

Boltzmann Equation and Angular Momentum Conservation

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The form of the Boltzmann equation presently being used to describe phenomena dependent upon the internal angular momentum states of molecules in the gas phase is inconsistent in that angular momentum is not conserved. Thus, the internal angular momentum relaxation is correctly described by this equation but the resulting production of angular momentum in the translational degrees of freedom just does not appear at all. This work is aimed at extending the Boltzmann equation to give a consistent description of all conserved quantities. It is shown that this is not a trivial matter and that some truncation of an expansion in position gradients is required. The simplest choice is discussed. In the development, a central role is played by sum rules which arise from the assumed localized nature of the intermolecular potential.

KEY WORDS: Boltzmann equation; conservation laws; nuclear magnetic relaxation; gaseous state; Wigner distribution function; density matrix; transport phenomena; angular momentum.

1. INTRODUCTION

For simple fluids, the equations of change for the various hydrodynamic densities, such as mass, momentum, and energy, can be readily derived from the Boltzmann equation. However, complications arise if the molecules of the fluid possess internal angular momentum. For such a system, it is possible to define a local internal angular momentum density $\mathbf{s}(\mathbf{r}, t)$. The equation of change of $\mathbf{s}(\mathbf{r}, t)$ and the resulting irreversible thermodynamics of such a system have been discussed by several authors. In particular, Curtiss⁽¹⁾ developed a kinetic theory for a dilute gas of rigid nonspherical molecules in which, because of the localized nature of the collision operator, no coupling between internal angular momentum and the angular momentum of fluid flow occurs. On the other hand, the standard text by De Groot and Mazur⁽²⁾ on

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irreversible thermodynamics discusses the coupling of internal and fluid-flow angular momentum but ignores the possibility of internal angular momentum flux. The earlier articles by Grad⁽³⁾ do, in fact, consider a general statistical-mechanical formulation for both the internal angular momentum flux and the coupling between internal and fluid-flow angular momentum. Quite recently, Snider and Lewchuk⁽⁴⁾ have discussed quite generally the equations of motion and the irreversible thermodynamics of a one-component fluid whose molecules possess internal angular momentum. In the absence of any external force or torque, their equation of change for the internal angular momentum density (or spin density, if spin states are involved) is

$$\rho \left(\frac{D}{Dt} \mathbf{s}(\mathbf{r}, t) \right) = -\nabla \cdot \mathbf{L} - 2\mathbf{P}^a \quad (1)$$

where ρ is the fluid density, \mathbf{L} is the conductive spin flux tensor, and \mathbf{P}^a is the pseudo-vector equivalent to the antisymmetric part of the pressure tensor P , namely $\mathbf{P}^a = -\frac{1}{2}\epsilon : P$. Here, ϵ is the completely antisymmetric, isotropic third-rank tensor.⁽⁵⁾ Finally, D/Dt is the substantial time derivative

$$D/Dt \equiv \partial/\partial t + \mathbf{v}_0 \cdot \nabla \quad (2)$$

Equation (1) shows that, in general, there is a spin-relaxation term arising from the antisymmetric part of the pressure tensor.

To obtain the correct equation of change for the internal angular momentum, it is necessary, then, to utilize a Boltzmann equation which can have a nonsymmetric pressure tensor. Moreover, as the internal degrees of freedom (such as spin or rotation) must be treated quantum-mechanically at ordinary temperatures, it is necessary to use a quantum-mechanical Boltzmann equation. For such a system, the appropriate function to describe the fluid consists of a set of one-particle Wigner distribution functions, one for each of the terms in a matrix of internal states, i.e., a Wigner-distribution-function density matrix $f(\mathbf{r}, \mathbf{p}, t)$ which is a distribution function in position-momentum space and a density operator ("matrix") in internal-state space. Since the internal states are degenerate (e.g., spin or rotation), it is necessary to use the full density-matrix formalism for these states. A quantum-mechanical Boltzmann equation which is appropriate for describing degenerate internal states has been derived by Waldmann⁽⁶⁾ and independently by Snider.⁽⁷⁾ Unfortunately, the pressure tensor as derived from this Waldmann-Snider (W-S) equation is symmetric (see, e.g., McCourt⁽⁸⁾). To obtain the correct equation of change for the spin density, Hess and Waldmann⁽⁹⁾ phenomenologically added an appropriate term containing the vorticity to this equation so that the Barnett effect is correctly described. Again by phenomenology, they identify the antisymmetric part of the pressure tensor from this spin equation and add this to the kinetic pressure tensor obtained from the W-S equation. In a later paper, Hess⁽¹⁰⁾ also obtains a spin relaxation from a generalized Boltzmann equation having a nonlocal collision term. This is identified by making a moment expansion of $f(\mathbf{r}, \tau, t)$ about total equilibrium (uniform gas). It should be mentioned that Grad⁽³⁾ had previously noted that the antisymmetric part of the pressure tensor arises only from collisional momentum transfer and thus appears as a dense-gas correction to the hydrodynamic equations.

The present paper begins with a nonlocal collision term, here called the generalized Boltzmann equation (Section 2), while approximate localizations of the collision term are considered in Section 3. This involves position-gradient contributions to the collision term. In particular, the linearly extended W-S equation has the usual W-S collision term plus two corrections each linear in position gradients. These latter terms reduce in special cases to the corrections of Hoffmann *et al.*⁽¹¹⁾ and to the terms in the Boltzmann-Landau equation recently derived by Baerwinkel and Grossmann.⁽¹²⁾ The contributions of the correction terms to the fluxes and productions of mass, linear momentum, energy, and internal angular momentum are discussed in Section 4. It is found that neither the W-S equation nor the linearly extended W-S equation gives a consistent set of equations of change for these quantities, in the sense that they are not in agreement with the equations of fluid dynamics. In the discussion (Section 5), a suggestion is made for choosing an extended W-S equation which is consistent with fluid dynamics, namely to keep one of the two linear-in-gradients corrections, but not the other. A gas obeying this latter equation is not ideal, that is, the gas has a second virial coefficient.

2. GENERALIZED BOLTZMANN EQUATION AND THE LOCALITY SUM RULE

For completeness, the fundamental equations used in deriving the usual W-S equation are repeated here. For a system of N identical particles (Boltzmann statistics will be used) the von Neumann equation can be written as

$$i\hbar \partial \rho / \partial t = L^{(N)} \rho^{(N)} \quad (3)$$

where $\rho^{(N)}(1, 2, \dots, N)$ is the N -particle density operator normalized to $N!$ and $L^{(N)}$ is the N -particle superoperator "commutator of $H^{(N)}$ with." The Hamiltonian $H^{(N)}$ is taken to be

$$H^{(N)} = \sum_{i=1}^N H^{(1)}(i) + \frac{1}{2} \sum_{i \neq j} V_{ij} \quad (4)$$

where $H^{(1)}(i)$ is the one-particle Hamiltonian acting on the i th particle and V_{ij} is the short-range potential responsible for collision between the i th and j th particles. Since the particles are identical, reduced density operators $\rho^{(M)}(1, 2, \dots, M)$ can be defined in M -particle space ($M < N$). The first BBGKY equation can then be written (for particle 1) as

$$i\hbar \partial \rho(1) / \partial t - [H^{(1)}(1), \rho^{(1)}(1)]_- = \text{Tr}_{(2)} [V\{1, 2\}, \rho^{(2)}(1, 2)]_- \quad (5)$$

with normalization $\text{Tr}_{(1)} \rho^{(1)}(1) = N$, $\text{Tr}_{(1,2)} \rho^{(1)}(1, 2) = N(N-1)$. The hierarchy is then truncated by choosing the two-particle density operator to be a functional of the one-particle density operators. Snider⁽⁷⁾ has shown that, for a short-range potential and a dilute gas, a reasonable choice for the two-particle density operator is

$$\rho(1, 2) = \Omega(1, 2) \rho^{(1)}(1) \rho^{(1)}(2) \Omega^+(1, 2) \quad (6)$$

where $\rho^{(1)}$ is the single-particle density operator and $\Omega(1, 2)$ is the Moeller wave operator, which transforms free-particle states into scattering states. It can be formally defined as the strong operator limit

$$\Omega(1, 2) = \lim_{t \rightarrow -\infty} \exp[iH^{(2)}(1, 2)t] \exp[-iK(1, 2)t] \quad (7)$$

where $H^{(2)}(1, 2)$ is the total two-particle Hamiltonian (including the interaction potential) and $K(1, 2) = H^{(1)}(1) + H^{(1)}(2)$ is the "free-particle" Hamiltonian for two particles. Further, $\Omega^\dagger(1, 2)$ is the adjoint of $\Omega(1, 2)$. Finally, Eq. (6) is substituted into Eq. (5) to give the generalized Boltzmann equation for the singlet density operator $\rho^{(1)}(1)$ for particle 1,

$$i\hbar \partial \rho^{(1)}(1) / \partial t - [H^{(1)}(1), \rho^{(1)}(1)]_- = \text{Tr}_{(2)} [V(1, 2), \Omega(1, 2) \rho^{(1)}(1) \rho^{(1)}(2) \Omega^\dagger(1, 2)]_- \quad (8)$$

Equation (8) is identical to Eq. (23) of Ref. 6 and is the starting point for the derivation of the usual W-S equation. The basic difference is that the collision term, right-hand side, of Eq. (8) is nonlocal, while the W-S collision term is localized and more conveniently expressed in terms of the Wigner distribution function. Equation (8) can also be expressed in terms of the corresponding Wigner distribution function by making a Weyl correspondence between $\rho^{(1)}$ and $f(\mathbf{r}, \mathbf{p}, t)$, namely

$$f(\mathbf{r}, \mathbf{p}, t) = (1/\hbar)^3 \int \exp(i\mathbf{q} \cdot \mathbf{r}/\hbar) \langle \mathbf{p} + \frac{1}{2}\mathbf{q} | \rho^{(1)} | \mathbf{p} - \frac{1}{2}\mathbf{q} \rangle d\mathbf{q} \quad (9)$$

