moderately dense gas are obtained, based on a recently derived density corrected quantum Boltzmann equation. Linearization of the equations determining the pair correlation and the ''free'' singlet density operators about local equilibrium is discussed first. The rate of change of the pair correlations is treated as dynamic effects for pairs of particles relaxing to local equilibrium via a relaxation time model arising from interactions with ''third particles.'' In contrast, the singlet density operator satisfies a Boltzmann equation with binary collisions. Spatially inhomogeneous corrections to the collision superoperator are included. Contributions to the transport coefficients arise from the perturbation from local equilibrium through fluxes associated with kinetic, collisional and, for the thermal conductivity, potential energy mechanisms. A comparison is made between the classical limit of the transport coefficient expressions obtained here and the classical expressions previously derived from the Boltzmann equation with the nonlocal collision corrections of Green and Bogoliubov. © *1996 American Institute of Physics.* [S0021-9606(96)51132-3]

I. INTRODUCTION

A density corrected quantum Boltzmann equation has recently been proposed.[1] The novel feature of this equation is the role of pair correlations, not only in determining the detailed nature of binary collisions, but also contributing to a density correction to the singlet density operator. The preceding paper[2] [Equations labelled (I.⋯) refer to paper I.] describes the local equilibrium properties of such a system in the presence of weak inhomogeneities. The object of the present paper is to linearize the pair correlation and Boltzmann equations, solve the resulting equations following the Chapman–Enskog procedure[3–7] and to obtain expressions for the transport coefficients. It should be emphasized that for a moderately dense gas (one that includes density effects up to the second virial coefficient), this gives only part of the density (second virial) corrections to the transport coefficients. There are also bound state[8,9] and triple collision effects[9,10] that contribute to the transport coefficients at the same order of density. A treatment of all these effects based on a unified starting point is still to be accomplished. The inclusion of the effects of both bound states and pair correlations is the object of the recent thesis by Wei.[11]

As previously emphasized,[2] the separation of macroscopic and microscopic motion is conveniently formulated with a phase space description of the translational motion, namely using the Wigner equivalent representation of the various density operators. The correlations are determined by an equation governed, in part, by a decay to their local equilibrium form, modelled using a decay time τ. Linearization of this equation about local equilibrium introduces the perturbation Φ and its solution by a Chapman–Enskog[3–7] type of approach is carried out in Section II. That is, the time derivatives are eliminated using an appropriate set of equations of change for the variables that parameterize the local equilibrium state for the pair correlations. Only the simplest approximate solution for Φ (keeping only the lowest Sonine polynomials) is discussed in this work. The corresponding linearization and solution of the Boltzmann equation (including contributions from pair correlations) is carried out in Section III. Here it is the standard method of eliminating the time derivatives by the use of the equations of change for the hydrodynamic variables of mass, momentum and energy densities that is employed. These relations are complicated by the presence of second virial type density corrections. The resulting integral (Chapman–Enskog) equation for the perturbation ϕ thus contains as part of its driving term, contributions from pair correlation effects, both directly as new terms from the left hand side of the Boltzmann equation and indirectly from the elimination of the time derivatives.

Expressions for the transport coefficients are obtained in Section IV. These are affected by the presence of pair correlations. The paper ends with a short general discussion on the approach that has been taken in this work to obtain the density corrections to the transport coefficients, comparing with the previous classical expressions and pointing out those added contributions that arise by explicitly including pair correlations.

II. LINEARIZED EQUATION FOR THE PAIR CORRELATIONS

Equation (I.17) governing the pair correlation density operator is first cast into Wigner function form for the center of mass motion, remaining an operator in relative motion, compare Eqs. (I.29) and (I.37). This is written as

$$\frac{\partial f_{c12}}{\partial t} + \frac{\mathbf{P}}{2m} \cdot \boldsymbol{\nabla} f_{c12} = -i\mathscr{L}_{\mathrm{rel}} f_{c12} - i\mathscr{V}_{12} f_{f12}$$

$$+ \frac{f_{c12}^e - f_{c12}}{\tau}, \qquad (1)$$

where f_{f12} is the properly transformed product of free density operators. Since it is the Wigner function form of the free density operator, Eqs. (I.24) and (I.25), that has been used to express the local equilibrium and small gradient behaviour of the free particles, the two particles can be localized at different positions and a gradient expansion of the product is appropriate. On carrying out this computation f_{f12} is given by

$$f_{f12}(\mathbf{R},\mathbf{P},t) \equiv f_{f12}^{lh} + f_{f12}^{lnh} + f_{f12}^{lh}(\phi_1 + \phi_2)$$

$$= \frac{n_f^2 e^{-K_{\mathrm{CM}}/kT_f}}{(4\pi mkT_f)^{3/2}} \Lambda_r^3 \left\{ e^{-K_{\mathrm{rel}}/kT_f} \right.$$

$$+ \left[\frac{e^{-K_{\mathrm{rel}}/kT_f}}{2kT_f} \mathbf{p}_{\mathrm{op}}, \mathbf{r}_{\mathrm{op}} \right]_+ : \boldsymbol{\nabla}\mathbf{v}_f$$

$$+ (\mathbf{P} - 2m\mathbf{v}_f) \cdot \left[\frac{e^{-K_{\mathrm{rel}}/kT_f}}{4mkT_f} \mathbf{p}_{\mathrm{op}}, \mathbf{r}_{\mathrm{op}} \right]_+ \cdot \boldsymbol{\nabla}\ln T_f$$

$$\left. + e^{-K_{\mathrm{rel}}/kT_f}(\phi_1 + \phi_2) \right\} \qquad (2)$$

while the "equilibrium" form for the pair correlation function is

$$f_{c12}^e(\mathbf{R},\mathbf{P},t) = \frac{n_f^2 e^{-K_{\mathrm{CM}}/kT_f}}{(4\pi mkT_f)^{3/2}} \Lambda_r^3 U(T_f), \qquad (3)$$

on the basis that this is the form that would occur if the pair correlations were at complete equilibrium with the free particle motion through interactions with a third "free" particle. The particle momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ in the perturbation terms ϕ_1 and ϕ_2 are to be interpreted in terms of center of mass and relative momenta according to $\frac{1}{2}\mathbf{P} \mp \mathbf{p}_{\mathrm{op}}$. The correlation equation (1) is now solved within the philosophy of the Chapman Enskog procedure.

The time derivative in Eq. (1) is to scale as a gradient. Thus the left hand side of (1) is to be evaluated with the local equilibrium pair correlation function (I.29) in order to be linear in gradients implying in particular that the time derivative is completely expressed in terms of the time dependence of the parameters specifying the density of correlated particles n_c, their mean velocity $\mathbf{v}_c$ and their local temperature T_c. These are in turn obtained from the equations of change derived by taking the appropriate moments of Eq. (1). In writing down the Wigner function for the correlations, Eqs. (I.29) and (I.37), the correlation density, temperature and mean velocity have all been taken as independent variables. Since these can differ from their values when the correlations are in equilibrium with the freely moving particles, these differences depend on the nonuniformity of the gas and thus scale with gradients as do the perturbations ϕ and Φ. Rather

than introducing separate parameters, it would be equivalent to include the differences as part of the perturbation Φ. But having introduced explicit parameters, it is necessary to recognize that to avoid redundancy, the perturbation Φ must not contribute to these parameters. As a consequence the three auxiliary conditions

$$\mathrm{Tr}_{\mathrm{rel}} \int f_c^{le} \Phi \, d\mathbf{P} = 0,$$

$$\mathrm{Tr}_{\mathrm{rel}} \int \mathbf{P} f_c^{le} \Phi \, d\mathbf{P} = \mathbf{0},$$

$$\mathrm{Tr}_{\mathrm{rel}} \int \left[\frac{(\mathbf{P} - 2m\mathbf{v}_c)^2}{4m} + H_{\mathrm{rel}} \right] f_c^{le} \Phi \, d\mathbf{P} = 0 \qquad (4)$$

on Φ are imposed. These are almost the same as the correlation contributions to the general auxiliary conditions discussed in Sec. IV of Ref. 2. With these conditions, integrating Eq. (1) over $\mathbf{P}$ and tracing over the relative motion, an equation of change for n_c is obtained

$$\frac{\partial n_c}{\partial t} + \boldsymbol{\nabla} \cdot (n_c \mathbf{v}_c) = \frac{n_c^e - n_c}{\tau}. \qquad (5)$$

Here $n_c^e \equiv n_f^2 \Lambda_r^3(T_f) \mathrm{Tr}_{\mathrm{rel}} U(T_f)$ is the equilibrium density of pair correlations as determined by ρ_f. The corresponding equation for the velocity $\mathbf{v}_c$ is, from the $\mathbf{P}/2m$ moment of Eq. (1) and after eliminating a contribution from $\partial n_c/\partial t$,

$$\frac{\partial \mathbf{v}_c}{\partial t} + \mathbf{v}_c \cdot \boldsymbol{\nabla}\mathbf{v}_c + \frac{1}{2n_c m} \boldsymbol{\nabla} \cdot \mathsf{P}_c = \frac{n_c^e(\mathbf{v}_f - \mathbf{v}_c)}{n_c \tau}, \qquad (6)$$

with the correlation pressure tensor

$$\mathsf{P}_c = \frac{1}{2m} \mathrm{Tr}_{\mathrm{rel}} \int (\mathbf{P} - 2m\mathbf{v}_c)(\mathbf{P} - 2m\mathbf{v}_c) f_{c12} \, d\mathbf{P}. \qquad (7)$$

Finally the equation of change for the temperature is obtained from the equation of change for the correlation energy

$$\varepsilon_{\mathrm{corr}} \equiv \varepsilon_{\mathrm{CM}} + \varepsilon_{\mathrm{rel}} = \frac{1}{n_c} \mathrm{Tr}_{\mathrm{rel}} \int \left[\frac{(\mathbf{P} - 2m\mathbf{v}_c)^2}{4m} + H_{\mathrm{rel}} \right] f_{c12} \, d\mathbf{P}. \qquad (8)$$

