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The Boltzmann Equation for a Polyatomic Gas

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A formulation of the kinetic theory of dilute, classical polyatomic gases is given which parallels the Waldmann development for structureless molecules. In the first section the Boltzmann equation is written in terms of the specific rates of inelastic collision processes and then the properties of these rates and those of the corresponding collision cross sections are examined. The dependence of the distribution function on the dynamical variables is discussed and the equations of change for the gas are derived. Finally, a study is made of the properties of the linearized Boltzmann collision operation. In the second section the Boltzmann equation is deduced from a rigorous statistical–mechanical point of view and discussed in terms of the basic ideas of Bogoliubov. The computationally important special case of impulsive interactions is then considered.

KEY WORDS: Boltzmann equation for polyatomic gases; transition rates for polyatomic molecules; differential cross sections for polyatomic molecules; free-flight invariants; symmetries of collision operator; external field effects on gas transport and relaxation; time scales (for evolution of statistical ensembles); Liouville equation (for polyatomic gases); collision integrals.

1. INTRODUCTION

The last two decades has been a period of significant growth for the kinetic theory of polyatomic gases. It was initiated by Grad's$^{(1)}$ investigation of the statistical mechanics of systems with internal degrees of freedom, transformed into a quantitative tool by Curtiss'$^{(2)}$ development of the classical kinetic theory of rigid nonspherical molecules, and nourished by Waldmann's$^{(3)}$ and Snider's$^{(4)}$ independent derivations of a rigorous quantum kinetic equation for polyatomic species. Within this same

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interval Mason and Monchick(5) tested, amended, and generalized the semiquantal theory of Wang Chang and Uhlenbeck,(6) while Kagan and Afanas'ev(7) and Dahler and his co-workers(8,8a) performed a similar service with regard to Curtiss' classical theory. Finally, there has been an explosive growth of activity stimulated by Beenakker's(9) studies of responses to external magnetic and electric fields which are specific to polyatomic gases.

Indeed, so much has been learned that it is now possible to place the kinetic theory of polyatomic gases on as firm a foundation as that which underlies the theory of monatomic species. Yet, most studies have been devoted to specific models and no general, systematic examination of the structure of the classical Boltzmann equation has appeared. It is the purpose of the present paper to remedy this.

A cataloging of the properties of the Boltzmann equation for structureless molecular species has been presented in very elegant form by Waldmann.(10) The second section of this paper is an attempt to extend his approach to polyatomic species. The third section is devoted to an examination of the formal statistical-mechanical basis of the Boltzmann equation and also to the establishment of the relationship between the general theory and that for species which interact impulsively.

2. PHENOMENOLOGICAL THEORY OF THE BOLTZMANN EQUATION

We consider a gas so dilute that the vast majority of the collisional events which occur can be treated as isolated binary encounters. These collisions involve pairs of molecules in states which we assume to be uncorrelated—the assumption of "molecular chaos"—prior to their mutual interaction and the associated scattering event. Under these circumstances the macroscopic state of the fluid can be characterized wholly in terms of single-particle fields and the microstate can be described fully by the set of singlet distribution functions specific to the various chemical species. In particular, f_α is the density at time t and at the point $\mathbf{x}$ of molecules of type α in the dynamical state $(\mathbf{c}, I)$, which includes the velocity $\mathbf{c}$ of the molecular center of mass and the coordinates and conjugate momenta I which are descriptive of the molecule's internal degrees of freedom. The variables I are selected to be canonical, so that we later can invoke the conservation of extension in phase which is appropriate to variables of this sort. For the moment we leave unanswered the interesting and important question of how these internal-state variables are to be chosen. Frequently we shall employ the contracted notation $f_\alpha(t\mathbf{x}i)$ or simply $f_\alpha(i)$ in place of the more explicit $f_\alpha(t\mathbf{x}\mathbf{c}_i I_i)$.

The basic postulate of the Boltzmann theory is that these distribution functions are governed by the set of kinetic equations

$$\left[\partial_t + \mathbf{c}_1 \cdot \frac{\partial}{\partial \mathbf{x}} + \mathbf{F}_{\alpha 1}^{(e)} \cdot \frac{\partial}{\partial \mathbf{c}_1}\right] f_\alpha(1) + [f_\alpha(1), \mathscr{H}_\alpha(1)] = \partial_c f_\alpha(1) \tag{1}$$

where $[u, v]$ denotes the Poisson bracket of the two functions u and v and where $\mathscr{H}_\alpha(1)$ is that portion of the single-particle Hamiltonian which depends exclusively upon the molecular internal degrees of freedom. Finally, $\mathbf{F}_{\alpha 1}^{(e)}$ stands for the external force per unit mass and

$$\partial_c f_\alpha(1) = \sum_\beta \iiint d1'\, d2'\, d2\, [w_{\alpha\beta}(12R \mid 1'2'R) f_\alpha(1') f_\beta(2') - w_{\alpha\beta}(1'2'R \mid 12R) f_\alpha(1) f_\beta(2)] \tag{2}$$

with $di = d^3c_i\, dI_i$ and where dI_i is the differential element of extension in the phase space associated with the internal degrees of freedom. The quantity $w_{\alpha\beta}(12R \mid 1'2'R)$ is the specific rate (unit concentrations in the reactant states and unit extension in the space of final states) of the binary collision process $(1_\alpha{}'2_\beta{}'R) \rightarrow (1_\alpha 2_\beta R)$. Here, the symbol R refers to a value of the intermolecular separation which is of the order of, but somewhat greater than, the effective range of the intermolecular forces. Since some of the internal-state variables (phases of vibrational modes and orientation of molecular axes) vary rapidly even when the molecules are in free flight, the introduction of this reference separation R is essential if the transition rate $w_{\alpha\beta}(1'2'R \mid 12R)$ is to be well defined.