In this, only the translational motion is transformed, while the internal-state operators remain operators. Thus, $f(\mathbf{r}, \mathbf{p}, t)$ is a function in phase space but simultaneously an operator in internal-state space. The inverse transform to Eq. (9) also exists, so that the resulting equation is entirely equivalent to the generalized Boltzmann equation, Eq. (8) [since the result is algebraically complicated, it was found that Baerwinkel and Grossmann's⁽¹²⁾ notation is somewhat more convenient for expressing the result]:

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{i}{\hbar} [H_{\text{int}}, f]_- = J(\mathbf{r}, \mathbf{p}, t) \quad (10)$$

where it has been assumed that

$$H^{(1)} = \frac{p^2}{2m} + H_{\text{int}} \quad (11)$$

and the internal-state Hamiltonian H_{int} is, for simplicity, position- and momentum-independent. The collision term is written as³

$$J(\mathbf{r}, \mathbf{p}) = \frac{-2^3 i}{\hbar} \left(\frac{2}{\hbar}\right)^3 \text{tr}_2 \int \exp\left[\frac{-2i}{\hbar} (\boldsymbol{\kappa} \cdot \mathbf{x} - \mathbf{q} \cdot \mathbf{y})\right] \mathfrak{I}(\boldsymbol{\beta} \mathbf{q} \mathbf{k} \boldsymbol{\kappa}) f_1\left(\mathbf{r} + \frac{\mathbf{y} - \mathbf{x}}{2}, \mathbf{p} + \boldsymbol{\beta} - \mathbf{k}\right) \\ \times f_2\left(\mathbf{r} + \frac{\mathbf{y} + \mathbf{x}}{2}, \mathbf{p} + \boldsymbol{\beta} + \mathbf{k}\right) d\mathbf{k} d\boldsymbol{\kappa} d\boldsymbol{\beta} d\mathbf{q} d\mathbf{y} d\mathbf{x} \quad (12)$$

³ tr_2 designates a trace over the internal states of the second particle—this is to be contrasted with Tr_2 , which is a trace over all states, translational and internal, as, for example, in Eq. (5). The subscripts 1 and 2 on f are retained to designate which internal states occur with $+\mathbf{k}$ and $+\mathbf{x}$ and vice versa.

where the superoperator (operator on operators) $\mathfrak{I}(\beta\mathbf{q}\mathbf{k}\varkappa)$ is defined by

$$\begin{aligned} \mathfrak{I}(\beta\mathbf{q}\mathbf{k}\varkappa) f_1\left(\mathbf{r} + \frac{\mathbf{y} - \mathbf{x}}{2}, \mathbf{p} + \beta - \mathbf{k}\right) f_2\left(\mathbf{r} + \frac{\mathbf{y} + \mathbf{x}}{2}, \mathbf{p} + \beta + \mathbf{k}\right) \\ = \langle \beta + \mathbf{q} | V\Omega | \mathbf{k} + \varkappa \rangle f_1\left(\mathbf{r} + \frac{\mathbf{y} - \mathbf{x}}{2}, \mathbf{p} + \beta - \mathbf{k}\right) \\ \times f_2\left(\mathbf{r} + \frac{\mathbf{y} + \mathbf{x}}{2}, \mathbf{p} + \beta + \mathbf{k}\right) \langle \mathbf{k} - \varkappa | \Omega^\dagger | \beta - \mathbf{q} \rangle \\ - \langle \beta + \mathbf{q} | \Omega | \mathbf{k} + \varkappa \rangle f_1\left(\mathbf{r} + \frac{\mathbf{y} - \mathbf{x}}{2}, \mathbf{p} + \beta - \mathbf{k}\right) \\ \times f_2\left(\mathbf{r} + \frac{\mathbf{y} + \mathbf{x}}{2}, \mathbf{p} + \beta + \mathbf{k}\right) \langle \mathbf{k} - \varkappa | \Omega^\dagger V | \beta - \mathbf{q} \rangle \end{aligned} \quad (13)$$

The position vector \mathbf{x} plays the role of the distance between the particles when they collide, the nonlocality of the collision, while $(\frac{1}{2}\mathbf{y})$ is the difference between the center of mass of the colliding pair and the position of one of the particles; β is the relative momentum of the colliding pair after collision, while \mathbf{k} is the average relative momentum before the collision [average in the sense that a matrix element $\langle \mathbf{p} | A | \mathbf{p}' \rangle$ of an operator A has two momenta \mathbf{p} and \mathbf{p}' and it is the average $\frac{1}{2}(\mathbf{p} + \mathbf{p}')$ of these]; \mathbf{q} is a measure of the off-diagonality in total momentum of the pair density matrix (before collision); and \varkappa measures the relative contribution to this from the two different particles. It should also be noted that, since V and Ω are independent of the center-of-mass motion, the center-of-mass momenta do not appear in the matrix elements for these quantities. Lastly, if spin particles are being dealt with, $H_{\text{int}} = 0$ and K refers to translational kinetic energy only. In this case, use of the intertwining relation

$$(K + V)\Omega = \Omega K \quad (14)$$

allows $\mathfrak{I}(\beta\mathbf{q}\mathbf{k}\varkappa)$ to be written as

$$\begin{aligned} \mathfrak{I}(\beta\mathbf{q}\mathbf{k}\varkappa) f_1\left(\mathbf{r} + \frac{\mathbf{y} - \mathbf{x}}{2}, \mathbf{p} + \beta - \mathbf{k}\right) f_2\left(\mathbf{r} + \frac{\mathbf{y} + \mathbf{x}}{2}, \mathbf{p} + \beta + \mathbf{k}\right) \\ = \frac{2}{\mu} (-\beta \cdot \mathbf{q} + \mathbf{k} \cdot \varkappa) \langle \beta + \mathbf{q} | \Omega | \mathbf{k} + \varkappa \rangle f_1 f_2 \langle \mathbf{k} - \varkappa | \Omega^\dagger | \beta - \mathbf{q} \rangle \end{aligned} \quad (15)$$

with $f_1 f_2$ having the same argument as the line above. Except for the requirement that Ω and f are still operators and their order must therefore be preserved, the form of Eq. (15) is identical to that given by Baerwinkel and Grossmann.⁽¹²⁾ The superoperator $\mathfrak{I}(\beta\mathbf{q}\mathbf{k}\varkappa)$ can be thought of as a superoperator parameterized by the four vectors $\beta, \mathbf{q}, \mathbf{k}, \varkappa$ which can act on any operator in the internal-state space of a pair of particles,

$$\begin{aligned} \mathfrak{I}(\beta\mathbf{q}\mathbf{k}\varkappa) A \equiv \langle \beta + \mathbf{q} | V\Omega | \mathbf{k} + \varkappa \rangle A \langle \mathbf{k} - \varkappa | \Omega^\dagger | \beta - \mathbf{q} \rangle \\ - \langle \beta + \mathbf{q} | \Omega | \mathbf{k} + \varkappa \rangle A \langle \mathbf{k} - \varkappa | \Omega^\dagger V | \beta - \mathbf{q} \rangle \end{aligned} \quad (16)$$

Some properties of the superoperator \mathfrak{I} will now be discussed. On the assumption

that the transition operator $t \equiv V\Omega$ is bounded and that A is of trace class, then $\mathfrak{S}(A)$ is also of trace class. Since a scalar product⁴

$$(B, A) \equiv \text{tr } B^*A \quad (17)$$

between bounded operators $B \in \mathfrak{B}$ and trace-class (nuclear) operators $A \in \mathfrak{R}$ can be defined, a matrix element of \mathfrak{S} between these spaces reads

$$(B, \mathfrak{S}A) \equiv \text{tr } B^*\mathfrak{S}A = \text{tr}(\mathfrak{S}^*B)^*A = (\mathfrak{S}^*B, A) \quad (18)$$

and \mathfrak{S}^* is the superoperator adjoint to \mathfrak{S} . By direct calculation, \mathfrak{S}^* is given by

$$\begin{aligned} \mathfrak{S}(\beta\mathbf{q}\mathbf{k}\boldsymbol{\kappa})^*B &= \langle \mathbf{k} + \boldsymbol{\kappa} | \Omega^+V | \beta + \mathbf{q} \rangle B \langle \beta - \mathbf{q} | \Omega | \mathbf{k} - \boldsymbol{\kappa} \rangle \\ &\quad - \langle \mathbf{k} + \boldsymbol{\kappa} | \Omega^+ | \beta + \mathbf{q} \rangle B \langle \beta - \mathbf{q} | V\Omega | \mathbf{k} - \boldsymbol{\kappa} \rangle \end{aligned} \quad (19)$$

since

$$\langle \beta + \mathbf{q} | \Omega | \mathbf{k} + \boldsymbol{\kappa} \rangle^* = \langle \mathbf{k} + \boldsymbol{\kappa} | \Omega^+ | \beta + \mathbf{q} \rangle \quad (19')$$

and similarly for $V\Omega$.