The rate of the change for this energy per particle is

$$\frac{\partial \varepsilon_{\mathrm{corr}}}{\partial t} + \mathbf{v}_c \cdot \boldsymbol{\nabla} \varepsilon_{\mathrm{corr}} = -\frac{1}{n_c} \mathsf{P}_c : \boldsymbol{\nabla}\mathbf{v}_c - \frac{1}{n_c} \boldsymbol{\nabla} \cdot \mathbf{q}_c + \frac{\sigma_c}{n_c}$$

$$+ \frac{n_c^e}{n_c} \frac{\varepsilon_{\mathrm{corr}}^e - \varepsilon_{\mathrm{corr}}}{\tau}, \qquad (9)$$

with correlation energy heat flux

$$\mathbf{q}_c \equiv \mathrm{Tr}_{\mathrm{rel}} \int \frac{\mathbf{P} - 2m\mathbf{v}_c}{2m} \left[\frac{(\mathbf{P} - 2m\mathbf{v}_c)^2}{4m} + H_{\mathrm{rel}} \right] f_{c12} \, d\mathbf{P} \qquad (10)$$

and correlation energy production

$$\sigma_c \equiv -\frac{1}{m}\mathrm{Tr}_{\mathrm{rel}}\int (\mathbf{p}_{\mathrm{op}}\cdot\boldsymbol{\nabla} V + \boldsymbol{\nabla} V\cdot\mathbf{p}_{\mathrm{op}})f_{f12}\,d\mathbf{P}$$

$$\simeq -\frac{n_f^2\Lambda_r^3(T_f)}{2mkT_f}\mathrm{Tr}_{\mathrm{rel}}(\mathbf{p}_{\mathrm{op}}\cdot\boldsymbol{\nabla} V + \boldsymbol{\nabla} V\cdot\mathbf{p}_{\mathrm{op}})$$

$$\times[e^{-K_{\mathrm{rel}}/kT_f}\mathbf{p}_{\mathrm{op}},\mathbf{r}_{\mathrm{op}}]_+ : \boldsymbol{\nabla}\mathbf{v}_f = +n_f^2\int V\,d\mathbf{r}_{\mathrm{rel}}\boldsymbol{\nabla}\cdot\mathbf{v}_f. \tag{11}$$

The approximation is the result of using Eq. (2) and the subsequent evaluation of the trace. Equation (9) also involves the "equilibrium" correlation energy, which is obtained from Eqs. (3) and (8) as

$$\varepsilon_{\mathrm{corr}}^e \equiv \frac{3}{2}kT_f + \frac{\mathrm{Tr}_{\mathrm{rel}}H_{\mathrm{rel}}U(T_f)}{\mathrm{Tr}_{\mathrm{rel}}U(T_f)}. \tag{12}$$

At local equilibrium, the correlation energy is determined solely by the temperature T_c so that with the correlation heat capacity $C_{\mathrm{corr}}=\partial\varepsilon_{\mathrm{corr}}/\partial T_c$, the energy equation of change is equivalent to an equation of change for T_c.

Eliminating the time dependence in the correlation equation by means of the above results and retaining at most linear in gradient terms, this equation can be written

$$\frac{\partial f_{c12}^{le}}{\partial t} + \frac{\mathbf{P}}{2m}\cdot\boldsymbol{\nabla} f_{c12}^{le} - f_{c12}^{le}\frac{n_c^e - n_c}{n_c\tau}$$

$$= f_{c12}^{le}[\mathbf{L}_{T_c}\cdot\boldsymbol{\nabla}\ln T_c + \mathsf{L}_{vc}^{(2)}:[\boldsymbol{\nabla}\mathbf{v}_c]^{(2)} + L_{vc}^{(0)}\boldsymbol{\nabla}\cdot\mathbf{v}_c]$$

$$+ \frac{n_c^e}{n_c}f_{c12}^{le}\left\{\frac{\mathbf{P}-2m\mathbf{v}_c}{kT_c}\cdot\frac{\mathbf{v}_f-\mathbf{v}_c}{\tau} + \left[\mathscr{G}^2 - \frac{3}{2}\right.\right.$$

$$\left.\left. + U^{-1}T_cU_{T_c} - \frac{E^U}{kT_c}\right]\frac{\varepsilon_{\mathrm{corr}}^e - \varepsilon_{\mathrm{corr}}}{C_{\mathrm{corr}}T_c\tau}\right\}$$

$$= -i\mathscr{L}_{\mathrm{rel}}[f_{c12}^{le}(1+\Phi_{12})] - i\mathscr{V}_{12}f_{f12}^{lh}(1+\phi_1+\phi_2)$$

$$- \frac{i(\mathbf{P}-2m\mathbf{v}_f)}{4mkT_f}\cdot\mathscr{V}_{12}[f_{f12}^{lh}\mathbf{p}_{\mathrm{op}},\mathbf{r}_{\mathrm{op}}]_+\cdot\boldsymbol{\nabla}\ln T_f$$

$$- \frac{i}{2kT_f}\mathscr{V}_{12}[f_{f12}^{lh}\mathbf{p}_{\mathrm{op}},\mathbf{r}_{\mathrm{op}}]_+ : \boldsymbol{\nabla}\mathbf{v}_f$$

$$+ \frac{1}{\tau}\left\{f_{c12}^e - \frac{n_c^e}{n_c}f_{c12}^{le} - f_{c12}^{le}\Phi_{12}\right\}. \tag{13}$$

Here $[\boldsymbol{\nabla}\mathbf{v}_c]^{(2)}$ is the symmetric traceless part[12] of the second rank tensor $\boldsymbol{\nabla}\mathbf{v}_c$, E^U is the energy associated with the Ursell operator, see Eq. (I.A11), and the dimensionless center of mass momentum $\mathscr{G}\equiv(\mathbf{P}-2m\mathbf{v}_c)/\sqrt{4mkT_c}$ has been introduced to simplify the notation. It is noted that there is no term involving the gradient of n_c in this equation, consistent with the notion that the perturbations are due solely to temperature and velocity gradients. The three expansion coefficients appearing in this equation are

$$\mathbf{L}_{Tc} = \left(\mathscr{G}^2 - \frac{5}{2} + U^{-1}T_cU_{T_c} - \frac{E^U}{kT_c}\right)\sqrt{\frac{kT_c}{m}}\mathscr{G}, \tag{14}$$

$$\mathsf{L}_{vc}^{(2)} = 2[\mathscr{G}]^{(2)}, \tag{15}$$

and

$$L_{vc}^{(0)} = \left(\frac{2}{3} - \frac{k}{C_{\mathrm{corr}}}\right)\left(\mathscr{G}^2 - \frac{3}{2}\right) - \frac{k}{C_{\mathrm{corr}}}\left(U^{-1}T_cU_{T_c} - \frac{E^U}{kT_c}\right)$$

$$+ \left(\mathscr{G}^2 - \frac{3}{2} + U^{-1}T_cU_{T_c} - \frac{E^U}{kT_c}\right)\frac{n_f^2\int V d\mathbf{r}_{\mathrm{rel}}}{n_cC_{\mathrm{corr}}T_c}. \tag{16}$$

Consistent with the gradient expansions of the perturbations, Eqs. (I.26) and (I.38), all terms in Eq. (13) should be proportional to a gradient. Those that are not explicitly of this form involve the differences between the corresponding correlated and free parameters, for example $T_c - T_f$. Since these differ only because of the spatial nonuniformity of the gas, these differences must be expressible in terms of gradients. As there are only the temperature and velocity gradients available, rotational symmetry requires that each difference can only depend on one gradient, specifically

$$n_c - n_c^e = n_c^e\Delta_c\boldsymbol{\nabla}\cdot\mathbf{v}_0,$$

$$T_c - T_f = T\tau_c\boldsymbol{\nabla}\cdot\mathbf{v}_0,$$

$$\mathbf{v}_c - \mathbf{v}_f = D_c\boldsymbol{\nabla}\ln T. \tag{17}$$

The first combination of quantities that needs to be explicitly expressed in terms of the gradients is [$\mathscr{G}_f$ is the dimensionless center of mass momentum using the free particle temperature T_f]

$$-i\mathscr{L}_{\mathrm{rel}}f_{c12}^{le} - i\mathscr{V}_{12}f_{f12}^{lh}$$

$$= i\mathscr{V}_{12}\left[\frac{n_ce^{-\mathscr{G}^2}e^{-K_{\mathrm{rel}}/kT_c}}{(4\pi mkT_c)^{3/2}\mathrm{Tr}_{\mathrm{rel}}U(T_c)}\right.$$

$$\left. - \frac{n_f^2h^3e^{-\mathscr{G}_f^2}e^{-K_{\mathrm{rel}}/kT_f}}{(2\pi mkT_f)^3}\right]$$

$$\simeq i\mathscr{V}_{12}f_{f12}^{lh}\left\{\left[\left(\mathscr{G}^2 - \frac{3}{2} + \frac{K_{\mathrm{rel}}-E^U}{kT}\right)\tau_c + \Delta_c\right]\boldsymbol{\nabla}\cdot\mathbf{v}_0\right.$$

$$\left. + D_c\frac{\mathbf{P}-2m\mathbf{v}_0}{kT}\cdot\boldsymbol{\nabla}\ln T\right\}. \tag{18}$$

The other combination is

$$f_{c12}^e - \frac{n_c^e}{n_c}f_{c12}^{le} = -f_{c12}^e\left[\sqrt{\frac{4m}{kT}}D_c\mathscr{G}\cdot\boldsymbol{\nabla}\ln T + \left(\mathscr{G}^2 - \frac{3}{2}\right.\right.$$

$$\left.\left. + U^{-1}T_cU_{T_c} - \frac{E^U}{kT_c}\right)\tau_c\boldsymbol{\nabla}\cdot\mathbf{v}_0\right]. \tag{19}$$

Subsequent to making this expansion of the difference between free and correlated parameters, there is no need for further distinction between these parameters so that, for simplification, all temperatures $T_f = T_c = T$ are subsequently expressed by the same symbol, as are the mean velocities $\mathbf{v}_f = \mathbf{v}_c = \mathbf{v}_0$.