Implicit in our formulation of the Boltzmann equations (2) is the assumption that the durations and spatial extensions of the collisonal events which cause these transitions can be ignored. This assumption manifests itself here through the appearance in (2) of distribution functions $f_\alpha(1)$, $f_\beta(2)$, $f_\alpha(1')$, and $f_\beta(2')$, all of which are to be evaluated at the same instant and at a single space point.

According to these Boltzmann equations, the evolution of the singlet distribution functions is a first-order Markov process. The randomizing events which are responsible for this stochastic behavior are collisions among the molecules. Therefore, it is t_c, the duration of a collision, and ω_f, the frequency with which these collisions occurs, which fix the time scale of definition for the distribution functions. This means that there is an intrinsic lower limit to the time resolution of the events which contribute to the Boltzmann equation. Stated somewhat differently, the distribution functions to which the Boltzmann equations pertain are not instantaneous densities, but averages over a time which is greater than the duration of an individual collision but less than the interval which elapses between successive collisions. These functions contain no information whatsoever about fluctuations with frequencies in excess of t_c^{-1}. To be somewhat more precise, let us for the moment assume that the intermolecular forces have a finite range R. At the low densities to which the Boltzmann equations apply the free path length $\lambda_f = 1/nR^2$ may be a hundred or a thousand times greater than R itself. Therefore, the interval between successive collisions, the so-called free-path transit time, $t_f = \omega_f^{-1} = \lambda_f/\bar{c} = \lambda_f/(8kT/\pi m)^{1/2}$, exceeds the duration of a collision, $t_c \approx R/\bar{c}$, by several orders of magnitude. Since we have assumed that the distribution functions of the Boltzmann equations do not change significantly in a period of the order of t_c ($\ll t_f$), neither will they vary over distances of the order of $\bar{c}t_c \approx R$. This argument establishes the internal consistency of our assignment of the same time and place coordinates to each of the singlet distribution functions of (2). Later we shall see that similar considerations permit us to determine the dependence of the distribution function upon the coordinates which describe the internal degrees of freedom.

2.1. The Properties of $w_{\alpha\beta}(12R \mid 1'2'R)$

The properties of the transition-rate matrix w are determined completely by the dynamics of binary encounters. From its definition as a transition rate it follows that $w_{\alpha\beta}(12R \mid 1'2'R)$ must be real and nonnegative. Furthermore, it is obvious that these rate coefficients must be such that $w_{\alpha\beta}(12R \mid 1'2'R) = w_{\beta\alpha}(21R \mid 2'1'R)$. In addition to these there are other constraints upon the transition rates:

(1) If these rates are to exhibit Galilean invariance, then $w_{\alpha\beta}(12R \mid 1'2'R)$ can depend upon the particle velocities only in the combinations $\mathbf{c}_{21}$ ($\equiv \mathbf{c}_2 - \mathbf{c}_1$), $\mathbf{c}'_{21}$, and $\mathbf{G} - \mathbf{G}'$, where $\mathbf{G} = (m_\alpha \mathbf{c}_1 + m_\beta \mathbf{c}_2)/(m_\alpha + m_\beta)$ is the velocity of the center of mass of the pair. (Later we shall see that there are other, more subtle restrictions which arise from the requirements of rotational invariance.)

(2) Conservation of linear momentum demands that w be diagonal with respect to the total (pair) momentum, i.e., that $w_{\alpha\beta}(12 \mid 1'2')$ be proportional to the Dirac delta function $\delta_3(\mathbf{G} - \mathbf{G}')$.

(3) Conservation of energy implies that w is proportional to

$$\delta_1(E_{1\alpha} + E_{2\beta} - E_{1\alpha'} - E_{2\beta'}), \quad \text{with} \quad E_{i\gamma} = (1/2)\, m_\gamma c_i^2 + \epsilon_\gamma(i)$$

and where ϵ_γ is the energy associated with the internal degrees of freedom of a γ-species molecule.

(4) The assumption of "point collisions" implies that the only dependence of w upon $\mathbf{x}$ is that due to variation of the transition rate with the local value of the external field strength.

(5) Molecular systems exhibit parity and time-reversal invariance. Therefore, $w_{\alpha\beta}(12 \mid 1'2') = w_{\alpha\beta}(\hat{P}1\ \hat{P}2 \mid \hat{P}1'\ \hat{P}2')$ and $w_{\alpha\beta}(12 \mid 1'2') = w_{\alpha\beta}(\hat{T}1'\ \hat{T}2' \mid \hat{T}1\ \hat{T}2)$, where $\hat{P}$ and $\hat{T}$ are the parity and time-reversal operators.

(6) As a consequence of time-reversal invariance, the transition rate satisfies the condition,

$$\iint d1'\, d2'\, w_{\alpha\beta}(12 \mid 1'2') = \iint d1'\, d2'\, w_{\alpha\beta}(1'2' \mid 12) \tag{3}$$

of "bilateral normalization."(11)
There can be little question about the first four of these conditions but the fifth and sixth deserve further comment:

Time-Reversal Invariance. Consider a mechanical event a → b. Define a state $\hat{T}$a which differs from a only in that the algebraic signs of all velocities are opposite to those of a. (If there is a magnetic field, then its sign is also to be reversed.) The equations of motion for a conservative system are such that when the algebraic signs of the velocities are reversed, the motions are reversed, i.e., the events of a sequence are unaltered, but their order of occurrence is reversed. Hence, the specific rate of the process a → b is identical to that of $\hat{T}$b → $\hat{T}$a, or $w_F(\mathrm{b} \mid \mathrm{a}) = w_{\hat{T}F}(\hat{T}\mathrm{a} \mid \hat{T}\mathrm{b})$. Here the subscript F refers to an external field and $\hat{T}F$ to its time-reversed image ($\hat{T}\mathbf{E} = \mathbf{E}$, $\hat{T}\mathbf{H} = -\mathbf{H}$).