A basic property of \mathfrak{S} , and one which plays an important role in the hydrodynamic equations of change, arises from the local nature of the intermolecular potential V . Thus, if V is assumed to be independent of the linear momenta of the molecules, any operator $h(\mathbf{r})$ dependent only on the relative position will commute with V (h is the identity in internal state space), thus

$$Vh = hV \quad (20)$$

From this, it immediately follows that

$$\Omega^+Vh\Omega - \Omega^+hV\Omega = 0 \quad (21)$$

which can be expressed in matrix form for momentum space (still operators in internal-state space) as

$$\begin{aligned} 0 &= \langle \mathbf{k} + \boldsymbol{\kappa} | \Omega^+Vh\Omega - \Omega^+hV\Omega | \mathbf{k} - \boldsymbol{\kappa} \rangle \\ &= \int \langle \mathbf{k} + \boldsymbol{\kappa} | \Omega^+V | \mathbf{p} \rangle \langle \mathbf{p} | h | \mathbf{p}' \rangle \langle \mathbf{p}' | \Omega | \mathbf{k} - \boldsymbol{\kappa} \rangle d\mathbf{p} d\mathbf{p}' \\ &\quad - \int \langle \mathbf{k} + \boldsymbol{\kappa} | \Omega^+ | \mathbf{p} \rangle \langle \mathbf{p} | h | \mathbf{p}' \rangle \langle \mathbf{p}' | V\Omega | \mathbf{k} - \boldsymbol{\kappa} \rangle d\mathbf{p} d\mathbf{p}' \end{aligned} \quad (22)$$

Now, for the special case that

$$h(\mathbf{r}) = \exp(2i\mathbf{q} \cdot \mathbf{r}/\hbar) \quad (23)$$

it follows that

$$\langle \mathbf{p} | h | \mathbf{p}' \rangle = \delta(\mathbf{p}' - \mathbf{p} + 2\mathbf{q}) \quad (24)$$

⁴ The superscript ^{*} denotes adjoint in internal-state space, in contrast to the full adjoint [†] in translation and internal-state space.

and

$$\int [\langle \mathbf{k} + \boldsymbol{\kappa} | \Omega^\dagger V | \mathbf{p} \rangle \langle \mathbf{p} - 2\mathbf{q} | \Omega | \mathbf{k} - \boldsymbol{\kappa} \rangle - \langle \mathbf{k} + \boldsymbol{\kappa} | \Omega^\dagger | \mathbf{p} \rangle \langle \mathbf{p} - 2\mathbf{q} | V \Omega | \mathbf{k} - \boldsymbol{\kappa} \rangle] d\mathbf{p} = 0 \quad (25)$$

For \mathbf{p} replaced by $\boldsymbol{\beta} + \mathbf{q}$, this can be interpreted as

$$\int \Im(\boldsymbol{\beta} \mathbf{q} \mathbf{k} \boldsymbol{\kappa})^* d\boldsymbol{\beta} = 0 \quad (26)$$

This relation is hereafter referred to as the locality sum rule. In fact, it is a three-parameter set of sum rules, labeled by \mathbf{q} , \mathbf{k} , and $\boldsymbol{\kappa}$. In particular, if $\mathbf{q} = 0$, the integral over \mathbf{p} (or $\boldsymbol{\beta}$) can be performed and a trivial identity obtained. This special case is a generalization of the optical theorem as follows:

Defining the free-particle Green's function by

$$G(E) \equiv \lim_{\epsilon \rightarrow 0} \frac{1}{E - K + i\epsilon} \quad (27)$$

the Lippmann–Schwinger integral equation reads

$$\Omega = 1 + GV\Omega = 1 + Gt \quad (28)$$

with the understanding that E is the eigenvalue of K on which Ω acts. To indicate this more explicitly, Eq. (28) is rewritten as

$$\Omega | E \rangle = [1 + G(E)t] | E \rangle \quad (28')$$

where $| E \rangle$ is a ket whose eigenvalue of K is E . Then the trivial identity $\Omega^\dagger V \Omega = \Omega^\dagger V \Omega$ [this is Eq. (25) with $\mathbf{q} = 0$] becomes

$$\langle E' | t^\dagger \Omega - \Omega^\dagger t | E \rangle = \langle E' | t^\dagger - t + t^\dagger [G(E) - G^+(E')] t | E \rangle \quad (29)$$

On the energy shell, $E' = E$, the identity

$$G^+(E) - G(E) = 2\pi i \delta(E - K) \quad (30)$$

is applicable, and the optical theorem

$$t^\dagger - t = 2\pi i t^\dagger \delta(E - K) t \quad (31)$$

follows. Thus, Eq. (26) is the optical theorem for $\mathbf{q} = \boldsymbol{\kappa} = 0$ if $H_{\text{int}} = 0$ or at least when $\mathbf{q} = 0$ and \mathbf{k} and $\boldsymbol{\kappa}$ are related to the internal-state energies in such a manner that $\Im(\boldsymbol{\beta} \mathbf{0} \mathbf{k} \boldsymbol{\kappa})^* 1$ is diagonal in “ K -energy.”

An easy calculation shows that

$$(\Im(\boldsymbol{\beta} \mathbf{q} \mathbf{k} \boldsymbol{\kappa}) A)^* = -\Im(\boldsymbol{\beta}, -\mathbf{q}, \mathbf{k}, -\boldsymbol{\kappa}) A^\dagger \quad (32)$$

and this immediately implies that J is Hermitian, namely

$$J^*(\mathbf{r}, \mathbf{p}) = J(\mathbf{r}, \mathbf{p}) \quad (33)$$

on the basis that ρ is Hermitian and hence $f^\dagger = f$. Lastly, since the collisions involve two particles, there is the permutation symmetry of \mathfrak{S} to investigate. This changes the sign of any relative coordinate so that the symmetry

$$\mathfrak{S}(\beta \mathbf{q} \mathbf{k} \boldsymbol{\varkappa}) = P_{\text{int}} \mathfrak{S}(-\beta, -\mathbf{q}, -\mathbf{k}, -\boldsymbol{\varkappa}) P_{\text{int}} \quad (34)$$

is obtained. Here, P_{int} is the permutation operator on the two particles acting in internal-state space only.

3. LOCALIZATION OF THE COLLISION TERM

3.1. The Waldmann-Snider Equation

The basic difference between the generalized Boltzmann equation, Eqs. (10), (12), and (13), and the usual Boltzmann equation is, besides the more complicated handling of the internal states, the nonlocality of the collision integral. As explicitly displayed in Eq. (12), the two f 's are evaluated at different positions. On the basis that f is only macroscopically position-dependent it was assumed in Ref. 6 that both the \mathbf{y} and \mathbf{x} dependences could be dropped since these will contribute to the integral only over a distance of the magnitude of the range of the potential. If this is valid, then the \mathbf{x} and \mathbf{y} integrals can be performed in Eq. (12) and the Waldmann-Snider collision term is obtained, namely

$$\begin{aligned} J(\mathbf{r}, \mathbf{p}) &\rightarrow J_0(\mathbf{r}, \mathbf{p}) \\ &= -64i\pi^3 \hbar^2 \text{tr}_2 \int \mathfrak{S}(\beta, 0, \mathbf{k}, 0) f_1(\mathbf{r}, \mathbf{p} + \beta - \mathbf{k}) f_2(\mathbf{r}, \mathbf{p} + \beta + \mathbf{k}) d\mathbf{k} d\beta \\ &= -i(2\pi)^3 \hbar^2 \text{tr}_2 \int \mathfrak{S}\left(\frac{\mathbf{p}_2 - \mathbf{p}}{2}, 0, \frac{\mathbf{p} + \mathbf{p}_2}{2} - \mathbf{p}_1', 0\right) \\ &\quad \times f_1(\mathbf{r}, \mathbf{p}_1') f_2(\mathbf{r}, \mathbf{p} + \mathbf{p}_2 - \mathbf{p}_1') d\mathbf{p}_1' d\mathbf{p}_2 \\ &= (2\pi)^4 \hbar^2 \text{tr}_2 \int \left[\left\langle \frac{\mathbf{p}_2 - \mathbf{p}}{2} \mid t \mid \frac{\mathbf{p} + \mathbf{p}_2}{2} - \mathbf{p}_1' \right\rangle \right. \\ &\quad \times f_1(\mathbf{r}, \mathbf{p}_1') f_2(\mathbf{r}, \mathbf{p} + \mathbf{p}_2 - \mathbf{p}_1') \left. \left\langle \frac{\mathbf{p} + \mathbf{p}_2}{2} - \mathbf{p}_1' \mid t^\dagger \delta(E) \mid \frac{\mathbf{p}_2 - \mathbf{p}}{2} \right\rangle d\mathbf{p}_1' \right. \\ &\quad \left. + \frac{1}{2\pi i} \left\{ \left\langle \frac{\mathbf{p}_2 - \mathbf{p}}{2} \mid t \mid \frac{\mathbf{p}_2 - \mathbf{p}}{2} \right\rangle ff - ff \left\langle \frac{\mathbf{p}_2 - \mathbf{p}}{2} \mid t^\dagger \mid \frac{\mathbf{p}_2 - \mathbf{p}}{2} \right\rangle \right\} \right] d\mathbf{p}_2 \quad (35) \end{aligned}$$

In the last form, f must be diagonal in internal-state energy and $J(\mathbf{r}, \mathbf{p})$ must also be restricted to being diagonal in internal energy. The $\delta(E)$ designates that the "K-energy" of ff must be the same as the "K-energy" of fft^\dagger , while ff is short for

$$f_1(\mathbf{r}, \mathbf{p}) f_2(\mathbf{r}, \mathbf{p}_2).$$

For diagonal f , this reduces in the standard way to the Wang Chang-Uhlenbeck⁽¹³⁾ equation with degeneracy averaged cross sections and, if no internal states are present, to the usual Boltzmann equation with a quantum-mechanical cross section.

For internal states with angular momenta, this approximate localization of the collision term does not give a consistent picture of angular momentum conservation. That is, the W-S equation predicts an internal angular momentum relaxation but no corresponding production of translational angular momentum $\langle \mathbf{r} \times \mathbf{p} \rangle$, since the collision is localized and \mathbf{p} is a summational invariant. Equivalently, the formal expression for the pressure tensor that is obtained from the W-S equation consists of a kinetic contribution only and this is necessarily symmetric. A localization which would be consistent must take into account some of the nonlocalizability of the collision term, but what is attempted here is to use as little as possible. The starting point for making these corrections is to expand ff in a power series about the position \mathbf{r} . This gives various extensions of the W-S equation.