With these evaluations, the linear in gradients form for the correlation equation splits into three separate equations. This separation requires the perturbations ϕ and Φ to be

written as a combination of the gradients, see Eqs. (I.26) and (I.38). First is the equation for the scalar multiplying $\boldsymbol{\nabla} \cdot \mathbf{v}_0$,

$$f_{c12}^e L_{vc}^{(0)} = i\mathscr{L}_{\mathrm{rel}}[f_{c12}^e C_{c12}] + i\mathscr{V}_{12} f_{f12}^{lh}\left[\left(\mathscr{G}^2 - \frac{3}{2}\right.\right.$$
$$\left.\left. + \frac{K_{\mathrm{rel}} - E^U}{kT}\right)\tau_c + \Delta_c\right] - \frac{i}{6kT}\mathscr{V}_{12}[f_{f12}^{lh}\mathbf{p}_{\mathrm{op}}, \cdot \mathbf{r}_{\mathrm{op}}]_+$$
$$+ i\mathscr{V}_{12}[f_{f12}^{lh}(C_1 + C_2)] + \frac{1}{\tau}f_{c12}^e C_{c12}. \qquad (20)$$

Second is the equation for the vector multiplying $\boldsymbol{\nabla}\ln T$,

$$f_{c12}^e \mathbf{L}_{Tc} = i\mathscr{L}_{\mathrm{rel}}[f_{c12}^e \mathbf{A}_{c12}] - \frac{i}{\sqrt{4mkT_f}}\mathscr{G}\cdot\mathscr{V}_{12}[f_{f12}^{lh}\mathbf{p}_{\mathrm{op}}, \mathbf{r}_{\mathrm{op}}]_+$$
$$+ i\mathscr{V}_{12}[f_{f12}^{lh}(\mathbf{A}_1 + \mathbf{A}_2)] + iD_c\sqrt{\frac{4m}{kT}}\mathscr{G}\mathscr{V}_{12}f_{f12}^{lh}$$
$$+ \frac{1}{\tau}f_{c12}^e \mathbf{A}_{c12}. \qquad (21)$$

Lastly is the equation for the second rank symmetric trace-less tensor multiplying $[\boldsymbol{\nabla}\mathbf{v}_0]^{(2)}$,

$$f_{c12}^e \mathsf{L}_{vc}^{(2)} = i\mathscr{L}_{\mathrm{rel}}[f_{c12}^e \mathsf{B}_{c12}] - \frac{i}{2kT}\mathscr{V}_{12}[f_{f12}^{lh}\mathbf{p}_{\mathrm{op}}, \mathbf{r}_{\mathrm{op}}]_+^{(2)}$$
$$+ i\mathscr{V}_{12}[f_{f12}^{lh}(\mathsf{B}_1 + \mathsf{B}_2)] + \frac{1}{\tau}f_{c12}^e \mathsf{B}_{c12}. \qquad (22)$$

These three equations are to determine the three functions $C_c, \mathbf{A}_c$ and B_c arising in the gradient expansion of Φ

$$\Phi = -\mathbf{A}_c\cdot\boldsymbol{\nabla}\ln T_c - \mathsf{B}_c\mathbf{:}[\boldsymbol{\nabla}\mathbf{v}_c]^{(2)} - C_c\boldsymbol{\nabla}\cdot\mathbf{v}_c; \qquad (23)$$

see also Eq. (I.38). This will be done by picking appropriate functional forms for these functions and taking moments. It is to be noted that the time derivatives of Eq. (1) were eliminated by the use of moments associated with the number, velocity and energy averages and these required the auxiliary conditions (4). In terms of the three functions $C_c, \mathbf{A}_c,$ and B_c, these auxiliary conditions become

$$\mathrm{Tr}_{\mathrm{rel}}\int f_c^{le} C_c d\mathbf{P} = 0,$$

$$\mathrm{Tr}_{\mathrm{rel}}\int \mathscr{G}_c^{le}\mathbf{A}_c d\mathbf{P} = 0,$$

and

$$\mathrm{Tr}_{\mathrm{rel}}\int (K_{\mathrm{CM}} + H_{\mathrm{rel}})f_c^{le} C_c d\mathbf{P} = 0. \qquad (24)$$

It is easy to verify that on taking appropriate moments of Eqs. (20)–(22), these auxiliary conditions are consistent with these equations.

A one moment approximation to each of the three perturbation functions is now proposed. For this calculation it is assumed that the appropriate moments are proportional to the (energy production free parts of the) corresponding left hand side of Eqs. (20)–(22). Thus the form for C_c is taken as

$$C_c = \left[\left(\frac{2}{3} - \frac{k}{C_{\mathrm{corr}}}\right)\left(\mathscr{G}^2 - \frac{3}{2}\right) - \frac{k}{C_{\mathrm{corr}}}\left(U^{-1}TU_T - \frac{E^U}{kT}\right)\right]c_0^c \qquad (25)$$

with expansion coefficient c_0^c. This satisfies the two relevant auxiliary conditions of Eq. (24). The moment of Eq. (20) is taken with respect to

$$\frac{2}{3}\left(\mathscr{G}^2 - \frac{3}{2}\right) - \frac{H_{\mathrm{rel}} - \varepsilon_{\mathrm{rel}}}{C_{\mathrm{rel}}T} \qquad (26)$$

to give

$$c_0^c = \tau\left[1 + \frac{3}{2C_{\mathrm{rel}}T\Lambda_r^3\mathrm{Tr}_{\mathrm{rel}}U}\int V d\mathbf{r}_{\mathrm{rel}}\right], \qquad (27)$$

with the potential factor arising from the $[f_{f12}^{lh}\mathbf{p}_{\mathrm{op}}, \cdot \mathbf{r}_{\mathrm{op}}]_+$ term in Eq. (20). The analogous choice for the $\mathbf{A}_c$ moment satisfying Eq. (24) is

$$\mathbf{A}_c = \mathscr{G}\left(\mathscr{G}^2 - \frac{5}{2} + U^{-1}TU_T - \frac{E^U}{kT}\right)a_1^c. \qquad (28)$$

Taking the matrix element of Eq. (21) with

$$\left(\mathscr{G}^2 - \frac{5}{2} + \frac{H_{\mathrm{rel}} - \varepsilon_{\mathrm{rel}}}{kT}\right)\mathscr{G} \qquad (29)$$

gives

$$a_1^c = \tau\sqrt{\frac{kT}{m}}\left[1 - \frac{2}{\Lambda_r^3\mathrm{Tr}_{\mathrm{rel}}U(2C_{\mathrm{rel}} + 5k)T}\int V d\mathbf{r}_{\mathrm{rel}}\right]. \qquad (30)$$

The obvious choice for B_c is $[\mathscr{G}]^{(2)}b_0^c$. The expansion coefficient is obtained from the $[\mathscr{G}]^{(2)}$ matrix element of Eq. (22) to be $b_0^c = 2\tau$.

III. LINEARIZED BOLTZMANN EQUATION

The Boltzmann equation (I.2) is now cast into Wigner function form and linearized about local equilibrium. Again time derivatives are to be eliminated by use of the equations of continuity, motion and energy, so they are to be treated as linear in position gradient. The collision term in the Boltzmann equation (I.2) involves the initial positions of the colliding pair, so that gradient corrections can arise from the collision term because the particles start at different positions. Thomas et al.[13] have carried out the gradient expansion of the collision term as well as expressing the result in phase space representation, see also the work of Baerwinkel and Grossmann.[14] It is convenient to write this expansion as the combination $J_h + J_c + J_r$, where J_h is the collision term as if the system was homogeneous (with all particle positions the same) and the other two terms arise from gradients in the local equilibrium Wigner functions. The expansion of the Boltzmann equation then can be written in phase space representation as

$$\frac{\partial(f_{f1}^{le} + f_{c1}^{lh})}{\partial t} + \frac{\mathbf{p}}{m}\cdot\boldsymbol{\nabla}(f_{f1}^{le} + f_{c1}^{lh}) - J_h - J_c - J_r = J_{ne} \qquad (31)$$

with all terms determined solely by the local equilibrium state collected together before the equality sign and the terms dependent on the perturbation ϕ after the equality sign.

The collision terms J_h, J_c and J_r are calculated[13] using the local equilibrium free density operator. The purely local equilibrium contribution J_h vanishes according to

$$
\begin{aligned}
J_h = &-8i(2\pi)^3\hbar^2 \int\int d\mathbf{q}\,d\mathbf{k}\langle\mathbf{q}|[V,\Omega|\mathbf{k}\rangle \\
&\times f_{f1}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q}-\mathbf{k},t)f_{f2}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q}+\mathbf{k},t)\langle\mathbf{k}|\Omega^\dagger]_-|\mathbf{q}\rangle \\
= &-\frac{in_f^2\Lambda_r^6}{\hbar h^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}[V,e^{-H_{\mathrm{rel}}/kT}]_- \\
= &\frac{in_f^2\Lambda_r^6}{\hbar h^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}[K_{\mathrm{rel}},U]_- = 0.
\end{aligned}
\tag{32}
$$

The second equality makes use of the assumed lack of bound states in that $\Omega\Omega^\dagger=1$ while the third equality depends on the identity

$$
[V,e^{-H_{\mathrm{rel}}/kT}]_- = -[K_{\mathrm{rel}},U]_- .
\tag{33}
$$

The correction to the collision term associated with the displacement of the center of mass from the macroscopic position $\mathbf{r}$ is given by

$$
\begin{aligned}
J_c = &\nabla\cdot 2h^3\int\int d\mathbf{q}\,d\mathbf{k}\nabla_{\mathbf{q}'}[\langle\mathbf{q}+\mathbf{q}'|V\Omega|\mathbf{k}\rangle \\
&\times f_{f1}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q}-\mathbf{k},t)f_{f2}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q}+\mathbf{k},t)\langle\mathbf{k}|\Omega^\dagger|\mathbf{q}-\mathbf{q}'\rangle \\
&-\langle\mathbf{q}+\mathbf{q}'|\Omega|\mathbf{k}\rangle f_{f1}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q}-\mathbf{k},t)f_{f2}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q}+\mathbf{k},t) \\
&\times\langle\mathbf{k}|\Omega^\dagger V|\mathbf{q}-\mathbf{q}'\rangle]|_{\mathbf{q}'=0} \\
= &\nabla\cdot\frac{-in_f^2\Lambda_r^6}{4\hbar h^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}[\mathbf{r}_{\mathrm{op}},[V,e^{-H_{\mathrm{rel}}/kT}]_-]_+ ,
\end{aligned}
\tag{34}
$$

where the derivative with respect to $\mathbf{q}'$ has been evaluated by considering a position representation of the operators and carrying out the derivative to obtain the anticommutator $[\mathbf{r}_{\mathrm{op}},]_+$. Further simplification of this expression is accomplished by using Eq. (33) and the operator identity

$$
[A,[B,C]_-]_+ = [[A,B]_-,C]_+ + [B,[A,C]_+]_- ,
\tag{35}
$$

in the form

$$
\begin{aligned}
[\mathbf{r}_{\mathrm{op}},[V,e^{-H_{\mathrm{rel}}/kT}]_-]_+ &= -[\mathbf{r}_{\mathrm{op}},[K_{\mathrm{rel}},U]_-]_+ \\
&= \frac{2\hbar}{im}[\mathbf{p}_{\mathrm{op}},U]_+ - [K_{\mathrm{rel}},[\mathbf{r}_{\mathrm{op}},U]_+]_- .
\end{aligned}
\tag{36}
$$

On taking the trace, the collision term J_c can be written as

$$
\begin{aligned}
J_c = &-\nabla\cdot\frac{n_f^2\Lambda_r^6}{mh^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}\mathbf{p}_{\mathrm{op}}U \\
= &\mathbf{J}_{cn}\cdot\nabla\ln n_f + \mathbf{J}_{cv}:\nabla\mathbf{v}_0 + \mathbf{J}_{cT}\cdot\nabla\ln T
\end{aligned}
\tag{37}
$$

with

$$
\mathbf{J}_{cn} = \frac{-2n_f^2\Lambda_r^6}{mh^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}\mathbf{p}_{\mathrm{op}}U,
\tag{38}
$$

$$
\mathbf{J}_{cv} = \frac{-2n_f^2\Lambda_r^6}{mkTh^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}(\mathbf{p}_{\mathrm{op}}+\mathbf{p}-m\mathbf{v}_0)\mathbf{p}_{\mathrm{op}}U,
\tag{39}
$$

and

$$
\begin{aligned}
\mathbf{J}_{cT} = &-\frac{3}{2}\mathbf{J}_{cn} - \frac{n_f^2\Lambda_r^6}{mkTh^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}\mathbf{p}_{\mathrm{op}}(K_{\mathrm{CM}}U \\
&+kT^2 U_T).
\end{aligned}
\tag{40}
$$