Parity or Reflection Invariance. The state $\hat{P}\mathsf{a}$ is the image of a seen in a mirror. It differs from a in that every polar vector contained in a is replaced with its negative. Axial vectors (for example, the "vector product" of two polar vectors) are unaltered by reflection. It is obvious that the conventional laws of mechanics ensure the equality of rate of the process $\mathsf{a} \to \mathsf{b}$ and that of its mirrored image $\hat{P}\mathsf{a} \to \hat{P}\mathsf{b}$. Therefore, $w(\mathsf{a} \mid \mathsf{b}) = w(\hat{P}\mathsf{a} \mid \hat{P}\mathsf{b})$ or, more specifically, $w_{\alpha\beta}(12 \mid 1'2') = w_{\alpha\beta}(\hat{P}1\, \hat{P}2 \mid \hat{P}1'\, \hat{P}2')$.

Bilateral Normalization. A "complete set" of states $\{\mathsf{b}\}$ is one for which the associated fractional occupations (or occupational probabilities) $p(\mathsf{b})$ satisfy the condition $\int d\mathsf{b}\, p(\mathsf{b}) = 1$. If $\{\mathsf{b}\}$ is complete, then so also is $\{\hat{T}\mathsf{b}\}$. Therefore,

$$\int d\mathsf{b}\; w_F(\mathsf{b} \mid \mathsf{a}) = \int d(\hat{T}\mathsf{b})\; w_F(\mathsf{b} \mid \mathsf{a}) = \int d(\hat{T}\mathsf{b})\; w_{\hat{T}F}(\hat{T}\mathsf{a} \mid \hat{T}\mathsf{b})$$

If we now replace $\hat{T}\mathsf{b}$ with the label b, then we must simultaneously replace the related state $\hat{T}\mathsf{a}$ with $(\hat{T})^{-1}\hat{T}\mathsf{a} = \mathsf{a}$ and the field $\hat{T}F$ with F. Hence,

$$\int d\mathsf{b}\; w_F(\mathsf{b} \mid \mathsf{a}) = \int d\mathsf{b}\; w_F(\mathsf{a} \mid \mathsf{b})$$

The condition of bilateral normalization permits us to rewrite the Boltzmann equations (2) in the more familiar forms

$$\partial_c f_\alpha(1) = \sum_\beta \iiint d1'\, d2'\, d2\; w_{\alpha\beta}(12R \mid 1'2'R)[f_\alpha(1')\, f_\beta(2') - f_\alpha(1)\, f_\beta(2)] \qquad (4)$$

Rotational Invariance. We have examined the consequences of parity and of time-reversal invariance. The first of these symmetry conditions is essential to the proof of the Curie principle; the second leads to the Onsager relations and to the demonstration that the coefficients of viscosity, thermal conductivity, and diffusion are positive-definite.[3] The remaining symmetries to be investigated are those associated with rotation. The approach we adopt is patterned after that used with parity and time reversal. In the case of parity we compared an event $\mathsf{a} \to \mathsf{b}$ with its mirror image $\hat{P}\mathsf{a} \to \hat{P}\mathsf{b}$ and concluded that the corresponding specific rates must be equal. With time reversal we compared an event $\mathsf{a} \to \mathsf{b}$ to the "playback" $\hat{T}\mathsf{b} \to \hat{T}\mathsf{a}$ wherein the sequence of states was reversed and each velocity replaced with its negative. Then, since there was no experience to the contrary (in atomic and molecular physics), we demanded that the specific rates of these two processes be equal. A similar argument is relied upon in the case of rotational invariance. We imagine that a scattering event has been recorded by two observors who are attached to coordinate frames which are related to one another by a rigid rotation. The assertion of rotational invariance is that the description of the event is the same

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[3] See (b) and (c), (e), and (a), respectively, of the subsection, "Symmetry Conditions and Bracket Integrals," p. 539.

in one frame as in the other. Stated a bit differently, we compare an event a → b to another, $\hat{R}$a → $\hat{R}$b, wherein each variable is measured relative to a set of axes which are rotated with respect to those used in the description of a → b. Rotational invariance then implies the equality of the specific rates $w(\mathrm{b} \mid \mathrm{a})$ and $w(\hat{R}\mathrm{b} \mid \hat{R}\mathrm{a})$.

2.2. Scattering Cross Sections

The transition rate $w_{\alpha\beta}(12 \mid 1'2')$ is closely related to the differential cross section $\Sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2' \to \mathbf{c}I_1I_2)$ for scattering from a beam with the relative velocity $\mathbf{c}' = \mathbf{c}_2' - \mathbf{c}_1'$ into a final state with the relative velocity $\mathbf{c} = \mathbf{c}_2 - \mathbf{c}_1$. To establish the exact nature of this relationship, we have only to recall the definition of the cross section. Imagine, first, a uniform beam of β-species molecules, each in the state I_2' and each moving with the same velocity $\mathbf{c}'$ relative to an α-species molecule which is at rest and in the state I_1'. (Here it must be understood that the beam consists of molecules which are in the state I_2' at the instant when their centers of mass pierce a sphere of radius R centered on the target particle. Despite the impossibility of producing such a beam, it does offer some theoretical advantages which we wish to exploit before we focus our attention upon cross sections which correspond to physically accessible conditions.) The beam is assumed to be of unit concentration, that is, it contains one β-species particle per unit volume. Therefore, the current density of the beam is numerically equal to c'. A collection device which subtends an element of solid angle $d^2\hat{c}$ is positioned in the direction $\hat{c}$ from the target particle. The current of β-species particles which is collected by this device will be proportional to $d^2\hat{c}$ and to c'. The coefficient of proportionality for that portion of the current associated with collisions which result in the final relative velocity $\mathbf{c}$ and the final states I_1 and I_2 is the differential cross section $\Sigma_{\alpha\beta}$. Therefore, we conclude that

$$w_{\alpha\beta}(12 \mid 1'2')\, d^3c_1\, d^3c_2\, dI_1\, dI_2 = c'\Sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2' \to \mathbf{c}I_1I_2)\, d^2\hat{c}\, dI_1\, dI_2 \qquad (5)$$