3.2. Linearly Extended W-S Equation

On expanding f about \mathbf{r} , the linearly extended W-S equation is defined as that extension which keeps at most linear gradients in f . Thus, in Eq. (12), ff is replaced by

$$f_1 f_2 \rightarrow f_{1-} f_{2+} + \frac{1}{2} \mathbf{y} \cdot \nabla (f_{1-} f_{2+}) + \frac{1}{2} \mathbf{x} \cdot (f_{1-} \nabla f_{2+} - f_{2+} \nabla f_{1-}) \quad (36)$$

where

$$f_{\pm} \equiv f(\mathbf{r}, \mathbf{p} + \beta \pm \mathbf{k}) \quad (37)$$

designates the momentum variable, while subscripts 1 and 2 refer to which of the molecule's internal states are involved. The collision term J can now be written as a sum of three contributions: the W-S collision term J_0 , Eq. (35), and two extra terms J_{11} and J_{12} arising from the two correction terms in Eq. (36). On integrating over \mathbf{x} , \mathbf{y} , \mathbf{q} , and $\boldsymbol{\kappa}$, these terms become

$$J_{11}(\mathbf{r}, \mathbf{p}) = \nabla \cdot 2h^3 \text{tr}_2 \int \nabla_{\mathbf{q}} \mathfrak{I}(\beta \mathbf{q} \mathbf{k} 0)|_{\mathbf{q}=0} f_{1-} f_{2+} d\mathbf{k} d\beta \quad (38)$$

and

$$J_{12}(\mathbf{r}, \mathbf{p}) = 2h^3 \text{tr}_2 \int \nabla_{\boldsymbol{\kappa}} \mathfrak{I}(\beta 0 \mathbf{k} \boldsymbol{\kappa})|_{\boldsymbol{\kappa}=0} \cdot [f_{2+} \nabla f_{1-} - f_{1-} \nabla f_{2+}] d\mathbf{k} d\beta \quad (39)$$

The hydrodynamic equations of change are derived from this extended W-S equation

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{i}{\hbar} [H_{\text{int}}, f]_- = J_0 + J_{11} + J_{12} \quad (40)$$

in the next section and it is shown there that this equation is also not consistent in treating angular momentum conservation. However, if only the correction J_{11} is included but not the J_{12} , this does give a consistent equation for linear and angular momentum conservation.

4. HYDRODYNAMIC EQUATIONS

The expectation of any one-particle operator ϕ is determined entirely by the singlet density matrix, thus

$$\langle \phi \rangle = \text{Tr}_1 \phi \rho^{(1)} = \text{tr}_1 \iint \phi'(\mathbf{r}', \mathbf{p}) f_1(\mathbf{r}', \mathbf{p}) d\mathbf{p} d\mathbf{r}' \quad (41)$$

where $\phi'(\mathbf{r}', \mathbf{p})$ is the phase function (still an operator in internal states) related to ϕ by the Weyl correspondence. In particular, if ϕ is a density operator (quantity of something per particle), then $\phi'(\mathbf{r}', \mathbf{p})$ is proportional to the delta function $\delta(\mathbf{r}' - \mathbf{r})$, that is, $\phi'(\mathbf{r}', \mathbf{p}) = \delta(\mathbf{r}' - \mathbf{r}) \phi(\mathbf{r}, \mathbf{p})$, where \mathbf{r} is the position at which the density is desired to be known. If $\Phi(\mathbf{r})$ is the average of ϕ per unit mass, then

$$\rho(\mathbf{r})\Phi(\mathbf{r}) = \text{tr}_1 \int \phi_1(\mathbf{r}, \mathbf{p}) f_1(\mathbf{r}, \mathbf{p}) d\mathbf{p} \quad (42)$$

with $\rho(\mathbf{r})$ being the mass density of the gas (ρ is to be contrasted with the singlet density matrix $\rho^{(1)}$). From the Boltzmann equation, the equation of change for Φ becomes (ϕ is assumed time-independent)

$$\begin{aligned} \rho \frac{D\Phi}{Dt} + \nabla \cdot \mathbf{J}_{\phi K} + \frac{i}{\hbar} \text{tr}_1 \int [\phi, H_{\text{int}}]_- f(\mathbf{r}, \mathbf{p}) d\mathbf{p} - \left\langle \frac{\mathbf{p}}{m} \cdot \frac{\partial \phi}{\partial \mathbf{r}} \right\rangle \\ = \left(\frac{\partial \rho \Phi}{\partial t} \right)_{\text{coll}} \\ = \partial_0(\rho \Phi) + \partial_{11}(\rho \Phi) + \partial_{12}(\rho \Phi) \end{aligned} \quad (43)$$

where the last form denotes the three contributions to the collision term in the linearly extended W-S equation and $\mathbf{J}_{\phi K}$ is the kinetic contribution $\langle [(\mathbf{p}/m) - \mathbf{v}_0] \phi \rangle$ to the flux of ϕ .

The equation of continuity

$$\partial \rho / \partial t + \nabla \cdot (\rho \mathbf{v}_0) = 0 \quad (44)$$

has already been used in writing Eq. (43), but this is easily proved for the generalized Boltzmann equation, Eq. (12), since

$$\begin{aligned} \left(\frac{\partial \rho}{\partial t} \right)_{\text{coll}} &= \text{tr}_1 \int J(\mathbf{r}, \mathbf{p}) d\mathbf{p} = \int (1, J(\mathbf{r}, \mathbf{p})) d\mathbf{p} \\ &= \frac{(-i)(2)^6}{\hbar} \left(\frac{2}{\hbar} \right)^3 \int \left(\Im(\beta \mathbf{q} \mathbf{k} \boldsymbol{\kappa})^{\dagger 1}, f_1 \left(\mathbf{r} + \frac{\mathbf{y} - \mathbf{x}}{2}, \mathbf{p} - \mathbf{k} \right) f_2 \left(\mathbf{r} + \frac{\mathbf{y} + \mathbf{x}}{2}, \mathbf{p} + \mathbf{k} \right) \right) \\ &\quad \times \exp \left[-\frac{2i}{\hbar} (\boldsymbol{\kappa} \cdot \mathbf{x} - \mathbf{q} \cdot \mathbf{y}) \right] d\mathbf{k} d\boldsymbol{\kappa} d\mathbf{q} d\mathbf{y} d\mathbf{x} d\beta d\mathbf{p} = 0 \end{aligned} \quad (45)$$

by the sum rule, Eq. (26). Note that it was possible to eliminate β from ff by translating \mathbf{p} .

4.1. Linear Momentum Conservation

$\partial_0(\rho\mathbf{v}_0)$ can easily be shown to vanish (see the appendix) and thus the W-S equation is consistent with momentum conservation. The correction terms $J_{11} + J_{12}$ are also consistent with momentum conservation and their contribution to the momentum equation is now obtained. For $\phi(\mathbf{r}, \mathbf{p}) = \mathbf{p}$, $\Phi = \mathbf{v}_0$, the momentum equation is

$$\rho \frac{D\mathbf{v}_0}{Dt} + \nabla \cdot \mathbf{P}_K = \partial_{11}(\rho\mathbf{v}_0) + \partial_{12}(\rho\mathbf{v}_0) \quad (46)$$

with

$$\partial_{11}(\rho\mathbf{v}_0) = -\nabla \cdot \mathbf{P}_V \quad (47)$$

where \mathbf{P}_V is the collisional transfer contribution to the pressure tensor

$$\begin{aligned} \mathbf{P}_V &= -2h^3 \text{tr}_1 \text{tr}_2 \int \nabla_{\mathbf{q}} \mathfrak{S}(\beta\mathbf{q}\mathbf{k}0)|_{\mathbf{q}=0} f_{1-} f_{2+} \mathbf{p} \, d\mathbf{k} \, d\beta \, d\mathbf{p} \\ &= 2h^3 \text{tr}_1 \text{tr}_2 \int \nabla_{\mathbf{q}} \mathfrak{S}(\beta\mathbf{q}\mathbf{k}0)|_{\mathbf{q}=0} f_1(\mathbf{r}, \mathbf{p} - \mathbf{k}) f_2(\mathbf{r}, \mathbf{p} + \mathbf{k}) \beta d\beta \, d\mathbf{k} \, d\mathbf{p} \end{aligned} \quad (48)$$

A translation of \mathbf{p} by β has been made and then part of the term eliminated by the sum rule, Eq. (26). In general, this contribution to the pressure tensor can be non-symmetric; however, if there is no internal structure—in fact, just no vectorial internal structure—then \mathbf{P}_V is symmetric, as the following argument shows: With no vectors in \mathfrak{S} besides β , \mathbf{q} , and \mathbf{k} , the second-rank tensor

$$\mathbf{T} \equiv \int \nabla_{\mathbf{q}} \mathfrak{S}(\beta\mathbf{q}\mathbf{k}0)|_{\mathbf{q}=0} \beta \, d\beta \quad (49)$$

has even parity and depends only on the vector \mathbf{k} . Hence by symmetry, \mathbf{T} must be of the form

$$\mathbf{T} = \mathbf{U}g(k^2) + \mathbf{k}\mathbf{k}h(k^2) \quad (50)$$

with \mathbf{U} the unit tensor. Thus, \mathbf{T} and hence \mathbf{P}_V , is symmetric when there are no vectorial internal states.