The explicit expression for J_r is

$$
\begin{aligned}
J_r = &2h^3\int\int d\mathbf{q}\,d\mathbf{k}\nabla_{\mathbf{k}'}\cdot\langle\mathbf{q}|[V,\Omega|\mathbf{k}+\mathbf{k}'\rangle\{f_{f2}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q} \\
&+\mathbf{k},t)\nabla f_{f1}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q}-\mathbf{k},t) - f_{f1}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q} \\
&-\mathbf{k},t)\nabla f_{f2}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q}+\mathbf{k},t)\}\langle\mathbf{k}-\mathbf{k}'|\Omega^\dagger]_-|\mathbf{q}\rangle|_{\mathbf{k}'=0} \\
= &\frac{-in_f^2\Lambda_r^6}{2kT\hbar h^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}[V,\Omega[e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}},\mathbf{r}_{\mathrm{op}}]_+\Omega^\dagger]_- \\
&\times:\left[\nabla\mathbf{v}_0+\nabla\ln T\frac{\mathbf{p}+\mathbf{p}_{\mathrm{op}}-m\mathbf{v}_0}{m}\right] \\
= &\mathbf{J}_{rv}:\nabla\mathbf{v}_0 + \mathbf{J}_{rT}\cdot\nabla\ln T
\end{aligned}
\tag{41}
$$

with gradient corrections having velocity gradient coefficient

$$
\begin{aligned}
\mathbf{J}_{rv} = &\frac{-in_f^2\Lambda_r^6}{2kT\hbar h^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT} \\
&\times[V,\Omega[e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}},\mathbf{r}_{\mathrm{op}}]_+\Omega^\dagger]_-
\end{aligned}
\tag{42}
$$

and temperature gradient coefficient

$$
\begin{aligned}
\mathbf{J}_{rT} = &\frac{-in_f^2\Lambda_r^6}{2mkT\hbar h^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}(\mathbf{p}+\mathbf{p}_{\mathrm{op}}-m\mathbf{v}_0) \\
&\cdot[V,\Omega[e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}},\mathbf{r}_{\mathrm{op}}]_+\Omega^\dagger]_- .
\end{aligned}
\tag{43}
$$

Finally the collision term J_{ne} is written in terms of a linear relaxation operator

$$
\begin{aligned}
J_{ne}(\mathbf{r},\mathbf{p},t) \equiv &-f_f^{le}\mathscr{R}\phi \\
= &-8i(2\pi)^3\hbar^2\int\int d\mathbf{q}\,d\mathbf{k}\langle\mathbf{q}|[V,\Omega|\mathbf{k}\rangle \\
&\times f_{f1}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q}-\mathbf{k},t)f_{f2}^{le}(\mathbf{r},\mathbf{p}+\mathbf{q}+\mathbf{k},t) \\
&\times[\phi_1(\mathbf{p}+\mathbf{q}-\mathbf{k})+\phi_2(\mathbf{p}+\mathbf{q}+\mathbf{k})]\langle\mathbf{k}|\Omega^\dagger]_-|\mathbf{q}\rangle \\
= &\frac{-2i\pi n_f^2\Lambda_r^6}{h^4}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT} \\
&\times[V,\Omega[e^{-K_{\mathrm{rel}}/kT}(\phi_1+\phi_2)]\Omega^\dagger]_- .
\end{aligned}
\tag{44}
$$

This completes the description of all the terms in the linearized Boltzmann equation (31).

The time derivative in Eq. (31) involves both the free and correlated local equilibrium Wigner functions which are respectively parameterized by $n_f,\mathbf{v}_f,T_f$ and $n_c,\mathbf{v}_c,T_c$. Since

a time derivative is to scale as a position gradient in the Chapman–Enskog theory for the calculation of transport coefficients, then any deviation between the free and pair correlation sets of parameters is proportional to a gradient and can be ignored when estimating a time derivative. Thus both sets of parameters can be replaced by the fluid parameter set n, $\mathbf{v}_0$ and T. Moreover, it is noted that the time derivative always occurs in the combination $\partial/\partial t + \mathbf{p}/m \cdot \boldsymbol{\nabla}$ in the Boltzmann equation. The appropriate set of equations to be used in evaluating the time derivatives is examined first, then the resulting form of the Chapman Enskog equation is discussed.

From the equation of continuity (I.5), the rate of change of the full density is

$$\frac{\partial n}{\partial t} + \frac{\mathbf{p}}{m} \cdot \boldsymbol{\nabla} n = \frac{\mathbf{p} - m\mathbf{v}_0}{m} \cdot \boldsymbol{\nabla} n - n \boldsymbol{\nabla} \cdot \mathbf{v}_0. \tag{45}$$

The equation of motion (I.6) gives, to terms linear in the gradients,

$$\frac{\partial \mathbf{v}_0}{\partial t} + \frac{\mathbf{p}}{m} \cdot \boldsymbol{\nabla} \mathbf{v}_0 = \frac{\mathbf{p} - m\mathbf{v}_0}{m} \cdot \boldsymbol{\nabla} \mathbf{v}_0 - \frac{1}{nm} \boldsymbol{\nabla} P, \tag{46}$$

where $P = nkT(1 + nB)$ is the local equilibrium pressure with $n_f^2 \to n^2$ appropriate to keeping only second order in density terms. For the local energy per particle $\varepsilon \equiv \varepsilon^K + \varepsilon^V$, energy conservation, see Eqs. (I.7) and (I.8), implies that to terms linear in the gradients

$$\frac{\partial \varepsilon}{\partial t} + \frac{\mathbf{p}}{m} \cdot \boldsymbol{\nabla} \varepsilon = \frac{\mathbf{p} - m\mathbf{v}_0}{m} \cdot \boldsymbol{\nabla} \varepsilon - \frac{P}{n} \boldsymbol{\nabla} \cdot \mathbf{v}_0. \tag{47}$$

Now it is T and n_f that enter explicitly into the linearized Boltzmann equation. The rate of change of temperature is obtained from the energy equation while the equation for n_f is derived from the relation between n_f and n, Eqs. (I.39) and (I.A15). The temperature equation is considered first.

According to Eq. (I.43) the kinetic energy depends on both temperature T and density n_f, likewise the potential energy (ignoring gradient corrections)

$$n\varepsilon^V(\mathbf{r},t) = \tfrac{1}{2} \text{Tr}_{12} V_{12} \delta(\mathbf{r}_1 - \mathbf{r}) \Omega \rho_{f1} \rho_{f2} \Omega^\dagger$$
$$= \tfrac{1}{2} n_f^2 \Lambda_r^3 \text{Tr}_{\text{rel}} V e^{-H_{\text{rel}}/kT}, \tag{48}$$

compare Eq. (I.A8). By thermodynamics, and consistent with the relations between the local equilibrium quantities, the equilibrium energy per particle depends on volume $(1/n)$ and temperature T according to

$$d\varepsilon = C_v dT + \left(\frac{\partial \varepsilon}{\partial(1/n)}\right)_T d(1/n)$$
$$= C_v dT - \left[T\left(\frac{\partial P}{\partial T}\right)_n - P\right]\frac{1}{n^2} dn = C_v dT - kT^2 \frac{dB}{dT} dn, \tag{49}$$

with constant volume heat capacity $C_v = (\partial \varepsilon/\partial T)_n$, see Eq. (I.A5). On combining the equations of change for energy and number density, the equation

$$\frac{\partial T}{\partial t} + \frac{\mathbf{p}}{m} \cdot \boldsymbol{\nabla} T = \frac{\mathbf{p} - m\mathbf{v}_0}{m} \cdot \boldsymbol{\nabla} T - \frac{T}{nC_v}\left(\frac{\partial P}{\partial T}\right)_n \boldsymbol{\nabla} \cdot \mathbf{v}_0 \tag{50}$$

for the temperature is obtained. In a similar manner, the free density is also dependent on n and T through the equilibrium constraint (I.39), so that

$$\frac{\partial n_f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \boldsymbol{\nabla} n_f$$

$$= (1 + 4nB)\left(\frac{\partial n}{\partial t} + \frac{\mathbf{p}}{m} \cdot \boldsymbol{\nabla} n\right) + 2n^2 \frac{dB}{dT}\left(\frac{\partial T}{\partial t} + \frac{\mathbf{p}}{m} \cdot \boldsymbol{\nabla} T\right)$$

$$= (1 + 4nB)\frac{\mathbf{p} - m\mathbf{v}_0}{m} \cdot \boldsymbol{\nabla} n + 2n^2 \frac{dB}{dT}\frac{\mathbf{p} - m\mathbf{v}_0}{m} \cdot \boldsymbol{\nabla} T$$

$$- \left[n(1 + 4nB) + \frac{2n^2 kT}{C_v}\frac{dB}{dT}\right]\boldsymbol{\nabla} \cdot \mathbf{v}_0. \tag{51}$$

Since both the local equilibrium free Wigner function as well as f_{c1}^{lh} are parameterized by $n_f, \mathbf{v}_0$, and T, the latter through $n_c = n_f^2 \Lambda_r^3 \text{Tr}_{\text{rel}} U$, the above set of equations is sufficient for evaluating the time derivatives appearing in Eq. (31).

On carrying out the indicated time and space derivatives in Eq. (31) and eliminating the time derivatives with the relations in the last paragraph, the left hand side of this equation is formally linear in the gradients $\boldsymbol{\nabla} n$, $\boldsymbol{\nabla} \mathbf{v}_0$ and $\boldsymbol{\nabla} T$. Furthermore it is a necessary condition for consistency with the equation of continuity that there be no dependence on $\boldsymbol{\nabla} n$. As an aid to writing down the detailed expressions involving the gradients and to prove the lack of dependence on $\boldsymbol{\nabla} n$, the individual contributions are organized as follows:

$$d(f_{f1}^{le} + f_{c1}^{lh}) = F_n d\ln n_f + \mathbf{F}_v \cdot d\mathbf{v}_0 + F_T d\ln T \tag{52}$$

with derivatives with respect to $\ln n_f, \mathbf{v}_0$ and $\ln T$ given by

$$F_n = f_{f1}^{le} + 2f_{c1}^{lh}, \tag{53}$$

$$\mathbf{F}_v = \frac{\mathbf{p} - m\mathbf{v}_0}{kT} f_{f1}^{le} + \frac{2n_f^2 \Lambda_r^6}{kTh^3}\text{Tr}_r(\mathbf{p}_{\text{op}} + \mathbf{p} - m\mathbf{v}_0)e^{-K_{\text{CM}}/kT}U \tag{54}$$

and

$$F_T = \left(W^2 - \frac{3}{2}\right)f_{f1}^{le} + \frac{n_f^2 \Lambda_r^6}{h^3}\text{Tr}_r e^{-K_{\text{CM}}/kT}\left[\left(\frac{K_{\text{CM}}}{kT} - 3\right)U\right.$$
$$\left. + TU_T\right], \tag{55}$$

wherein the dimensionless momentum[3] $\mathbf{W} \equiv (\mathbf{p} - m\mathbf{v}_0)/\sqrt{2mkT}$ has been introduced.