Because energy and momentum are conserved in a collision, both $w_{\alpha\beta}$ and $\Sigma_{\alpha\beta}$ must be proportional to $\delta_3(\mathbf{G} - \mathbf{G}')\, \delta_1(E_{\alpha 1} + E_{\beta 2} - E_{\alpha 1'} - E_{\beta 2'})$. Therefore, it is convenient to extract the delta-function singularities from $\Sigma_{\alpha\beta}$ and introduce the differential cross section $\sigma_{\alpha\beta} = \Sigma_{\alpha\beta}/[\delta_3(\mathbf{G} - \mathbf{G}')\, d^3G\, \delta_1(E - E')\, dE]$ which is defined only on the energy–momentum shell. Here $E = \frac{1}{2}\mu_{\alpha\beta}c^2 + \epsilon_\alpha + \epsilon_\beta$ and $\mu_{\alpha\beta} = m_\alpha m_\beta/(m_\alpha + m_\beta)$ is the reduced mass of the colliding pair. In terms of the differential cross section $\sigma_{\alpha\beta}$ the relationship (5) becomes

$$w_{\alpha\beta}(12 \mid 1'2')\, d^3c_1\, d^3c_2 = c'\sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2' \to \mathbf{c}I_1I_2)\, d^2\hat{c}\, \delta_3(\mathbf{G} - \mathbf{G}')\, d^3G\, \delta_1(E - E')\, dE \qquad (6)$$

Then, since $d^3c_1\, d^3c_2 = d^3c\, d^3G = (c/\mu_{\alpha\beta})\, d^2\hat{c}\, dE\, d^3G$, it follows that

$$w_{\alpha\beta}(12 \mid 1'2') = \mu_{\alpha\beta}(c'/c)\, \sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2' \to cI_1I_2)\, \delta_3(\mathbf{G} - \mathbf{G}')\, \delta_1(E - E') \qquad (7)$$

and, furthermore, that the Boltzmann equations (4) can be written in the form

$$\partial_c f_\alpha(1) = \sum_\beta \int \cdots \int d^2c'\, d^3c_2\, dI_1'\, dI_2'\, dI_2$$
$$\times \{(c'^2/c)\, \sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2' \to \mathbf{c}I_1I_2)[f_\alpha(1')\, f_\beta(2') - f_\alpha(1)\, f_\beta(2)]\}_{EG} \qquad (8)$$

where the subscript EG indicates that the primed and unprimed states share common values of energy and momentum.

As a consequence of time-reversal invariance and parity, the differential cross sections satisfy the condition

$$\begin{aligned} c'^2\sigma_{\alpha\beta}(\mathbf{c}', I_1', I_2' \to \mathbf{c}, I_1, I_2) &= c^2\sigma_{\alpha\beta}(\hat{T}\{\mathbf{c}, I_1, I_2\}) \to \hat{T}\{\mathbf{c}', I_1', I_2'\}) \\ &= c^2\sigma_{\alpha\beta}(\mathbf{c}, \hat{T}\hat{P}I_1, \hat{T}\hat{P}I_2 \to \mathbf{c}', \hat{T}\hat{P}I_1', \hat{T}\hat{P}I_2') \end{aligned} \tag{9}$$

which is commonly referred to as microreversibility.

Construction of $w_{\alpha\beta}$ and $\sigma_{\alpha\beta}$. Let us suppose that a particular collision occurs at $t = 0$, that at that instant the separation of the molecular centers of mass is a minimum. The duration of the collision t_c is the length of time that the molecules lie within the effective range of their mutual interaction. We assume that this interaction has a very limited range. Therefore, the trajectory descriptive of the relative motion of the mass centers of the colliding molecules consists of two rectilinear segments,

$$\begin{aligned} \mathbf{r}^<(t) &= \mathbf{b}' + \mathbf{c}'t, \qquad t < -\tfrac{1}{2}t_c \\ \mathbf{r}^>(t) &= \mathbf{b} + \mathbf{c}t, \qquad t > +\tfrac{1}{2}t_c \end{aligned}$$

and a short connective path which passes through the region in space where the collision actually occurs.

The vectors $\mathbf{b}'$ and $\mathbf{b}$ (which are perpendicular to $\mathbf{c}'$ and $\mathbf{c}$, respectively) are called the pre- and postcollisional "impact parameters." The vector $\mathbf{b}'$ is the value which the vector separation of the two molecules would assume at the instant ($t = 0$) of closest approach if there were no intermolecular forces: $\mathbf{b}$ is a similarly defined parameter associated with the time-reversed image of the dynamical trajectory.

Now, prior to collision the relative orbital angular momentum of the pair is given by

$$\mathbf{l}' = \mathbf{r}^<(t) \times \mathbf{p}' = \mathbf{b}' \times \mathbf{p}', \qquad t < -\tfrac{1}{2}t_c$$

where $\mathbf{p}' = \mu_{\alpha\beta}\mathbf{c}'$. After the collision has occurred the angular momentum of the relative motion is equal to

$$\mathbf{l} = \mathbf{r}^>(t) \times \mathbf{p} = \mathbf{b} \times \mathbf{p}, \qquad t > +\tfrac{1}{2}t_c$$

Conservation of angular momentum implies that $\mathbf{l} + \mathbf{L}_1 + \mathbf{L}_2 = \mathbf{l}' + \mathbf{L}_1' + \mathbf{L}_2'$ where $\mathbf{L}_i$ is the "spin" or rotational angular momentum of molecule i. Then, since $\mathbf{l}' = \mathbf{b}' \times \mathbf{p}'$ and $\mathbf{b} = p^{-2}\mathbf{p} \times \mathbf{l}$, we see that $\mathbf{b}$ is related to the primed variables through the formula

$$\begin{aligned} \mathbf{b} &= p^{-2}\mathbf{p} \times [\mathbf{l}' + (\mathbf{L}_1' - \mathbf{L}_1) + (\mathbf{L}_2' - \mathbf{L}_2)] \\ &= p^{-2}\mathbf{p} \times [\mathbf{b}' \times \mathbf{p}' + (\mathbf{L}_1' - \mathbf{L}_1) + (\mathbf{L}_2' - \mathbf{L}_2)] \end{aligned}$$

where $p^2 = p'^2 + 2\mu_{\alpha\beta}[\{\epsilon_\alpha(I_1') - \epsilon_\alpha(I_1)\} + \{\epsilon_\beta(I_2') - \epsilon_\beta(I_2)\}]$.