For a Boltzmann distribution (Q the internal-state position function),

$$f(\mathbf{r}, \mathbf{p}) = \frac{n \exp[-p^2/2mkT - H_{\text{int}}/kT]}{(2\pi mkT)^{3/2} Q} \quad (51)$$

\mathbf{P}_V is just the second-virial-coefficient contribution to the pressure tensor. Thus, it is found that

$$\int f_1(\mathbf{r}, \mathbf{p} - \mathbf{k}) f_2(\mathbf{r}, \mathbf{p} + \mathbf{k}) \, d\mathbf{p} = \frac{n^2}{(4\pi mkT)^{3/2} Q^2} \exp \left[-\frac{k^2}{mkT} - \frac{H_{\text{int}}}{kT} - \frac{H_{2,\text{int}}}{kT} \right] \quad (52)$$

and consequently

$$\begin{aligned}
 & \int \Im(\beta \mathbf{q} \mathbf{k} 0) f_1(\mathbf{r}, \mathbf{p} - \mathbf{k}) f_2(\mathbf{r}, \mathbf{p} + \mathbf{k}) d\mathbf{p} d\mathbf{k} \\
 &= \frac{n^2}{(4\pi m k T)^{3/2} Q^2} \langle \beta + \mathbf{q} | \int [V \Omega | \mathbf{k} \rangle \langle \mathbf{k} | e^{-\mathbf{K}/kT} \Omega^\dagger - \Omega e^{-\mathbf{K}/kT} | \mathbf{k} \rangle \langle \mathbf{k} | \Omega^\dagger V] d\mathbf{k} | \beta - \mathbf{q} \rangle \\
 &= \frac{n^2}{(4\pi m k T)^{3/2} Q^2} \langle \beta + \mathbf{q} | [V e^{-H/kT} P_c - e^{-H/kT} P_c V] | \beta - \mathbf{q} \rangle \quad (53)
 \end{aligned}$$

where use has been made of the intertwining relation, Eq. (14), and the fact that $\Omega \Omega^\dagger = P_c$ is the projection onto the unbound states of the total relative Hamiltonian H . Finally, the equilibrium P_V reduces to

$$\begin{aligned}
 P_V^{\text{eq}} &= \frac{2n^2 h^3}{(4\pi m k T)^{3/2} Q^2} \text{tr}_1 \text{tr}_2 \int \nabla_{\mathbf{q}} (\langle \beta + \mathbf{q} | \mathbf{r} \rangle \langle \mathbf{r}' | \beta - \mathbf{q} \rangle) |_{\mathbf{q}=0} \beta d\beta \langle \mathbf{r} | V e^{-H/kT} P_c \\
 &\quad - e^{-H/kT} P_c V | \mathbf{r}' \rangle d\mathbf{r}' d\mathbf{r} \\
 &= \frac{2n^2 h^3}{(4\pi m k T)^{3/2} Q^2} \text{tr}_1 \text{tr}_2 \int (\mathbf{r} + \mathbf{r}') [\nabla_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}')] [V(\mathbf{r}) - V(\mathbf{r}')] \langle \mathbf{r} | e^{-H/kT} P_c | \mathbf{r}' \rangle d\mathbf{r} d\mathbf{r}' \\
 &= \frac{-4n^2 h^3}{(4\pi m k T)^{3/2} Q^2} \text{tr}_1 \text{tr}_2 \int \mathbf{r} \nabla_{\mathbf{r}} V \langle \mathbf{r} | e^{-H/kT} P_c | \mathbf{r} \rangle d\mathbf{r} \\
 &= -\frac{n^2 h^3}{2(\pi m k T)^{3/2} Q^2} \text{Tr}_{\text{rel}} \mathbf{r} (\nabla_{\mathbf{r}} V) e^{-H/kT} P_c \quad (54)
 \end{aligned}$$

where the trace Tr_{rel} is over relative translational coordinates and also over the internal states of the molecules. If there are no bound states, $P_c = 1$, and if there are no internal states, P_V is isotropic, $P_V = P_V \mathbf{U}$, so that P_V can be identified as $n^2 k T B$, where B is the second virial coefficient. However, even in equilibrium, if H_{int} is parameterized by an external polar vector (for example, the electric field), then P_V will, in general, not be isotropic. Furthermore, if there are bound states, P_V^{eq} listed above is only the continuum contribution to the second virial coefficient.

The remaining term of Eq. (46), $\partial_{12}(\rho \mathbf{v}_0)$, is easily shown to be zero as follows: By definition, this quantity is given by

$$\begin{aligned}
 \partial_{12}(\rho \mathbf{v}_0) &= 2h^3 \text{tr}_1 \text{tr}_2 \int \mathbf{p} \nabla_{\mathbf{x}} \Im(\beta 0 \mathbf{k} \mathbf{x}) |_{\mathbf{x}=0} \cdot (f_{2+} \nabla f_{1-} - f_{1-} \nabla f_{2+}) d\mathbf{k} d\beta d\mathbf{p} \\
 &= -2h^3 \text{tr}_1 \text{tr}_2 \int \beta \nabla_{\mathbf{x}} \Im(\beta 0 \mathbf{k} \mathbf{x}) |_{\mathbf{x}=0} d\beta \cdot [f_2(\mathbf{r}, \mathbf{p} + \mathbf{k}) \nabla f_1(\mathbf{r}, \mathbf{p} - \mathbf{k}) \\
 &\quad - f_1(\mathbf{r}, \mathbf{p} - \mathbf{k}) \nabla f_2(\mathbf{r}, \mathbf{p} + \mathbf{k})] d\mathbf{k} d\mathbf{p} \quad (55)
 \end{aligned}$$

where \mathbf{p} has been translated by β and Eq. (26) used where applicable. It is now shown that the β integral is symmetric to particle interchange, and since the remaining term $f_2 \nabla f_1 - f_1 \nabla f_2$ is odd to this transformation (\mathbf{k} changes sign), integration over \mathbf{k} and

tracing over internal states causes the term to vanish. Now, by changes of variable, it is seen that

$$\begin{aligned} \int \beta \nabla_x \mathfrak{I}(\beta \mathbf{0} \mathbf{k} \boldsymbol{\kappa})|_{\boldsymbol{\kappa}=0} d\beta &= \int \beta \nabla_x \mathfrak{I}(-\beta \mathbf{0} \mathbf{k} - \boldsymbol{\kappa})|_{\boldsymbol{\kappa}=0} d\beta \\ &= P_{\text{int}} \int \beta \nabla_x \mathfrak{I}(\beta \mathbf{0} - \mathbf{k} \boldsymbol{\kappa})|_{\boldsymbol{\kappa}=0} d\beta P_{\text{int}} \end{aligned} \quad (56)$$

where Eq. (34) has been used for the last equality. This shows that this quantity is even in \mathbf{k} (with simultaneous particle exchange) and the vanishing of $\partial_{12}(\rho \mathbf{v}_0)$ follows. Momentum conservation is thus assured since

$$\rho D\mathbf{v}_0/Dt = -\nabla \cdot P \quad (57)$$

with

$$P = P_K + P_V \quad (58)$$

4.2. Energy Balance

The equation of change for kinetic (more correctly, one-particle) energy is obtained from the generalized Boltzmann equation. As might be expected, there is a hydrodynamic source term, namely $\sigma_K \neq 0$, in

$$\rho DE_K/Dt = -\nabla \cdot \mathbf{q} + \sigma_K \quad (59)$$

where

$$\rho E_K(\mathbf{r}) \equiv \text{tr}_1 \int [(p^2/2m) + H_{\text{int}}] f_1(\mathbf{r}, \mathbf{p}) d\mathbf{p} \quad (60)$$

The reason for this is, of course, that the total energy, kinetic plus potential, is conserved rather than the kinetic energy by itself. It is shown that a consistent approximation can be made in evaluating the potential-energy density (\mathbf{r}_1 is the position operator of particle 1, which is to be contrasted with the macroscopic position parameter \mathbf{r}):

$$\rho E_V(\mathbf{r}) = \frac{1}{2} \text{Tr}_1 \text{Tr}_2 \delta(\mathbf{r} - \mathbf{r}_1) V \rho^{(2)} \quad (61)$$

so that

$$\rho DE_V/Dt = -\nabla \cdot \mathbf{q}' + \sigma_V \quad (62)$$

with

$$\sigma_K + \sigma_V = 0 \quad (63)$$

Thus, the conservation of total energy $E = E_K + E_V$ is verified. The kinetic energy equation is discussed first.

It is shown in the appendix that, if f is diagonal in internal energy, then J_0 does not contribute to the energy-balance equation. For the W-S equation, then, with diagonal in energy f , the σ_K of Eq. (59) vanishes and “kinetic” energy is conserved. This is the case usually assumed when calculating thermal conductivity and vis-

cosity.^(14,15) However, for nondiagonal-in-energy f 's, as required to describe high-density NMR experiments,⁽¹⁶⁾ J_0 contributes a production term

$$\partial_0(\rho E_K) = -64i\pi^3\hbar^2 \text{tr}_1 \text{tr}_2 \int \langle \mathbf{k} | \Omega^\dagger V \Omega | \mathbf{k} \rangle [H_{\text{int}}, f_1(\mathbf{p} - \mathbf{k}) f_2(\mathbf{p} + \mathbf{k})]_- d\mathbf{p} d\mathbf{k} \quad (64)$$

to σ_K . J_{11} contributes to the heat flux so that

$$\mathbf{q} = \mathbf{q}_K + \mathbf{q}_V \quad (65)$$

with \mathbf{q}_K arising from the drift terms on the left-hand side of the Boltzmann equation

$$\mathbf{q}_K = \text{tr}_1 \int \left(\frac{\mathbf{p}}{m} - \mathbf{v}_0 \right) \left(\frac{p^2}{2m} + H_{\text{int}} \right) f_1(\mathbf{r}, \mathbf{p}) d\mathbf{p} \quad (66)$$

and a collisional transfer term from J_{11}

$$\mathbf{q}_V = -2\hbar^3 \text{tr}_1 \text{tr}_2 \int \left(\frac{p^2}{2m} + H_{\text{int}} \right) \nabla_{\mathbf{a}} \mathfrak{I}(\beta \mathbf{q} \mathbf{k} \mathbf{0})|_{\mathbf{a}=0} f_{1-} f_{2+} d\mathbf{k} d\beta d\mathbf{p} \quad (67)$$