With this breakdown of the various contributions, the dependence of the left hand side of Eq. (31) on the gradients can be explicitly obtained. But as stated earlier, there should be no dependence on $\boldsymbol{\nabla} n$. That this is the case is now demonstrated. Dependence on $\boldsymbol{\nabla} n$ arises from the time and space derivatives of n_f and also through the pressure gradient associated with the time derivative of $\mathbf{v}_0$. Collecting these contributions together gives as the coefficient of $\boldsymbol{\nabla} n$,

$$\frac{\mathbf{p}-m\mathbf{v}_0}{n_f m}(1+4nB)F_n - \frac{1}{nm}\left(\frac{\partial P}{\partial n}\right)_T \mathbf{F}_v - \frac{1}{n_f}(1+4nB)\mathbf{J}_{cn}$$

$$= \frac{1+2nB}{nm}[(\mathbf{p}-m\mathbf{v}_0)F_n - kT\mathbf{F}_v - m\mathbf{J}_{cn}] = \mathbf{0}, \qquad (56)$$

to terms linear in n. The terms in F_n and $\mathbf{F}_v$ involving f_{f1}^{le} clearly cancel and on examining the various contributions from pair correlations these are also easily shown to cancel.

On collecting the various contributions, the linearized Boltzmann equation (31) can be written in the form

$$\mathbf{L}_T \cdot \boldsymbol{\nabla} \ln T + \mathsf{L}_v^{(2)} \mathbin{:} [\boldsymbol{\nabla}\mathbf{v}_0]^{(2)} + L_v^{(0)}\boldsymbol{\nabla}\cdot\mathbf{v}_0 = -\mathscr{R}\phi, \qquad (57)$$

where[12] $[\boldsymbol{\nabla}\mathbf{v}_0]^{(2)}$ is the symmetric traceless part of the second rank tensor $\boldsymbol{\nabla}\mathbf{v}_0$. The general weight factor f_{f1}^{le} has been removed so that the linearized Boltzmann equation can be treated as an operator equation in a Hilbert space with inner product

$$\langle\langle A|B\rangle\rangle = \int A f_{f1}^{le}(\mathbf{r},\mathbf{p},t)B\,d\mathbf{p}. \qquad (58)$$

In the general case the coefficients of the generalized forces are given explicitly by retaining only terms up to second order in the density

$$f_{f1}^{le}\mathbf{L}_T = \left(F_T + 2n^2 T\frac{dB}{dT}\frac{F_n}{n_f}\right)\frac{\mathbf{p}-m\mathbf{v}_0}{m} - \mathbf{F}_v\frac{kT}{m}\left(1+nB+nT\frac{dB}{dT}\right) - \mathbf{J}_{cn}\frac{2n^2}{n_f}T\frac{dB}{dT} - \mathbf{J}_{cT} - \mathbf{J}_{rT}$$

$$= \left[W^2 - \frac{5}{2} - nB + nT\frac{dB}{dT}\right]\frac{\mathbf{p}-m\mathbf{v}_0}{m}f_{f1}^{le} - \mathbf{J}_{rT} + \frac{n^2\Lambda_r^6}{h^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}\frac{\mathbf{p}_{\mathrm{op}}+\mathbf{p}-m\mathbf{v}_0}{m}\left[\left(\frac{K_{\mathrm{CM}}}{kT}-5\right)U+TU_T\right], \qquad (59)$$

$$f_{f1}^{le}\mathsf{L}_v^{(2)} = \left[\mathbf{F}_v\frac{\mathbf{p}-m\mathbf{v}_0}{m} - \mathsf{J}_{cv} - \mathsf{J}_{rv}\right]^{(2)} = 2[\mathbf{W}_1]^{(2)}f_{f1}^{le} + \frac{2n^2\Lambda_r^6}{mkTh^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}[\mathbf{p}_{\mathrm{op}}+\mathbf{p}-m\mathbf{v}_0]^{(2)}U$$

$$+ \frac{in_f^2\Lambda_r^6}{2kT\hbar h^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}[V,\Omega[e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}},\mathbf{r}_{\mathrm{op}}]_+^{(2)}\Omega^\dagger]_-, \qquad (60)$$

where irreducible Cartesian tensors such as $[\mathbf{W}]^{(2)}$ are defined in Ref. 12, and

$$f_{f1}^{le}L_v^{(0)} = \frac{1}{3}\mathbf{F}_v\cdot\left(\frac{\mathbf{p}-m\mathbf{v}_0}{m}\right) - \frac{F_n}{n_f}\left[n(1+4nB)+\frac{2n^2kT}{C_v}\frac{dB}{dT}\right] - \frac{k}{C_v}F_T\left(1+nB+nT\frac{dB}{dT}\right) - \frac{1}{3}\mathsf{U}\mathbin{:}(\mathsf{J}_{cv}+\mathsf{J}_{rv})$$

$$= \frac{kf_{f1}^{le}}{C_v}\left[\left(\frac{2C_v}{3k}-1-nB-nT\frac{dB}{dT}\right)\left(W^2-\frac{3}{2}\right) - 3nB - 2nT\frac{dB}{dT}\right] - \frac{n^2k\Lambda_r^6}{C_v h^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}TU_T$$

$$+ \frac{in^2\Lambda_r^6}{6kT\hbar h^3}\mathrm{Tr}_r e^{-K_{\mathrm{CM}}/kT}[V,\Omega[e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}},\cdot\mathbf{r}_{\mathrm{op}}]_+\Omega^\dagger]_-. \qquad (61)$$

This completes the identification of the terms in the Chapman–Enskog equation (57).

The linear equation (57) is to be solved for the perturbation ϕ. According to the Fredholm alternative,[15,16] a solution exists only if the given function (left hand side of the equation) is orthogonal to the left invariants (left eigenvectors having zero eigenvalue) of $\mathscr{R}$, and to make the solution unique, some condition on the perturbation is required for each right invariant. Just as for the standard Boltzmann equation, it is first verified that the left and right invariants are the mass, momentum and (kinetic) energy. It follows easily that the left hand side of Eq. (57) is orthogonal to these invariants and the standard Chapman–Enskog method requires that the perturbation does not contribute to the mass, momentum or energy densities, see Eqs. (I.40), (I.42) and (I.45) together with Eqs. (4), thus making the solution unique.

In order to verify the invariants of $\mathscr{R}$ it is appropriate to begin by studying matrix elements of the linear superoperator $\mathscr{R}$. From the definition of inner product (58), the contribution to the collisional rate of change of observable ψ associated with perturbation ϕ is

$$\langle\langle\psi|\mathscr{R}|\phi\rangle\rangle = \frac{in^2\Lambda_r^6}{2\hbar h^3}\int d\mathbf{p}\,\mathrm{Tr}_r(\psi_1+\psi_2)e^{-K_{\mathrm{CM}}/kT}$$

$$\times[V,\Omega e^{-K_{\mathrm{rel}}/kT}(\phi_1+\phi_2)\Omega^\dagger]_-. \qquad (62)$$

Here a symmetrization of ψ between particles has been carried out. Since V commutes with the center of mass motion, the commutator can be changed into the corresponding commutator with the combination of ψ's, namely $[\psi_1+\psi_2,V]_-$. For mass and linear momentum this commutator immediately vanishes, thus these four quantities are left invariants of $\mathscr{R}$. For ψ equal to the (kinetic) energy $H^{(1)}$, the combination of ψ's is equal to the sum of center of mass and relative (kinetic) energies. The former commutes with V so can not contribute. The relative kinetic energy contribution can be written in the following form:

$$\int d\mathbf{p} \ \mathrm{Tr_r} K_{\mathrm{rel}} e^{-K_{\mathrm{CM}}/kT}[V, \Omega X \Omega^\dagger]_-$$

$$= \int d\mathbf{p} \ \mathrm{Tr_r} e^{-K_{\mathrm{CM}}/kT}[K_{\mathrm{rel}}, V]_- \Omega X \Omega^\dagger$$

$$= \int d\mathbf{p} \ \mathrm{Tr_r} e^{-K_{\mathrm{CM}}/kT}[H_{\mathrm{rel}}, V]_- \Omega X \Omega^\dagger$$

$$= -\int d\mathbf{p} \ \mathrm{Tr_r} e^{-K_{\mathrm{CM}}/kT} V[H_{\mathrm{rel}}, \Omega X \Omega^\dagger]_-$$

$$= -\int d\mathbf{p} \ \mathrm{Tr_r} e^{-K_{\mathrm{CM}}/kT} V \Omega [K_{\mathrm{rel}}, X]_- \Omega^\dagger. \tag{63}$$

Thus, if X commutes with K_{rel}, equivalently the perturbation being a function solely of the particles momentum, then the kinetic energy is a left invariant of $\mathscr{R}$. It should be emphasized that any position dependence of ϕ is to be treated as a *parameter* for the linearized collision operator, thus a constant as far as the collision is concerned. Collision nonlocality effects, which are in particular responsible for conversion between kinetic and potential energy, have already been accounted for by the presence of J_c and J_r in Eq. (31). Thus the kinetic energy provides a fifth left invariant for the linearized Boltzmann equation.

The identification of right invariants requires looking at which ϕ's give a zero contribution to the matrix element (62). For each of mass, momentum and kinetic energy, the sum of ϕ's is either constant, the center of mass momentum or the sum of center of mass and relative kinetic energies. In all cases, the Møller operators act to change the combination $e^{-K_{\mathrm{rel}}/kT}(\phi_1 + \phi_2)$ into a function of center of mass momentum and ''total'' relative (H_{rel}) energy operator. Such a quantity commutes with H_{rel}, so that for each of mass, momentum and kinetic energy, the $\mathscr{R}$ matrix element can be replaced by

$$\langle\langle \psi | \mathscr{R} | \phi \rangle\rangle = -\frac{i n^2 \Lambda_r^6}{2\hbar h^3} \int d\mathbf{p} \ \mathrm{Tr_r}(\psi_1 + \psi_2) e^{-K_{\mathrm{CM}}/kT}$$
$$\times [K_{\mathrm{rel}}, \Omega e^{-K_{\mathrm{rel}}/kT}(\phi_1 + \phi_2)\Omega^\dagger]_-. \tag{64}$$

This vanishes provided ψ is a function of momentum, since the combination of ψ's then commutes with K_{rel}. Thus, since the collision operator $\mathscr{R}$ is localized at one position and acts only to transform the momentum dependence of the Wigner function, its left and right invariants are the standard mass, momentum and kinetic energy. The possibility of a collision inhomogeneity complicates this identification. In this work this problem is overcome by explicitly expanding the inhomogeneity effects and treating them in a different manner.