We now denote by Z the ensemble density associated with the steadystate scattering experiment described previously. This function must be that solution of the two-particle Liouville equation, $[Z, H^{(2)}] = 0$, which satisfies the boundary condition $Z(1, 2) = \delta(1' - 1)\,\delta(2' - 2)$ on the "precollision hemisphere" $\{|\,\mathbf{x}_{21}\,| = R;\ \mathbf{x}_{21} \cdot \mathbf{c}'_{21} < 0\}$. Here $H^{(2)}$ is the Hamiltonian function for a system of two interacting molecules and $\delta(i' - i) \equiv \delta_3(\mathbf{c}_i' - \mathbf{c}_i)\,\delta(I_i' - I_i)$. Now a dynamical trajectory which emerges from the collision sphere in the state $(12\mathbf{b}, R)$ is connected to a unique state $(1^\star 2^\star \mathbf{b}^\star, R)$ on the precollision hemisphere. Therefore, since the values of the ensemble density are propagated along the characteristic curves (dynamical trajectories) of the Liouville equation, the desired solution of that equation assumes the form $Z(1, 2) = \delta(1' - 1^\star)\,\delta(2' - 2^\star)$ on the "postcollision hemisphere." The current density of scattered molecular pairs with impact parameters in the range $(\mathbf{b}, d\mathbf{b})$ is $c\,d^2b$. Consequently, $w_{\alpha\beta}(12R \mid 1'2'R)$, the specific rate at which pairs of molecules are scattered from the initial (primed) into the final (unprimed) states is equal to

$$w_{\alpha\beta}(12R \mid 1'2'R) = \int d^2b\; cZ = \int d^2b\; c\,\delta(1' - 1^\star)\,\delta(2' - 2^\star) \tag{10}$$

By comparing this result with (7) and recalling that $\delta_3(\mathbf{c}_1' - \mathbf{c}_1^\star)\,\delta_3(\mathbf{c}_2' - \mathbf{c}_2^\star) = (\mu_{\alpha\beta}/c)\,\delta_2(\hat{\mathbf{c}}' - \hat{\mathbf{c}}^\star)\,\delta_3(\mathbf{G} - \mathbf{G}')\,\delta_1(E - E')$, we conclude that

$$\sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2'R \to \mathbf{c}I_1I_2R) = (c/c')^2 \int d^2b\; \delta_2(\hat{\mathbf{c}}' - \hat{\mathbf{c}}^\star)\,\delta(I_1' - I_1^\star)\,\delta(I_2' - I_2^\star) \tag{11}$$

Because of time-reversal invariance, it is possible to express the transition rate and differential cross section in the alternate forms

$$w_{\alpha\beta}(12R \mid 1'2'R) = \int d^2b'\; c'\,\delta(1 - 1^*)\,\delta(2 - 2^*) \tag{12}$$

and

$$\sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2'R \to \mathbf{c}I_1I_2R) = \int d^2b'\; \delta_2(\hat{\mathbf{c}} - \hat{\mathbf{c}}^*)\,\delta(I_1 - I_1^*)\,\delta(I_2 - I_2^*) \tag{13}$$

where the asterisks refer to the unique final state on the postcollisional hemisphere which evolves from the initial state $(\mathbf{c}_1', I_1', \mathbf{c}_2', I_2', \mathbf{b}', R)$. The cross section, as expressed by (13), can be identified with the area in the precollision $\mathbf{b}'$-plane which scatters into unit solid angle about the direction $\hat{c}$. By changing the variables of integration from $\mathbf{b}'$ to $\hat{\mathbf{c}}^*$ (and exercising care if $\mathbf{b}'$ is not a single-valued function of $\hat{\mathbf{c}}^*$), we obtain the relationship

$$\sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2'R \to \mathbf{c}I_1I_2R) = \left|\, \partial(\mathbf{b}')/\partial(\hat{\mathbf{c}}^*)\right|_{\hat{\mathbf{c}}^* = \hat{\mathbf{c}}}\,\delta(I_1 - I_1^*)\,\delta(I_2 - I_2^*) \tag{14}$$

between the differential cross section and the Jacobian of the transformation from $\mathbf{b}'$ to $\hat{\mathbf{c}}^*$.

Finally, as a consequence of parity and time-reversal invariance it can be shown that to each event $(\mathbf{b}', \mathbf{p}', I_1', I_2') \to (\mathbf{b}, \mathbf{p}, I_1, I_2)$ there corresponds the unique event $(\hat{T}\hat{P}\mathbf{b}, \hat{T}\hat{P}\mathbf{p}, \hat{T}\hat{P}I_1, \hat{T}\hat{P}I_2) \to (\hat{T}\hat{P}\mathbf{b}', \hat{T}\hat{P}\mathbf{p}', \hat{T}\hat{P}I_1', \hat{T}\hat{P}I_2')$ or $(-\mathbf{b}, \mathbf{p}, \hat{T}\hat{P}I_1, \hat{T}\hat{P}I_2) \to (-\mathbf{b}', \mathbf{p}', \hat{T}\hat{P}I_1', \hat{T}\hat{P}I_2')$. The algebraic signs of the impact parameters and of the angular momenta and axial orientations are opposite in the "direct" and "$\hat{T}\hat{P}$-imaged" events: if the direct collision changes the relative momentum from $\mathbf{p}'$ to $\mathbf{p}$, then the $\hat{T}\hat{P}$-imaged collision causes scattering from $\mathbf{p}$ to $\mathbf{p}'$; if the direct collision changes the spins $\mathbf{L}_1'$ and $\mathbf{L}_2'$ to $\mathbf{L}_1$ and $\mathbf{L}_2$, respectively, then the $\hat{T}\hat{P}$-imaged process is accompanied by transitions from $-\mathbf{L}_1$ and $-\mathbf{L}_2$ to $-\mathbf{L}_1'$ and $-\mathbf{L}_2'$.