The remaining term, $\partial_{12}(\rho E_K)$, also contributes to the energy production

$$\partial_{12}(\rho E) = 2\hbar^3 \text{tr}_1 \text{tr}_2 \int \left(\frac{p^2}{2m} + H_{\text{int}} \right) \nabla_{\mathbf{x}} \mathfrak{I}(\beta \mathbf{0} \mathbf{k} \mathbf{x})|_{\mathbf{x}=0} (f_{2+} \nabla f_{1-} - f_{1-} \nabla f_{2+}) d\mathbf{k} d\beta d\mathbf{p} \quad (68)$$

and thus,

$$\sigma_K = \partial_0(\rho E_K) + \partial_{12}(\rho E_K) \quad (69)$$

The potential-energy density depends on $\rho^{(2)}$, or equivalently, could be expressed in terms of the pair Wigner distribution function $f^{(2)}$. However, since the object here is merely to show that σ_K is canceled by a potential-energy production σ_V and furthermore, since the operator manipulations are slightly simpler, the equation of change for E_V is obtained by density-matrix methods and then expressed in terms of the singlet Wigner distribution functions. The equation of change for the pair density matrix $\rho^{(2)}$ for a pair of interacting particles is, ignoring triple collisions,

$$i\hbar \partial \rho^{(2)} / \partial t = [H^{(2)}, \rho^{(2)}]_- \quad (70)$$

From this, the equation for E_V is

$$\begin{aligned} i\hbar \partial \rho E_V / \partial t &= \frac{1}{2} \text{Tr}_1 \text{Tr}_2 [\delta(\mathbf{r} - \mathbf{r}_1) V, H^{(2)}]_- \rho^{(2)} \\ &= \frac{1}{2} \text{Tr}_1 \text{Tr}_2 [\delta(\mathbf{r} - \mathbf{r}_1) V, K]_- \rho^{(2)} \\ &= \frac{1}{4} \text{Tr}_1 \text{Tr}_2 [\delta(\mathbf{r} - \mathbf{r}_1), K]_- [\rho^{(2)}, V]_+ - \frac{1}{4} \text{Tr}_1 \text{Tr}_2 [K, \delta(\mathbf{r} - \mathbf{r}_1)]_+ [V, \rho^{(2)}]_- \end{aligned} \quad (71)$$

where the fact that V commutes with $\delta(\mathbf{r} - \mathbf{r}_1)$ is used as well as the equality $H^{(2)} = K + V$. The first term in the last expression is of the form of a gradient, and so, consistent with the molecular chaos assumption, Eq. (6), this term becomes

$$(1/4i\hbar) \text{Tr}_1 \text{Tr}_2 [\delta, K]_- [\rho^{(2)}, V]_+ = (-1/8m) \nabla_{\mathbf{r}} \cdot \text{Tr}_1 \text{Tr}_2 [\mathbf{p}_1, \delta(\mathbf{r} - \mathbf{r}_1)]_+ [\rho^{(2)} V]_+ \quad (72)$$

Since $\rho^{(2)}$ and V are symmetric to particle interchange, the expression $[K, \delta(\mathbf{r} - \mathbf{r}_1)]_+$ in the last term of Eq. (71) can be replaced by

$$\begin{aligned} [K, \delta(\mathbf{r} - \mathbf{r}_1)]_+ &= [H_1^{(1)}, \delta(\mathbf{r} - \mathbf{r}_1)]_+ + [H_2^{(1)}, \delta(\mathbf{r} - \mathbf{r}_1)]_+ \\ &= [H_1^{(1)}, \delta(\mathbf{r} - \mathbf{r}_1)]_+ + [H_2^{(1)}, \delta(\mathbf{r} - \mathbf{r}_2)]_+ + [H_2^{(1)}, \delta(\mathbf{r} - \mathbf{r}_1) - (\mathbf{r} - \mathbf{r}_2)]_+ \\ &\sim 2[H_1^{(1)}, \delta(\mathbf{r} - \mathbf{r}_1)]_+ - \nabla_{\mathbf{r}} \cdot [H_1^{(1)}, \mathbf{r}_{21} \delta(\mathbf{r} - \mathbf{r}_1)]_+ \end{aligned} \quad (73)$$

where in the last line \sim designates equivalent contributions to the expectation value when the difference between δ -functions has been expanded to keep only linear position gradients. The first term of Eq. (73) is a one-particle operator and can thus be expressed in terms of $\mathfrak{S}(\beta \mathbf{q} \mathbf{k} \kappa)$ provided the ansatz, Eq. (6), is inserted for $\rho^{(2)}$. It is easily shown that, on dropping quadratic position derivatives, the Weyl correspondence of $\frac{1}{2}[H^{(1)}, \delta(\mathbf{r} - \mathbf{r}_1)]_+$ is the one-particle energy density in phase space. Thus, this contribution to $\rho DE_V/Dt$ just cancels the collision contributions

$$\partial_0(\rho E_K) + \partial_{11}(\rho E_K) + \partial_{12}(\rho E_K) \text{ to } \rho DE_K/Dt,$$

that is, on collecting terms,

$$\begin{aligned} \partial(\rho E_V)/\partial t &= \nabla \cdot \mathbf{q}_V - \sigma_K - \nabla \cdot \left\{ \frac{1}{8m} \text{Tr}_1 \text{Tr}_2 [\mathbf{p}_1, \delta(\mathbf{r} - \mathbf{r}_1)]_+ [\rho^{(2)}, V]_+ \right. \\ &\quad \left. + \frac{-1}{4i\hbar} \text{Tr}_1 \text{Tr}_2 [H_1^{(1)}, \mathbf{r}_{21} \delta(\mathbf{r} - \mathbf{r}_1)]_+ [V, \rho^{(2)}]_- \right\} \\ &= -\nabla \cdot (\mathbf{q}' + \rho \mathbf{v}_0 E_V) + \sigma_V \end{aligned} \quad (74)$$

In this way, it is clearly seen that $\sigma_V = -\sigma_K$, while

$$\begin{aligned} \mathbf{q}' &= \frac{\hbar^3}{4m} \text{tr}_1 \text{tr}_2 \int (\mathbf{p} - m\mathbf{v}_0) [\langle \beta | \mathbf{t} | \mathbf{k} \rangle f_{1-} f_{2+} \langle \mathbf{k} | \Omega^\dagger | \beta \rangle \\ &\quad + \langle \beta | \Omega | \mathbf{k} \rangle f_{1-} f_{2+} \langle \mathbf{k} | \mathbf{t}^\dagger | \beta \rangle] d\mathbf{k} d\beta d\mathbf{p} \end{aligned} \quad (75)$$

where only the localized collision term is kept in \mathbf{q}' since this already appears as a gradient in the hydrodynamic equations. Thus, on taking into account the potential energy in a manner consistent with the way the collisions were treated, a conservation law for total energy is obtained, namely

$$\rho D(E_K + E_V)/Dt = -\nabla \cdot (\mathbf{q} + \mathbf{q}') \quad (76)$$

4.3. Angular Momentum

Internal angular momentum (hereafter called spin, although it may arise from rotation of a diatomic or polyatomic molecule) is not conserved during collision

processes since the translational degrees of freedom also carry angular momentum about the center of mass of a relative colliding pair. The average spin per unit mass of the fluid is denoted by $\mathbf{s}(\mathbf{r}, t)$ and this is related to f by

$$\rho \mathbf{s} = \text{tr}_1 \int \mathbf{J}_1 f_1(\mathbf{r}, \mathbf{p}) d\mathbf{p} \quad (77)$$

where \mathbf{J} is the internal angular momentum operator. The equation of change for \mathbf{s} is, using Eq. (40),

$$\rho D\mathbf{s}/Dt = -\nabla \cdot (\mathbf{L}_K + \mathbf{L}_V) + \boldsymbol{\sigma}_s \quad (78)$$

where

$$\mathbf{L}_K = \text{tr}_1 \int [(\mathbf{p}/m) - \mathbf{v}_0] \mathbf{J}_1 f_1(\mathbf{r}, \mathbf{p}) d\mathbf{p} \quad (79)$$

$$\mathbf{L}_V = -2h^3 \text{tr}_1 \text{tr}_2 \int \mathbf{J}_1 \nabla_{\mathbf{q}} \mathfrak{I}(\boldsymbol{\beta} \mathbf{q} \mathbf{k} 0)|_{\mathbf{q}=0} f_{1-} f_{2+} d\mathbf{k} d\boldsymbol{\beta} d\mathbf{p} \quad (80)$$

and

$$\boldsymbol{\sigma}_s = \partial_0(\rho \mathbf{s}) + \partial_{12}(\rho \mathbf{s}) \quad (81)$$

In the appendix, Eq. (A12), it is shown that the W-S collision term gives

$$\begin{aligned} \partial_0(\rho \mathbf{s}) &= 2h^3 \text{tr}_1 \text{tr}_2 \int \boldsymbol{\beta} \times \nabla_{\mathbf{q}} \mathfrak{I}(\boldsymbol{\beta} \mathbf{q} \mathbf{k} 0)|_{\mathbf{q}=0} f_{1-} f_{2+} d\boldsymbol{\beta} d\mathbf{q} d\mathbf{p} \\ &= \boldsymbol{\epsilon} : \mathbf{P}_V = \boldsymbol{\epsilon} : \mathbf{P} \equiv -2\mathbf{P}^a \end{aligned} \quad (82)$$

with the identification made with \mathbf{P}_V of Eq. (48). Since \mathbf{P}_K is symmetric, this can be added to \mathbf{P}_V . Although the term $\partial_{12}(\rho \mathbf{s})$ can be identified with a contribution to the antisymmetric pressure tensor due to terms of higher order in position gradients—in other words, a term quadratic in gradients in the momentum-balance equation—this evaluation will not be made here. Suffice it to say at this point that $\partial_{12}(\rho \mathbf{s})$ is nonzero and does not come from the pressure tensor \mathbf{P} in the linear-in-gradients approximate localization of the collision term. This point is discussed further in the last section. For the complete, linearly extended W-S equation, the equation of change of internal angular momentum reads

$$\rho D\mathbf{s}/Dt = -\nabla \cdot \mathbf{L} - 2\mathbf{P}^a + \partial_{12}(\rho \mathbf{s}) \quad (83)$$

and thus it is seen that the linearly extended W-S equation is not consistent with the equations of fluid dynamics.