As stated earlier, the solvability of the linearized Boltzmann equation (57) requires that the left hand side be orthogonal to the left invariants of $\mathscr{R}$. These requirements are now discussed. Since the equations of change for n and $\mathbf{v}_0$ have been based on the moments of Eq. (31), these equations are exactly the requirements that the left hand side of Eq. (57) be orthogonal to the left invariants. Detailed evaluation of the orthogonality conditions using the coefficients

$\mathbf{L}_T$, $\mathsf{L}_v^{(2)}$ and $L_v^{(0)}$ confirm these properties. The equation of change for the kinetic energy was not used in the elimination of the time derivatives to arrive at Eq. (57) so the orthogonality of the left hand side of Eq. (57) to the kinetic energy needs to be explicitly examined. For the kinetic energy only the $L_v^{(0)}$ orthogonality is not automatically satisfied by rotational invariance. The immediate integral of this orthogonality condition leads to

$$\int \mathbf{W}_1^2 f_{f1}^{le} L_v^{(0)} d\mathbf{p}_1 = \frac{3 n_f k}{2 C_v}\left[\frac{2 C_v}{3k} - 1 - 4 n B - 3 n T \frac{dB}{dT}\right]$$
$$- \frac{n^2 k T \Lambda_r^3}{2 C_v}\mathrm{Tr_{rel}}\left(\frac{3}{2} + \frac{K_{\mathrm{rel}}}{kT}\right) U_T$$
$$+ \frac{n^2 \Lambda_r^3}{12 m (kT)^2}\mathrm{Tr_{rel}}[\mathbf{p}_{\mathrm{op}}, \cdot \boldsymbol{\nabla} V]_+$$
$$\times \Omega [e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}}, \cdot \mathbf{r}_{\mathrm{op}}]_+ \Omega^\dagger. \tag{65}$$

After making use of the explicit form for $B(T)$, Eq. (I.A2), and retaining at most terms of second order in the density, this is simplified to

$$\int \mathbf{W}_1^2 f_{f1}^{le} L_v^{(0)} d\mathbf{p}_1 = \frac{n^2 \Lambda_r^3}{3(kT)^2}\mathrm{Tr_{rel}} V H_{\mathrm{rel}} e^{-H_{\mathrm{rel}}/kT}$$
$$+ \frac{n^2 \Lambda_r^3}{12 m (kT)^2}\mathrm{Tr_{rel}}[\mathbf{p}_{\mathrm{op}}, \cdot \boldsymbol{\nabla} V]_+$$
$$\times \Omega [e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}}, \cdot \mathbf{r}_{\mathrm{op}}]_+ \Omega^\dagger. \tag{66}$$

The identity of Appendix A shows that this combination vanishes, thus verifying that all of the orthogonality conditions are satisfied. Thus a solution to the linearized Boltzmann equation exists.

The presence of right invariants for the collision operator $\mathscr{R}$ implies that the solution ϕ to Eq. (57) is not unique. Uniqueness is obtained from the combination of auxiliary conditions (I.40), (I.42), (I.45) and (4). The auxiliary conditions (4) for the pair correlation Wigner function imply that the auxiliary conditions for ϕ reduce to the requirements that ϕ be orthogonal to mass, momentum and kinetic energy, namely the right invariants of $\mathscr{R}$. For the mass, this is an immediate consequence of Eqs. (4) and (I.40). For the momentum, the second equation in the set of Eq. (4) does not eliminate the total contribution of Φ to Eq. (I.42). But the specific form chosen for Φ [only the vector part, $\mathbf{A}_c$, could contribute to a momentum expectation value], see Eq. (28), gives no contribution to Eq. (I.42). Finally, to obtain the condition for the kinetic energy from Eq. (I.45), it is recognized that the independent particle contribution to the potential energy

$$\int \int \int V_{12} f_{f1}^{le} f_{f2}^{le}(\phi_1 + \phi_2) d\mathbf{r}_{12} \ d\mathbf{p}_1 \ d\mathbf{p}_2 \tag{67}$$

vanishes because of the separate auxiliary conditions (I.40) for ϕ_1 and ϕ_2 [after subtracting the appropriate correlation condition of Eq. (4)].

The auxiliary conditions imply certain constraints on the possible forms for **A**, B and C, in the gradient expansion (I.26) of ϕ. In particular the vector **A** is affected only by the momentum constraint, while the scalar C is affected by both the number density and energy constraint. These constraints are identical to those appearing in dilute gas kinetic theory,[3] or more comparably to those for a previous classical treatment[17] of moderately dense gas kinetic theory. As in that treatment, only the lowest order Sonine polynomials that are necessary to approximate the perturbation ϕ will be retained in this work. Thus the expansion functions are approximated by

$$\mathbf{A} = a_1 \mathbf{W}(\tfrac{5}{2} - W^2),$$

$$\mathsf{B} = b_0 [\mathbf{W}]^{(2)},$$

$$C = c_2(\tfrac{15}{8} - \tfrac{5}{2} W^2 + \tfrac{1}{2} W^4), \qquad (68)$$

having unknown coefficients a_1, b_0 and c_2.

The Chapman–Enskog equation (57) together with the form of the perturbation function (I.26) can be split into three equations according to the three different gradients. This gives separate equations for each of **A**, B and C. The magnitude a_1 of $\mathbf{A} = A\mathbf{W}$ is found by taking the component of the **A** equation along the **A** direction, thus

$$X_\lambda \equiv \int d\mathbf{p}(W^2 - \tfrac{5}{2})\mathbf{W} \cdot f_f^{le} \mathbf{L}_T$$

$$= -a_1 \langle\langle \mathbf{W}(W^2 - \tfrac{5}{2}) \cdot |\mathscr{R}|\mathbf{W}(W^2 - \tfrac{5}{2})\rangle\rangle$$

$$\equiv -\tfrac{15}{4} n_f^2 a_1 \bar{v} \mathfrak{S}_\lambda, \qquad (69)$$

where $\bar{v} \equiv \sqrt{16kT/\pi m}$ is the mean velocity of relative motion and $\mathfrak{S}_\lambda$ is the appropriate "kinetic" cross section for thermal conductivity λ. The driving term X_λ can be partially evaluated. After some simplification, this can be written as, neglecting terms of order n^3,

$$X_\lambda = \frac{15}{4}\sqrt{\frac{2kT}{m}} n_f + \frac{5 n_f^2 \Lambda_r^3}{4}\sqrt{\frac{kT}{2m}} \mathrm{Tr}_{\mathrm{rel}}\left[\left(\gamma^2 - \frac{3}{2}\right)TU_T\right.$$

$$-\left(\frac{5}{2}\gamma^2 - \frac{21}{4}\right)U\right] + \frac{in_f^2 \Lambda_r^3}{8\hbar\sqrt{2mkT}}\mathrm{Tr}_{\mathrm{rel}}[\gamma^2 \mathsf{U}$$

$$+ 2\mathscr{GG}, V]_- : \Omega[e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}}, \mathbf{r}_{\mathrm{op}}]_+ \Omega^\dagger. \qquad (70)$$

The equation for B reduces to an equation for the scalar b_0,

$$X_\eta \equiv \int d\mathbf{p}[\mathbf{W}]^{(2)} : \mathsf{L}_v^{(2)} f_f^{le}$$

$$= b_0 \langle\langle [\mathbf{W}]^{(2)} : |\mathscr{R}|[\mathbf{W}]^{(2)}\rangle\rangle \equiv \tfrac{5}{2} n_f^2 b_0 \bar{v} \mathfrak{S}(20). \qquad (71)$$

Since the polarization is the same here as in the dilute gas case, the cross section for viscosity is written in standard[7]

notation as $\mathfrak{S}(20)$. For the determination of b_0, there remains only the reduction of X_η to simpler form. This is accomplished in the same manner as previous reductions, to give

$$X_\eta = 5n_f(1 - n_f B) + \frac{n_f^2 \Lambda_r^3}{4m(kT)^2}$$

$$\times \mathrm{Tr}_{\mathrm{rel}}[\mathbf{p}, \boldsymbol{\nabla} V]_+^{(2)} : \Omega[e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}}, \mathbf{r}_{\mathrm{op}}]_+^{(2)} \Omega^\dagger. \qquad (72)$$

Finally, for the calculation of c_2, there is the determining equation

$$X_\kappa \equiv \int d\mathbf{p}(\tfrac{15}{8} - \tfrac{5}{2} W^2 + \tfrac{1}{2} W^4) f_f^{le} L_v^{(0)}$$

$$= c_2 \langle\langle (\tfrac{15}{8} - \tfrac{5}{2} W^2 + \tfrac{1}{2} W^4)|\mathscr{R}|(\tfrac{15}{8} - \tfrac{5}{2} W^2 + \tfrac{1}{2} W^4)\rangle\rangle$$

$$\equiv \tfrac{15}{8} c_2 n_f^2 \bar{v} \mathfrak{S}_\kappa. \qquad (73)$$

The driving term to order n^2 is calculated to be

$$X_\kappa = -\frac{n_f^2 \Lambda_r^3}{12}\mathrm{Tr}_{\mathrm{rel}}\left(\gamma^4 - 5\gamma^2 + \frac{15}{4}\right)TU_T + \frac{in_f^2 \Lambda_r^3}{48\hbar kT}$$

$$\times \mathrm{Tr}_{\mathrm{rel}}[\gamma^4 - 5\gamma^2, V]_- \Omega[e^{-K_{\mathrm{rel}}/kT}\mathbf{p}_{\mathrm{op}}, \cdot\mathbf{r}_{\mathrm{op}}]_+ \Omega^\dagger. \qquad (74)$$

Here $\boldsymbol{\gamma} \equiv \mathbf{p}_{\mathrm{op}}/\sqrt{mkT}$ is the dimensionless relative momentum operator. This completes a listing and reduction of all the quantities for a first order approximation of the perturbation expansion coefficients a_1, b_0 and c_2.

IV. TRANSPORT COEFFICIENTS

Density operator expressions for the heat flux and pressure tensor are given in Sec. IV of Ref. 2. Specifically the pressure tensor arises by means of kinetic and collisional transfer mechanisms while the heat flux has the additional contribution of a potential energy flux. As well, the kinetic contributions involve both free and correlated pair particle effects. From the standard dilute gas kinetic theory point of view, fluxes are expanded in powers of the spatial inhomogeneity. For a locally homogeneous system there is no heat flux but there is a local equilibrium pressure. It is the object of the present section to obtain expressions for these quantities. The present estimates are made assuming there is only one temperature $T_f = T_c = T$ and stream velocity $\mathbf{v}_f = \mathbf{v}_c = \mathbf{v}_0$, with the correlation density $n_c = n_f^2 \Lambda_r^3 \mathrm{Tr}_{\mathrm{rel}}U$ parameterizing the local equilibrium with the free particle density n_f. This appears appropriate since it is noticed from Sec. II that all conditions can be satisfied with these equalities, equivalently that there are no constraints requiring different temperatures or mean velocities for the free and pair correlations, or out of equilibrium pair correlation density.