2.3. Free-Flight Invariants

The transition rates and cross sections of the previous sections depend upon some variables whose values are not normally monitored in scattering experiments. For example, in the case of a rotor, one certainly is interested in collisional alterations of the molecular spin angular momentum, but one is neither concerned with nor able to measure molecular orientation. Also, when vibrations are involved it is the energy and not the phase of the motion which is of interest. Now the cross sections which are experimentally accessible are, in some sense, averages over the unmonitored variables and, as we shall see, it is precisely these averaged cross sections which are of importance in kinetic theory.

Much of what concerns us here is dependent upon the precise nature of the internal-state variables I_i. Thus far we have made no specific demands upon these variables other than to stipulate that they consist of generalized coordinates and the associated conjugate momenta. However, it is clear that we should choose these variables so that they separate into two categories, those which can and those which cannot be monitored in real scattering experiments. The former are "free-flight invariants," that is, variables whose values remain constant (in the absence of external fields) during the intervals between successive molecular collisions. This confronts us with the problems of determining the number of these free-flight invariants and of establishing a physical interpretation for each. There are no general, unqualified answers to these questions. However, it is possible to answer both provided that the Hamiltonian function (and/or the associated Hamilton–Jacobi equation) for the internal degrees of freedom of a single molecule is separable in some coordinate system. For, when this is so the motion of each conjugate coordinate–momentum pair (q_s, p_s) will be periodic and the associated action variable $J_s = \oint p_s\, dq_s$ (being equal to the phase volume enclosed within one orbit) will be a constant of the motion that is, a free-flight invariant.

It is possible for some of the frequencies associated with these n action variables to be degenerate, in which case there will exist $m \leqslant n - 1$ linearly independent commensurability relationships, $\sum_i a_{ki}\omega_i = 0$, with $k = 1,\ldots, m$. Here $\omega_i \equiv \dot{\phi}_i(J_1 \cdots J_n) = \partial\mathscr{H}(J_1 \cdots J_n)/\partial J_i$ is the frequency associated with one of the separable modes, ϕ_i is the angle conjugate to the momentum J_i, and the coefficients a_{ki} are integers. As a consequence of this degeneracy one is able to replace the original set of angle variables, $\{\phi_i\,; i = 1,\ldots, n\}$, with a set $\{\phi_i' = \sum_j a_{ij}\phi_j\,, i = 1,\ldots, m;$ $\phi_i\,, i = m + 1,\ldots, n\}$ which includes m angle variables each of which is of zero frequency and so identifiable as a constant of the free-flight motion. The Hamiltonian function for the internal degrees of freedom is dependent only upon those transformed action variables J_i', $i = m + 1,\ldots, n$, for which the corresponding frequencies $\omega_i' = \dot{\phi}_i$

are different from zero. Each commensurability relationship implies existence of a simply periodic motion in a two- or higher-dimensional subspace of the coordinates q_s ; $s = 1,..., n$. For example, if two frequencies ω_s and ω_t are commensurable, then the orbit in the $q_s q_t$-plane is closed; if these frequencies are incommensurable, the orbit densely fills a portion of this plane.

There are a few systems of special importance which deserve individual attention. In the case of a rigid, symmetric top the usual choices of coordinates and momenta are the Euler angles θ, ϕ, ψ and the corresponding momenta p_θ, p_ϕ, p_ψ. It is convenient to select these angles so that ϕ measures the precession of the (major) symmetry axis of the inertial ellipsoid about the fixed direction of **L**, the rotational angular momentum, that θ is the angle between this symmetry axis and **L**, and that ψ is the angle between the line of nodes and one of the degenerate principle axes of the inertial ellipsoid. The frequencies associated with these rotational coordinates are $\omega_\theta = 0$, $\omega_\phi = | \mathbf{L} |/2\pi\Gamma$, and $\omega_\psi = (K/2\pi)(\Gamma^{-1} - \Gamma'^{-1})$. Here, $K(\equiv L \cos\theta)$ is the component of angular momentum along the symmetry axis of the inertial ellipsoid, Γ is the principle moment of inertia about the symmetry axis, and Γ' the doubly-degenerate principle moment. Since the latter two of these frequencies are in no way related, there is only one commensurability relationship and so only four independent free-flight invariants. Although the choice of these four invariants is somewhat arbitrary, it is natural and convenient to select $K/L \equiv \cos\theta$ (or alternatively, K) and the three components of **L** measured along the axes of a space-fixed frame. In the case of a spherical top ($\Gamma \to \Gamma'$) the frequency ω_ψ is equal to zero, and so there are five free-flight invariants. The additional invariant can be chosen equal to ψ. In both of these cases it is natural to select ϕ, $\cos\theta$, ψ, and **L** as variables instead of the canonical set of Euler angles and conjugate momenta. It is readily established that $dI = d\theta\, d\phi\, d\psi\, dp_\theta\, dp_\phi\, dp_\psi = d(\cos\theta)\, d\phi\, d\psi\, d^3L$ and that for this choice of variables (1) becomes

$$\Big[\partial_t + \mathbf{c}_1 \cdot \frac{\partial}{\partial \mathbf{x}} + \mathbf{F}_{\alpha 1}^{(e)} \cdot \frac{\partial}{\partial \mathbf{c}_1} + \frac{|\mathbf{L}|}{\Gamma} \frac{\partial}{\partial \phi} + K(\Gamma^{-1} - \Gamma'^{-1}) \frac{\partial}{\partial \psi} + \mathbf{N}_{\alpha 1}^{(e)} \cdot \frac{\partial}{\partial \mathbf{L}}\Big] f_\alpha(1) = \partial_c f_\alpha(1)$$

where $\mathbf{N}_{\alpha 1}^{(e)}$ is the external torque on a molecule of species α. An analysis of this same sort is not strictly applicable to the asymmetric top because in that case there is no separable coordinate system. However, it is readily established that there are four free-flight invariants associated with an asymmetric top, the three components of **L** and the rotational energy.