5. DISCUSSION

The equations of change derived from the generalized Boltzmann equation, Eq. (8), give equations of conservation type for mass, linear momentum, and angular momentum. For energy conservation, this must be supplemented by a contribution from the potential energy and if this latter is governed by the pair Liouville equation,

Eq. (70), total energy conservation is obtained. This picture is thus consistent with all conservation equations. However, in this, the collision term is written in a highly nonlocal manner and an equation which reflects (at least partly) the localized nature of the collisions is desirable. This is aided by making a Weyl correspondence to a Wigner distribution function in the phase space for the translational degrees of freedom, maintaining all the while the operator formalism for internal states. The equivalent form, Eq. (10), has a collision term, Eq. (12), which includes integrals over the positions of the colliding pairs.

The completely local approximation to this is the Waldmann–Snider collision term, Eq. (35). This gives rise to the following set of equations of change:

$$\partial\rho/\partial t + \nabla \cdot (\rho\mathbf{v}_0) = 0 \quad (84)$$

$$\rho D\mathbf{v}_0/Dt = -\nabla \cdot \mathbf{P}_K \quad (85)$$

$$\rho DE_K/Dt = -\nabla \cdot \mathbf{q}_K + \partial_0(\rho E_K) \quad (86)$$

$$\rho Ds/Dt = -\nabla \cdot \mathbf{L}_K - 2\mathbf{P}_V^a \quad (87)$$

It is immediately seen that the equations for mass and linear momentum are of conservation type, it being assumed that no external forces or torques are present. If f is required to be diagonal in internal energy, $\partial_0(\rho E_K)$ vanishes and then energy is also conserved. However, spin angular momentum is not conserved, which is perfectly correct, but the equations are inconsistent in that the spin production term, $-2\mathbf{P}_V^a$, is related to an antisymmetric part of the pressure tensor which has no analog in the momentum equation. To remedy this, deviations from a completely localized collision term were considered. Keeping linear-in-gradients contributions to the collision term, this linearly extended W–S equation gives a more complete set of equations of change—mass balance being the same—the others are

$$\rho D\mathbf{v}_0/Dt = -\nabla \cdot (\mathbf{P}_K + \mathbf{P}_V) \quad (88)$$

$$\rho DE_K/Dt = -\nabla \cdot (\mathbf{q}_K + \mathbf{q}_V) + \sigma_K \quad (89)$$

and

$$\rho Ds/Dt = -\nabla \cdot (\mathbf{L}_K + \mathbf{L}_V) - 2\mathbf{P}_V^a + \partial_{12}(\rho s) \quad (90)$$

At this stage, energy is not conserved even if f is diagonal in internal energy. This can be remedied by adding the equation of change for potential energy, namely

$$\rho DE_V/Dt = -\nabla \cdot \mathbf{q}' - \sigma_K \quad (91)$$

However, the equation of change for spin density still is not consistent with the rest. Only by keeping an infinite set of gradients would it be expected that a consistent set of equations be obtained. But this would be equivalent to dealing with the generalized Boltzmann equation.

It is noticed, however, that the linearly extended equation

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{i}{\hbar} [H_{\text{int}}, f]_- = J_0 + J_{11} + J_{12} \quad (92)$$

has two corrections which differentiate it from the W-S equation. The term J_{11} gives only collisional transfer contributions to the fluxes, whereas the J_{12} term adds production terms. It is thus suggested that a properly extended W-S equation is

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{i}{\hbar} [H_{\text{int}}, f]_- = J_0 + J_{11} \quad (93)$$

and this has the consistent set of equations of change

$$\partial \rho / \partial t + \nabla \cdot (\rho \mathbf{v}_0) = 0 \quad (94)$$

$$\rho D\mathbf{v}_0/Dt = -\nabla \cdot (\mathbf{P}_K + \mathbf{P}_V) \quad (95)$$

$$\rho DE_K/Dt = -\nabla \cdot (\mathbf{q}_K + \mathbf{q}_V) \quad (96)$$

and

$$\rho D\mathbf{s}/Dt = -\nabla \cdot (\mathbf{L}_K + \mathbf{L}_V) - 2\mathbf{P}_V^a \quad (97)$$

This set of equations is valid provided that f is diagonal in internal energy. If this restriction is not met, it is again necessary to add a contribution to take into account the rate of change of the potential energy. For consistency, this last equation should be truncated to

$$\rho DE_V/Dt = -\nabla \cdot \mathbf{q}' - \partial_0(\rho E_K) \quad (98)$$

It is interesting to note that in this approximation there are collisional transfer contributions to the pressure tensor, heat-flux vector, and angular momentum flux tensor. In particular, the gas is nonideal in that it has a second virial coefficient, namely that contributed by the unbound pair states. It is also interesting to speculate on the effect that the J_{11} term would have in solving the Boltzmann equation to obtain transport coefficients and spin-relaxation times. Presumably, they may only be density corrections. However, it is important to start from a consistent set of equations, as has been pointed out by Green and Hoffman.⁽¹⁷⁾

APPENDIX

$\partial_0(\rho\Phi)$ is evaluated for momentum ($\Phi = \mathbf{v}_0$), "kinetic" energy ($\Phi = E_K$), and spin ($\Phi = \mathbf{s}$). For the operator-phase function $\phi(\mathbf{p})$, $\partial_0(\rho\Phi)$ is given by

$$\partial_0(\rho\Phi) = -64i\pi^3\hbar^2 \text{tr}_1 \text{tr}_2 \int \phi_1(\mathbf{p}) \mathfrak{I}(\boldsymbol{\beta}, 0, \mathbf{k}, 0) f_{1-} f_{2+} d\mathbf{k} d\boldsymbol{\beta} d\mathbf{p} \quad (\text{A1})$$

The first step in the corresponding classical proof is to symmetrize the integrand to particle interchange. Here, this uses Eq. (34), thus

$$\begin{aligned} & \text{tr}_1 \text{tr}_2 \int \phi_1(\mathbf{p}) \mathfrak{I}(\boldsymbol{\beta}, 0, \mathbf{k}, 0) f_{1-} f_{2+} d\mathbf{k} d\boldsymbol{\beta} d\mathbf{p} \\ &= \text{tr}_1 \text{tr}_2 \int \phi_2(\mathbf{p}) \mathfrak{I}(-\boldsymbol{\beta}, 0, \mathbf{k}, 0) f_{1-} f_{2+} d\mathbf{k} d\boldsymbol{\beta} d\mathbf{p} \\ &= \text{tr}_1 \text{tr}_2 \int \phi_2(\mathbf{p} + 2\boldsymbol{\beta}) \mathfrak{I}(\boldsymbol{\beta}, 0, \mathbf{k}, 0) f_{1-} f_{2+} d\mathbf{k} d\boldsymbol{\beta} d\mathbf{p} \\ &= \frac{1}{2} \text{tr}_1 \text{tr}_2 \int [\phi_1(\mathbf{p}) + \phi_2(\mathbf{p} + 2\boldsymbol{\beta})] \mathfrak{I}(\boldsymbol{\beta}, 0, \mathbf{k}, 0) f_{1-} f_{2+} d\mathbf{k} d\boldsymbol{\beta} d\mathbf{p} \quad (\text{A2}) \end{aligned}$$

The first equality has used Eq. (34), the effect of P_{int} , and the replacement of $-\mathbf{k}$ by \mathbf{k} , while the second equality replaces $\boldsymbol{\beta}$ by $-\boldsymbol{\beta}$ and translates \mathbf{p} to $\mathbf{p} + 2\boldsymbol{\beta}$.

For momentum, $\phi = \mathbf{p}$ and the sum $\phi_1 + \phi_2$ becomes

$$\phi_1(\mathbf{p}) + \phi_2(\mathbf{p} + 2\boldsymbol{\beta}) = 2(\mathbf{p} + \boldsymbol{\beta}) \quad (\text{A3})$$

which is just twice the combination of \mathbf{p} and $\boldsymbol{\beta}$ that appears in $f_{1-} f_{2+}$. Consequently, if \mathbf{p} is replaced by $\mathbf{p} - \boldsymbol{\beta}$, $\boldsymbol{\beta}$ appears only in \mathfrak{I} and nowhere else. The sum rule, Eq. (26) can then be applied to ensure that $\partial_0(\rho \mathbf{v}_0)$ vanishes.