The kinetic pressure tensor is calculated according to

$$\mathsf{P}^K = 2kT \int \mathbf{W}\mathbf{W} f^{(1)} d\mathbf{p} = \left(nkT + \frac{1}{3} n_f^2 kT\varepsilon_1 \right) \mathsf{U}$$

$$+ 2n_f kT \int \mathbf{W}\mathbf{W} \frac{e^{-W^2}}{\pi^{3/2}} \phi d\mathbf{W}$$

$$+ 2n_f^2 kT\Lambda_r^3 \int d\mathscr{G} \mathrm{Tr}_{\mathrm{rel}} \frac{e^{-\mathscr{G}^2}}{\pi^{3/2}} \mathbf{W}_1 \mathbf{W}_1 U\Phi_c$$

$$= P^K \mathsf{U} - 2\eta_K [\boldsymbol{\nabla}\mathbf{v}_0]^{(2)} - \kappa_K \boldsymbol{\nabla}\cdot\mathbf{v}_0 \mathsf{U}, \qquad (75)$$

to give contributions η_K and κ_K to the shear and bulk viscosity coefficients. On identifying the coefficients of $[\boldsymbol{\nabla}\mathbf{v}_0]^{(2)}$ and $\boldsymbol{\nabla}\cdot\mathbf{v}_0$ and simplifying the resulting expressions, the kinetic contributions to the shear and bulk viscosity coefficients become

$$\eta_K = \tfrac{1}{2} kT [n_f b_0 + \tfrac{1}{2} n_c b_0^c] \qquad (76)$$

and

$$\kappa_K = \frac{2n_c kTc_0^c}{3C_{\mathrm{corr}}} C_U^V. \qquad (77)$$

Here the heat capacity $C_U^V = d\varepsilon_U^V/dT$ associated with the potential energy $\varepsilon_U^V \equiv \tfrac{1}{2}\mathrm{Tr}_{\mathrm{rel}} VU/\mathrm{Tr}_{\mathrm{rel}} U$ per particle for the pair correlations has been introduced. The collisional transfer part of the pressure tensor reduces to

$$\mathsf{P}_{\mathrm{coll}} = P_{\mathrm{virial}} \mathsf{U} - 2\eta_{\mathrm{coll}} [\boldsymbol{\nabla}\mathbf{v}_0]^{(2)} - \kappa_{\mathrm{coll}} \boldsymbol{\nabla}\cdot\mathbf{v}_0 \mathsf{U} \qquad (78)$$

with virial pressure $P_{\mathrm{virial}} = n_f^2 kT(B - \varepsilon_1/3)$, shear viscosity

$$\eta_{\mathrm{coll}} = \frac{n_f^2 \Lambda_r^3}{40kT} \mathrm{Tr}_{\mathrm{rel}} [\mathbf{r}_{\mathrm{op}} \boldsymbol{\nabla} V]^{(2)} : \Omega [e^{-K_{\mathrm{rel}}/kT} \mathbf{p}_{\mathrm{op}}, \mathbf{r}_{\mathrm{op}}]_+ \Omega^\dagger$$

$$- b_0 \frac{n_f^2 \Lambda_r^3}{20} \mathrm{Tr}_{\mathrm{rel}} [\mathbf{r}_{\mathrm{op}} \boldsymbol{\nabla} V]^{(2)} : \Omega e^{-K_{\mathrm{rel}}/kT} [\boldsymbol{\gamma}]^{(2)} \Omega^\dagger, \qquad (79)$$

and bulk viscosity

$$\kappa_{\mathrm{coll}} = \frac{n_f^2 \Lambda_r^3}{36kT} \mathrm{Tr}_{\mathrm{rel}} \mathbf{r}_{\mathrm{op}} \cdot \boldsymbol{\nabla} V \Omega [e^{-K_{\mathrm{rel}}/kT} \mathbf{p}_{\mathrm{op}}, \cdot\mathbf{r}_{\mathrm{op}}]_+ \Omega^\dagger - \frac{n_f^2 \Lambda_r^3}{24}$$

$$\times c_2 \mathrm{Tr}_{\mathrm{rel}} \mathbf{r}_{\mathrm{op}} \cdot \boldsymbol{\nabla} V e^{-H_{\mathrm{rel}}/kT} \left[\frac{H_{\mathrm{rel}}^2}{(kT)^2} - 5\frac{H_{\mathrm{rel}}}{kT} + \frac{15}{4} \right]. \qquad (80)$$

The kinetic heat flux vector is

$$\mathbf{q}^K = \sqrt{\frac{2kT}{m}} kT \int d\mathbf{p} \, \mathbf{W}W^2 f_f^{le} \phi + \sqrt{\frac{2kT}{m}} kT$$

$$\times \int d\mathbf{P} \, \mathrm{Tr}_{\mathrm{rel}} \mathbf{W}_1 W_1^2 f_{c12}^{le} \Phi_{c12} = -\lambda_K \boldsymbol{\nabla} T \qquad (81)$$

with kinetic contribution to the thermal conductivity

$$\lambda_K = -\frac{5}{4} n_f k \sqrt{\frac{2kT}{m}} a_1 + \frac{5}{8} n_c k \sqrt{\frac{kT}{m}} a_1^c \left[1 + \frac{4}{3} \frac{\mathrm{Tr}_{\mathrm{rel}} K_{\mathrm{rel}} U_T}{kT\mathrm{Tr}_{\mathrm{rel}} U} \right], \qquad (82)$$

while the collisional heat flux

$$\mathbf{q}_{\mathrm{coll}} = -\lambda_{\mathrm{coll}} \boldsymbol{\nabla} T \qquad (83)$$

has thermal conductivity contribution

$$\lambda_{\mathrm{coll}} = \frac{n_f^2 \Lambda_r^3}{24T} \mathrm{Tr}_{\mathrm{rel}} \mathbf{r}_{\mathrm{op}} \boldsymbol{\nabla} V : \Omega [e^{-K_{\mathrm{rel}}/kT} \mathbf{p}_{\mathrm{op}}, \mathbf{r}_{\mathrm{op}}]_+ \Omega^\dagger$$

$$- \frac{ka_1}{2\sqrt{2mkT}} \left[T\frac{dP_{\mathrm{virial}}}{dT} - P_{\mathrm{virial}} \right.$$

$$\left. - \frac{n_f^2 \Lambda_r^3}{3} \mathrm{Tr}_{\mathrm{rel}} \mathbf{r}_{\mathrm{op}} \boldsymbol{\nabla} V : \Omega e^{-K_{\mathrm{rel}}/kT} \mathscr{G}\mathscr{G}\Omega^\dagger \right]. \qquad (84)$$

Finally, the potential energy heat flux

$$\mathbf{q}^V = \frac{1}{2} n_f^2 \Lambda_r^3 \sqrt{\frac{kT}{m}} \mathrm{Tr}_{\mathrm{rel}} \int d\mathscr{G} \frac{e^{-\mathscr{G}^2}}{\pi^{3/2}} \mathscr{G} V$$

$$\times [e^{-K_{\mathrm{rel}}/kT}(\phi_1 + \phi_2) + U\Phi_{c12}]$$

$$= -\lambda_V \boldsymbol{\nabla} T \qquad (85)$$

has thermal conductivity contribution

$$\lambda_V = -\frac{5}{12} n_f^2 \Lambda_r^3 a_1 \sqrt{\frac{k}{2mT}} \mathrm{Tr}_{\mathrm{rel}} V e^{-K_{\mathrm{rel}}/kT} \left(\frac{K_{\mathrm{rel}}}{kT} - \frac{3}{2} \right)$$

$$+ \frac{1}{2} n_c \sqrt{\frac{kT}{m}} C_U^V a_1^c. \qquad (86)$$

Several different contributions to the transport coefficients have been found. Collected together, the shear viscosity is

$$\eta = \eta_K + \eta_{\mathrm{coll}}, \qquad (87)$$

with detailed formulae given by Eqs. (76) and (79). For the bulk viscosity,

$$\kappa = \kappa_K + \kappa_{\mathrm{coll}}, \qquad (88)$$

with formulae Eqs. (77) and (80). Finally, for the thermal conductivity,

$$\lambda = \lambda_K + \lambda_{\mathrm{coll}} + \lambda_V, \qquad (89)$$

with formulae from Eqs. (82), (84) and (86).

V. DISCUSSION

A recently proposed[1] density corrected quantum Boltzmann equation emphasizes the distinction between free particle and pair correlation effects. The singlet density operator is influenced by both effects. The free density operator is determined by solving the quantum Boltzmann equation while a separate equation (I.17) based on the second BBGKY equation has been introduced[2] for the determination of the operator describing the pair correlations. In unpublished work, a formal solution of that equation involving a long time limit, specifically a generalization of Eq. (I.3), was used for the pair correlations but had the consequence that the derived expressions for the transport coefficients did not reduce at low density to those associated with the solution of the dilute gas Boltzmann equation. Thus it was considered that an alternate method for solving equation (I.17) for the pair correlations was needed. Section II has cast this equation into Wigner function form, linearized it about local equilib-

rium and solved it in a Chapman–Enskog manner. The quantum Boltzmann equation (I.2) was treated in the same manner in Section III. In general these equations would have to be solved simultaneously but using the simplest form for the perturbation functions, the equations uncouple and can be solved independently. Expressions for the transport coefficients consistent with these solutions were given in Section IV. A comparison of these expressions with the classical mechanical results[17,18] obtained from solving the classical Boltzmann equation with nonlocal collision corrections first obtained by Green[19] and Bogoliubov[20] is given in the following paragraphs. Rainwater[23] has also considered the reduction of the quantum formalism to the classical. His starting point is the quantum treatment by Thomas and Snider[13] so it does not have the pair correlation effects as presented in this work.

The classical treatment[17,18] had no separate equations for the pair correlations so all transport coefficients in that work are expressed in terms of the solution of the Boltzmann equation. In both treatments the solution of the Boltzmann equation is parameterized by the three expansion coefficients a_1, b_0 and c_2. Reduction of the quantum expressions (69)–(74) to their classical limit gives exact agreement with the classical result. It should be stated that many of the classical results are partly expressed in terms of the second virial coefficient $B(T)$ and its temperature derivatives. To arrive at such expressions, it was assumed that the intermolecular potential supported no bound states and is moreover monotonically repulsive, so this also is an input into the comparison. Thus the present solution of the quantum Boltzmann equation is the quantum analog of the classical solution. This is reasonable since the two equations express the same essential features. Where they might have disagreed would be in the presence of the pair correlations. But these only appear in the quantum Chapman–Enskog equation (57) through their local equilibrium contribution to the singlet Wigner function, which essentially reduces classically to part of the local Maxwellian distribution. As a consequence, no difference arises when the quantum solution is reduced to the classical.