One free-flight invariant can be associated with each pure vibrational mode. If this invariant is selected to be the vibrational energy, then the associated angle variable is the phase of the vibrational motion. When two vibrational frequencies are degenerate, there will be an additional constant of the motion. For example, in the case of a linear triatomic molecule with two degenerate bending modes this constant can be identified with the phase difference between the vibrations in and out of the plane of **L** and the molecular axis. Although such invariants are usually of limited importance in kinetic theory, we shall retain them along with the others and then later indicate how they can be eliminated from the formalism.

The previous considerations now permit us to be rather specific concerning the types of variables which fall into the category of free-flight invariants and those which do not. Thus, we assume that the canonical variables I can be separated into a set of invariants $\mathscr{J}$ consisting of action variables and of angles with zero frequencies, and a set η consisting of angle variables which vary linearly with time. The frequencies associated with the members of the set η are typically of the order of 10^{11} sec^{-1} or greater.

We have mentioned previously that the distribution function of the Boltzmann equation is the average over an interval of time which is long compared to the duration of a collision, but less than the interval between successive collisions. From this we concluded that the Boltzmann distribution function was independent of variations which occur with frequencies in excess of the collision frequency $\omega_f \approx 10^9$ sec^{-1}. Since the frequencies of the η variables are greater than ω_f we must assume that the Boltzmann distribution function is independent of these variables, i.e., that

$$f_\alpha(t\mathbf{x}\mathbf{c}I) \to (1/\Delta_\alpha)\, F_\alpha(t\mathbf{x}\mathbf{c}\mathscr{J})$$

where $\Delta_\alpha = \int d\eta$.

Then, to determine the collisional rate of change of $F_\alpha(t\mathbf{x}\mathbf{c}_1\mathscr{J}_1) \equiv F_\alpha(t\mathbf{x}\bar{1})$ we integrate (4) over the range of the variables η_1 and obtain

$$\partial_c F_\alpha(t\mathbf{x}\bar{1}) = \sum_\beta \iiint d\bar{1}'\, d\bar{2}'\, d\bar{2}\; w_{\alpha\beta}(\bar{1}\bar{2} \mid \bar{1}'\bar{2}')[F_\alpha(\bar{1}')\, F_\beta(\bar{2}') - F_\alpha(\bar{1})\, F_\beta(\bar{2})] \tag{15}$$

with $\bar{i} = (\mathbf{c}_i\,, \mathscr{J}_i)$, $d\bar{i} = d^3c_i\, d\mathscr{J}_i$, and

$$w_{\alpha\beta}(\bar{1}\bar{2} \mid \bar{1}'\bar{2}') = (1/\Delta_\alpha\, \Delta_\beta) \iiiint d\eta_1\, d\eta_2\, d\eta_1'\, d\eta_2'\; w_{\alpha\beta}(12R \mid 1'2'R) \tag{16}$$

This transition rate and the corresponding differential cross section,

$$\sigma_{\alpha\beta}(\mathbf{c}'\mathscr{J}_1'\mathscr{J}_2' \to \mathbf{c}\mathscr{J}_1\mathscr{J}_2) = (1/\Delta_\alpha\, \Delta_\beta) \iiiint d\eta_1\, d\eta_2\, d\eta_1'\, d\eta_2'\; \sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2'R \to \mathbf{c}I_1I_2R) \tag{17}$$

are defined in terms of the unweighted averages over initial and final values of the variables η_i of the rate of scattering of β-species molecules in the state $\mathscr{J}_2'$ by α-species molecules in the state $\mathscr{J}_1'$. Thus, if Z' is the solution of the steady-state Liouville equation $[Z', H^{(2)}] = 0$ which satisfies the precollision boundary condition $Z'(\bar{1}, \bar{2}) = (\Delta_\alpha\, \Delta_\beta)^{-1}\, \delta(\bar{1}' - \bar{1})\, \delta(\bar{2}' - \bar{2})$, then the specific rate of the scattering process $(\mathbf{c}'\mathscr{J}_1'\mathscr{J}_2') \to (\mathbf{c}\mathscr{J}_1\mathscr{J}_2)$ is given by

$$w_{\alpha\beta}(\bar{1}\bar{2} \mid \bar{1}'\bar{2}') = (1/\Delta_\alpha\, \Delta_\beta) \iint d\eta_1\, d\eta_2 \int d^2b\; cZ'$$

in agreement with (16). It is important to recognize that $w_{\alpha\beta}(\bar{1}\bar{2} \mid \bar{1}'\bar{2}')$, unlike $w_{\alpha\beta}(12R \mid 1'2'R)$, is independent of the value of the parameter R.