For energy, $\phi(\mathbf{p}) = (p^2/2m) + H_{\text{int}}$ and thus the sum has the form

$$\begin{aligned} \phi_1(\mathbf{p}) + \phi_2(\mathbf{p} + 2\boldsymbol{\beta}) &= \frac{p^2}{2m} + \frac{(\mathbf{p} + 2\boldsymbol{\beta})^2}{2m} + H_{1,\text{int}} + H_{2,\text{int}} \\ &= \frac{(\mathbf{p} + \boldsymbol{\beta})^2}{m} + \frac{\boldsymbol{\beta}^2}{m} + H_{1,\text{int}} + H_{2,\text{int}} \end{aligned} \quad (\text{A4})$$

The $(\mathbf{p} + \boldsymbol{\beta})^2$ term gives a zero contribution for the same reason as discussed for momentum, while the remaining term can be recognized as an eigenvalue of K (in relative coordinates for translational motion). On recognizing that Eq. (A1) involves the quantity

$$\begin{aligned} \text{tr}_1 \text{tr}_2 \int &\left(\frac{\boldsymbol{\beta}^2}{m} + H_{1,\text{int}} + H_{2,\text{int}} \right) \mathfrak{I}(\boldsymbol{\beta}0\mathbf{k}0) f_1(\mathbf{p} - \mathbf{k}) f_2(\mathbf{p} + \mathbf{k}) d\boldsymbol{\beta} \\ &= \int \left(\frac{\boldsymbol{\beta}^2}{m} + H_{1,\text{int}} + H_{2,\text{int}} \right) \mathfrak{I}(\boldsymbol{\beta}0\mathbf{k}0) f_1(\mathbf{p} - \mathbf{k}) f_2(\mathbf{p} + \mathbf{k}) d\boldsymbol{\beta} \\ &= \int \left(\mathfrak{I}(\boldsymbol{\beta}0\mathbf{k}0)^\dagger \left[\frac{\boldsymbol{\beta}^2}{m} + H_{1,\text{int}} + H_{2,\text{int}} \right] f_1(\mathbf{p} - \mathbf{k}) f_2(\mathbf{p} + \mathbf{k}) \right) d\boldsymbol{\beta} \end{aligned} \quad (\text{A5})$$

it is necessary to evaluate

$$\int \mathfrak{I}(\boldsymbol{\beta}0\mathbf{k}0)^\dagger \left[\frac{\boldsymbol{\beta}^2}{m} + H_{1,\text{int}} + H_{2,\text{int}} \right] d\boldsymbol{\beta}$$

This is explicitly

$$\begin{aligned} &\int \langle \mathbf{k} | t^\dagger | \boldsymbol{\beta} \rangle \left[\frac{\boldsymbol{\beta}^2}{m} + H_{1,\text{int}} + H_{2,\text{int}} \right] \langle \boldsymbol{\beta} | \Omega | \mathbf{k} \rangle d\boldsymbol{\beta} \\ &\quad - \int \langle \mathbf{k} | \Omega^\dagger | \boldsymbol{\beta} \rangle \left[\frac{\boldsymbol{\beta}^2}{m} + H_{1,\text{int}} + H_{2,\text{int}} \right] \langle \boldsymbol{\beta} | t | \mathbf{k} \rangle d\boldsymbol{\beta} \\ &= \langle \mathbf{k} | t^\dagger K \Omega - \Omega^\dagger K t | \mathbf{k} \rangle \end{aligned} \quad (\text{A6})$$

Now, the operator in this equation can be rewritten in the following form if use is made of the intertwining relation, Eq. (14):

$$\begin{aligned} t^\dagger K \Omega - \Omega^\dagger K t &= \Omega^\dagger (VK - KV) \Omega \\ &= \Omega^\dagger (VH - HV) \Omega = [\Omega^\dagger V \Omega, K]_- \end{aligned} \quad (\text{A7})$$

Since the matrix element (A6) is diagonal in translational kinetic energy, this part of K drops out, leaving

$$\begin{aligned} \partial_0(\rho E_K) &= -32i\pi^3\hbar^2 \text{tr}_1 \text{tr}_2 \int \langle \mathbf{k} | \Omega^\dagger V \Omega | \mathbf{k} \rangle \\ &\quad \times [H_{1,\text{int}} + H_{2,\text{int}}, f_1(\mathbf{p} - \mathbf{k}) f_2(\mathbf{p} + \mathbf{k})]_- d\mathbf{p} d\mathbf{k} \end{aligned} \quad (\text{A8})$$

This vanishes if f is diagonal in internal energy, but in general this is not the case.

Lastly, for internal angular momentum, ϕ is \mathbf{J} , so that, after symmetrization,

$$\begin{aligned} \partial_0(\rho s) &= -32i\pi^3\hbar^2 \int (\mathbf{J}_1 + \mathbf{J}_2, \Im(\beta_0 \mathbf{k} 0) f_{1-} f_{2+}) d\mathbf{k} d\beta d\mathbf{p} \\ &= -32i\pi^3\hbar^2 \int (\Im(\beta_0 \mathbf{k} 0)^* [\mathbf{J}_1 + \mathbf{J}_2], f_1(\mathbf{p} - \mathbf{k}) f_2(\mathbf{p} + \mathbf{k})) d\beta d\mathbf{k} d\mathbf{p} \end{aligned} \quad (\text{A9})$$

Now, conservation of angular momentum means that

$$[\mathbf{J}_1 + \mathbf{J}_2 + \mathbf{L}, V]_- = 0 \quad (\text{A10})$$

where $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is the relative translational angular momentum. Thus,

$$\mathbf{J}_{\text{tot}} \equiv \mathbf{J}_1 + \mathbf{J}_2 + \mathbf{L}$$

commutes with K , V , Ω , and also t . Adding \mathbf{L} to $\mathbf{J}_1 + \mathbf{J}_2$ before doing the β integral in Eq. (A9) gives the result

$$\begin{aligned} &\int \Im(\beta_0 \mathbf{k} 0)^* [\mathbf{J}_1 + \mathbf{J}_2 + \mathbf{L}] d\beta \\ &= \int \{ \langle \mathbf{k} | t^\dagger | \beta \rangle [\mathbf{J}_1 + \mathbf{J}_2 - i\hbar \beta \times \partial/\partial \beta] \langle \beta | \Omega | \mathbf{k} \rangle \\ &\quad - \langle \mathbf{k} | \Omega^\dagger | \beta \rangle [\mathbf{J}_1 + \mathbf{J}_2 - i\hbar \beta \times \partial/\partial \beta] \langle \beta | t | \mathbf{k} \rangle \} d\beta \\ &= \langle \mathbf{k} | t^\dagger \mathbf{J}_{\text{tot}} \Omega - \Omega^\dagger \mathbf{J}_{\text{tot}} t | \mathbf{k} \rangle = \langle \mathbf{k} | \mathbf{J}_{\text{tot}} [t^\dagger \Omega - \Omega^\dagger t] | \mathbf{k} \rangle = 0 \end{aligned} \quad (\text{A11})$$

Hence, the W-S production term for internal angular momentum becomes

$$\begin{aligned} \partial_0(\rho s) &= 32\pi^3\hbar^3 \text{tr}_1 \text{tr}_2 \int \beta \times \left[\left(\frac{\partial}{\partial \beta} \langle \beta | t | \mathbf{k} \rangle \right) ff \langle \mathbf{k} | \Omega^\dagger | \beta \rangle \right. \\ &\quad \left. - \left(\frac{\partial}{\partial \beta} \langle \beta | \Omega | \mathbf{k} \rangle \right) ff \langle \mathbf{k} | t^\dagger | \beta \rangle \right] d\beta d\mathbf{k} d\mathbf{p} \\ &= 2\hbar^3 \text{tr}_1 \text{tr}_2 \int \beta \times \nabla_q \Im(\beta \mathbf{q} \mathbf{k} 0)|_{\mathbf{q}=0} f_{1-} f_{2+} d\beta d\mathbf{k} d\mathbf{p} \end{aligned} \quad (\text{A12})$$

The change from the β to the \mathbf{q} derivative is accomplished by first utilizing the reality of $\partial_0(\rho s)$ to symmetrize between the first expression of Eq. (A12) and its adjoint, with a subsequent identification of the combination of β derivatives with a \mathbf{q} derivative of $\Im(\beta \mathbf{q} \mathbf{k} 0)$. Here, ff is short for $f_1(\mathbf{p} - \mathbf{k}) f_2(\mathbf{p} + \mathbf{k})$.

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REFERENCES

1. C. F. Curtiss, *J. Chem. Phys.* **24**:225 (1956).
2. S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland Publishing Company, Amsterdam (1962).
3. H. Grad, *Commun. Pure Appl. Math.* **5**:455 (1952); *J. Phys. Chem.* **56**:1039 (1952).
4. R. F. Snider and K. S. Lewchuk, *J. Chem. Phys.* **46**:3163 (1967).
5. J. A. R. Coope, R. F. Snider, and F. R. McCourt, *J. Chem. Phys.* **43**:2269 (1965).
6. L. Waldmann, *Z. Naturforsch.* **12a**:660 (1957).
7. R. F. Snider, *J. Chem. Phys.* **32**:1051 (1960).
8. F. R. McCourt, "Transport Properties of Gases with Rotational States," Dissertation, The University of British Columbia (1966).
9. S. Hess and L. Waldmann, *Z. Naturforsch.* **21a**:1529 (1966).
10. S. Hess, *Z. Naturforsch.* **22a**:187 (1967).
11. D. K. Hoffmann, J. F. Mueller, and C. F. Curtiss, *J. Chem. Phys.* **43**:2878 (1965).
12. K. Baerwinkel and S. Grossmann, *Z. Physik* **198**:277 (1967); K. Baerwinkel, *Z. Naturforsch.* **24a**:22, 38 (1969).
13. C. S. Wang Chang and G. E. Uhlenbeck, "Transport Phenomena in Polyatomic Gases," University of Michigan Report, CM-681 (1951).
14. F. R. McCourt and R. F. Snider, *J. Chem. Phys.* **46**:2387 (1967).
15. F. R. McCourt and R. F. Snider, *J. Chem. Phys.* **47**:4117 (1967).
16. F. M. Chen and R. F. Snider, *J. Chem. Phys.* **50**:4082 (1969).
17. H. S. Green and D. K. Hoffmann, *J. Chem. Phys.* **49**:2600 (1968).