Comparison of the expressions for the transport coefficients is not so straightforward. Expressions (77) and (80) for the bulk viscosity are easiest to compare. The classical treatment has no c_0^c so there is no kinetic contribution to the bulk viscosity for spherical particles. Moreover, the quantum collisional contribution to the bulk viscosity reduces in the classical limit to the result in Ref. 18. Since the bulk viscosity measures the transfer of energy from one form of energy to another, the presence of pair correlations provides a possibility for such energy exchange while the classical treatment had no such possibility. Thus the difference in κ_K is a reasonable result.

The present treatment has kinetic contributions to the shear viscosity, Eq. (76), from both the free density operator (Boltzmann equation) and the pair correlations while the classical treatment has no extra pair correlation structure. Simply setting $b_0^c = 0$ does not lead to agreement since in the present treatment b_0 is multiplied by the free density while in the classical case the full gas density appears. Agreement is

obtained if it is assumed that $b_0^c = 2b_0$, with a possible rationale that the pair correlations involve the effect of two particles, thus the perturbation should be twice as big as the free. The quantum expression for the collisional contribution to the shear viscosity reduces to the classical expression given in Ref. 18 except that the expression for $H_\lambda + R_\lambda$ of that work should have a factor of 2 multiplying the ''Y'' contribution to this quantity. This missing 2 is an error in that paper. Since its contribution to the shear viscosity (and thermal conductivity) is second order in the gas density, this factor appears to not yet have been numerically used in the calculation of the transport coefficients, for example, in Refs. 21 and 23.

Finally is the comparison of expressions for the thermal conductivity. These are quite different in structure. First is the kinetic contribution λ_K. This can be made to agree with the classical expression if $a_1^c = -2a_1$, compare the discussion of the shear viscosity, together with ignoring the correction factor in Eq. (82) involving U_T. The classical limit of Eq. (84) gives, in the notation of Ref. 18,

$$\lambda_{\text{coll}}|_{\text{class}} = \frac{1}{3} n_f^2 k \sigma^3 \sqrt{\pi m k T} (H_\lambda + R_\lambda)$$
$$- \frac{1}{4} n^2 k \sqrt{\frac{2kT}{m}} a_1 \left[T \frac{dB}{dT} - \frac{4\pi\sigma^3}{3} N_\lambda \right]. \quad (90)$$

[Note the error in $H_\lambda + R_\lambda$ mentioned above.] This contains part of the density corrections in Eq. (26) of Ref. 18 for the thermal conductivity. A direct classical reduction of Eq. (86) gives zero for the first term and the second term does not correspond to terms found in the classical treatment. The main new element here is that the potential energy cannot be derived from the Boltzmann equation but involves a separate calculation using the pair density operator (classically the pair distribution function). In the classical treatment the pair distribution function was calculated using the Green-Bogoliubov procedure of following a pair of free particles into the collision regime, just as was done for the binary collision term. The quantum analog is to set the pair density operator equal to

$$\rho_{12}^{(2)} = \Omega \rho_{f1} \rho_{f2} \Omega^\dagger, \quad (91)$$

compare the collision term in the Boltzmann equation (I.2). Within a linear-in-gradients evaluation of the potential heat flux, the localization of the pair of interacting particles can be placed at the center of mass of the pair, see the first two lines of Eq. (I.50). Inserting the above expression for the pair density operator into the potential heat flux equation gives contributions both from the perturbation functions $\phi_1 + \phi_2$ and from the different localizations of the free singlet density operators. After taking the classical limit, the latter gives the I_λ term in Eq. (26) of Ref. 18 while the former can be completely expressed in terms of the second virial coefficient (for monotonic repulsive potentials), thus

$$\lambda_V|_{\text{class}} = \frac{5 n_f^2 a_1 k}{6} \sqrt{\frac{kT}{2m}} \left[2T \frac{dB}{dT} + T^2 \frac{d^2 B}{dT^2} \right]$$

$$-\frac{n^2 k \sigma^4}{3}\sqrt{\frac{\pi kT}{m}}I_\lambda. \qquad (92)$$

With this change in interpretation of how to estimate the potential heat flux, the combination $\lambda_K + \lambda_{\text{coll}} + \lambda_V$ reduces to the classical expression for the thermal conductivity. [Note that T_λ is given with an overall wrong sign, in Eq. (30) of Ref. 18, which was first noted by Bennett and Curtiss.[21]]

From the above discussion it is seen that the present treatment of the kinetic theory of a moderately dense quantum gas has similarities to the previous classical treatment. The explicit need in quantum mechanics to account for pair correlation corrections to the singlet density operator vanishes in the classical limit and all other quantities in the quantum Boltzmann equation have classical analogs. It is in the evaluation of expectation values where the distinction between the treatments arises. In the present quantum treatment, the Boltzmann equation determines only the non (local-)equilibrium part of the free density operator, so that it is necessary, even for one particle observables, to calculate the nonequilibrium part of the pair correlations so that their contribution to all expectation values may be obtained. The present treatment has considered these pair correlation effects to be somewhat diffusive, long ranged effects rather than as hard, short ranged collision type effects. Thus a separate equation for the pair correlations has been proposed, and solved within the Chapman–Enskog approach. In contrast, the earlier classical treatment used the same collisional ansatz, the classical limit of Eq. (91), for the full pair distribution function as for the collision term in the Boltzmann equation, which reflects hard, percussive collisions. But in ending this discussion, it is emphasized that the two approaches are not all that different. While it is the linearization, Eq. (13), of the pair correlation equation (I.17) within the Chapman–Enskog procedure that is used in this work, if the three particle decay effects are ignored, then it is easy to integrate the pair correlation equation to give Eq. (I.3), see Appendix B, a result consistent with Eq. (91). This approach was not followed in the present treatment since it was found that the resulting pair correlation density operator was unbounded if the free singlet density operator is parameterized with a position dependent temperature and stream velocity.

It is remarked that the classical kinetic theory of moderately dense gases has been extended in a number of ways so it is not as limited as the above discussion may imply. The generalization to include non-monotonic intermolecular potentials has been carried out by Rainwater.[9] In cooperation with co-workers[22] he has also approximately incorporated the role of three particle collisions and the presence of bound states. These papers should be referred to for a detailed discussion of the methods and literature of the approaches that they use.

ACKNOWLEDGMENTS

APPENDIX A: A TRACE IDENTITY

It is to be shown that in the absence of bound states

$$Z \equiv \frac{-1}{4m}\text{Tr}_{\text{rel}}[\mathbf{p}_{\text{op}},\cdot\boldsymbol{\nabla}V]_+ \Omega[e^{-K_{\text{rel}}/kT}\mathbf{p}_{\text{op}},\cdot\mathbf{r}_{\text{op}}]_+\Omega^\dagger$$

$$= \text{Tr}_{\text{rel}}VHe^{-H_{\text{rel}}/kT}. \qquad (A1)$$

The first anticommutator is identified as the result of the commutator

$$[K_{\text{rel}},V]_- = \frac{\hbar}{im}[\mathbf{p}_{\text{op}}\cdot\boldsymbol{\nabla}V + \boldsymbol{\nabla}V\cdot\mathbf{p}_{\text{op}}], \qquad (A2)$$

which can be further written as $[H_{\text{rel}},V]_-$ since the commutator of V with itself vanishes. Inserting this relation into Eq. (A1) and using the cyclic invariance of the trace to flip the commutator gives

$$Z = \frac{i}{4\hbar}\text{Tr}_{\text{rel}}V[H_{\text{rel}},\Omega[e^{-K_{\text{rel}}/kT}\mathbf{p}_{\text{op}},\cdot\mathbf{r}_{\text{op}}]_+\Omega^\dagger]_-$$

$$= \frac{i}{4\hbar}\text{Tr}_{\text{rel}}V\Omega[K_{\text{rel}},[e^{-K_{\text{rel}}/kT}\mathbf{p}_{\text{op}},\cdot\mathbf{r}_{\text{op}}]_+]_-\Omega^\dagger, \qquad (A3)$$

with the second equality arising from the intertwining relation when there are no bound states. Now the K_{rel} commutator affects only $\mathbf{r}_{\text{op}}$ according to

$$[K_{\text{rel}},\mathbf{r}_{\text{op}}]_- = \frac{2\hbar}{im}\mathbf{p}_{\text{op}}. \qquad (A4)$$

Z now reduces to

$$Z = \tfrac{1}{2}\,\text{Tr}_{\text{rel}}V\Omega[e^{-K_{\text{rel}}/kT}2K_{\text{rel}}]\Omega^\dagger. \qquad (A5)$$

Finally the intertwining relation changes any function of K_{rel} into the corresponding function of H_{rel}. The unitarity of Ω in the absence of bound states implies that $\Omega\Omega^\dagger = 1$ resulting in the equality that was to be proven.

APPENDIX B: COLLISIONAL INTEGRATION OF THE PAIR CORRELATION EQUATION

Without the relaxation term, Eq. (I.17) takes the form

$$i\frac{\partial\rho_{c12}}{\partial t} = \mathscr{L}_{12}^{(2)}\rho_{c12} + \mathscr{V}_{12}\rho_{f1}\rho_{f2}. \qquad (B1)$$

This can immediately be formally integrated to

$$\rho_{c12}(t) = e^{-i\mathscr{L}_{12}^{(2)}(t-t_0)}\rho_{c12}(t_0)$$

$$-i\int_{t_0}^t e^{-i\mathscr{L}_{12}^{(2)}(t-t')}\mathscr{V}_{12}\rho_{f1}(t')\rho_{f2}(t')dt'. \qquad (B2)$$

If the time t_0 is taken so that the pair of particles are far apart, before interaction, then it is appropriate to set

$\rho_{c12}(t_0) = 0$. Moreover, if the presence of other particles is ignored, then the free density operators evolve freely over the time interval $t_0 \to t$, that is,

$$\rho_{f1}(t') = e^{-i\mathscr{L}_1^{(1)}(t'-t)}\rho_{f1}(t). \tag{B3}$$

Then the integral can be carried out

$$\rho_{c12}(t) = -\rho_{f1}(t)\rho_{f2}(t) + e^{-i\mathscr{L}_{12}^{(2)}(t-t_0)}$$
$$\times e^{-i(\mathscr{L}_1^{(1)}+\mathscr{L}_2^{(1)})(t_0-t)}\rho_{f1}(t)\rho_{f2}(t). \tag{B4}$$

Finally, if the time interval $t-t_0$ can be taken large compared to the time of duration of a collision, the product of evolution superoperators can be approximated by the Møller superoperator and Eq. (I.3) is obtained.

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