To prove this, we have only to note that

$$\frac{\partial}{\partial R}\, w_{\alpha\beta}(\overline{12} \mid \overline{1}'\overline{2}') = \frac{1}{\Delta_\alpha\, \Delta_\beta} \iiiint d\eta_1\, d\eta_2\, d\eta_1{}'\, d\eta_2{}' \Big\{ \sum_{i_1} \Big[\frac{\omega'_{i_1}}{c'} \frac{\partial}{\partial \phi'_{i_1}} - \frac{\omega_{i_1}}{c} \frac{\partial}{\partial \phi_{i_1}} \Big]$$

$$+ \sum_{i_2} \Big[\frac{\omega'_{i_2}}{c'} \frac{\partial}{\partial \phi'_{i_2}} - \frac{\omega_{i_2}}{c} \frac{\partial}{\partial \phi_{i_2}} \Big] \Big\}\, w_{\alpha\beta}(12R \mid 1'2'R) = 0$$

where the sums extend over all angle variables with nonzero frequencies, that is, over all variables included in the sets η_1 and η_2. Because of the simple relationships between the two pairs of functions, it is obvious that the phase-averaged transition rate and differential cross section exhibit the same symmetry and invariance properties as do $w_{\alpha\beta}(12R \mid 1'2'R)$ and $\sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2'R \to \mathbf{c}I_1I_2R)$.

By way of illustration, let us again examine the symmetric top. For convenience we replace the canonical set of action-angle variables with $\mathscr{J} = (L, K)$ and $\eta = (\psi, \phi)$. The Jacobian of this transformation is equal to L^{-1} and $\Delta_\alpha = (2\pi)^2$. Furthermore, in order to simulate a situation which is commonly encountered, let us assume the molecular interactions are such that the axial components of angular momentum are collisional invariants, i.e., that

$$w_{\alpha\beta}(\overline{12} \mid \overline{1}'\overline{2}') = \tilde{w}_{\alpha\beta}(\mathbf{c}_1\mathbf{L}_1\,,\, \mathbf{c}_2\mathbf{L}_2 \mid \mathbf{c}_1{}'\mathbf{L}_1{}',\, \mathbf{c}_2{}'\mathbf{L}_2{}')\, \delta(K_1 - K_1{}')\, \delta(K_2 - K_2{}')$$

Under these circumstances the distribution in K is unaltered by collisions. In practice this distribution will be sharp, so that $F_\alpha(t\mathbf{x}\mathbf{c}\mathbf{L}K)$ is of the form $F_\alpha(t\mathbf{x}\mathbf{c}L)\, \delta(K - K_\alpha)$. For example, if α denotes a diatomic species in a Π electronic state, K_α will be equal to $\hbar$. If K_α were equal to zero, the theory would be descriptive of the Σ electronic state of a diatomic species. Whichever the case, it follows from (15) that the collisional rate of change of $F_\alpha(\tilde{1}) \equiv F_\alpha(t\mathbf{x}\mathbf{c}_1\mathbf{L}_1)$ will be given by

$$\partial_c F_\alpha(\tilde{1}) = \sum_\beta \iiint d\tilde{1}'\, d\tilde{2}'\, d\tilde{2}\, \tilde{w}_{\alpha\beta}(\tilde{1}\tilde{2} \mid \tilde{1}'\tilde{2}')[F_\alpha(\tilde{1}')\, F_\beta(\tilde{2}') - F_\alpha(\tilde{1})\, F_\beta(\tilde{2})] \tag{18}$$

where $\tilde{i} = (\mathbf{c}_i\,, \mathbf{L}_i)$ and $d\tilde{i} = d^3c_i\, d^3\mathbf{L}_i/L_i$.

Now that we recognize how the functional dependence of the Boltzmann distribution function is regulated by the approximations implicit in the assumed form of the collisional term, we must perform a corresponding modification upon the "left-hand side" of the Boltzmann equation. In particular, we replace $f_\alpha(t\mathbf{x}1)$ with $F_\alpha(t\mathbf{x}\bar{1})(1/\Delta_\alpha)$ in (1) and integrate over the range of η_1 to obtain

$$\Big(\partial_t + \mathbf{c}_1 \cdot \frac{\partial}{\partial \mathbf{x}} + \bar{\mathbf{F}}^{(e)}_{\alpha 1} \cdot \frac{\partial}{\partial \mathbf{c}_1}\Big) F_\alpha(t\mathbf{x}\bar{1}) + \overline{[F_\alpha(t\mathbf{x}\bar{1})\, \mathscr{H}_\alpha(1)]} = \partial_c F_\alpha(t\mathbf{x}\bar{1}) \tag{19}$$

Here a bar above a function denotes its average over the η variables. Due to the definition of these variables, the average of $[F_\alpha\,, \mathscr{H}_\alpha]$ will vanish unless there is a dependence of the internal-state Hamiltonian $\mathscr{H}_\alpha$ upon an external field. For example, in the dipole approximation the interaction of a molecule with an electric or magnetic field is given by $-\boldsymbol{\mu} \cdot \mathbf{F}$, where $\mathbf{F}$ ($= \mathbf{E}$ or $\mathbf{H}$) is the local intensity of the external field. Corresponding to this term in $\mathscr{H}_\alpha$ is the contribution

$$[\bar{\boldsymbol{\mu}}_\alpha(\bar{1}) \times \mathbf{F} \cdot (\partial/\partial \mathbf{L}_1)]\, F_\alpha(t\mathbf{x}\bar{1})$$

to the average of $[F_\alpha , \mathscr{H}_\alpha]$.

Let us suppose that the molecules are symmetric tops and that each has an *electric* dipole moment of magnitude μ_0 directed along its symmetry axis. It then follows that

$$\boldsymbol{\mu} = \mu_0[\hat{\mathbf{L}} \cos\theta + \hat{\mathbf{M}} \sin\theta \cos\phi + \hat{\mathbf{N}} \sin\theta \sin\phi]$$

where $\hat{\mathbf{L}} = \mathbf{L}/L$, $\hat{\mathbf{M}}$, and $\hat{\mathbf{N}}$ form an orthonormal set of vectors. Therefore,

$$\bar{\boldsymbol{\mu}} = [1/(2\pi)^2] \iint d\psi\, d\phi\, \boldsymbol{\mu} = \mu_0 \hat{\mathbf{L}} \cos\theta = \gamma(K, L)\mathbf{L}$$

where $\gamma(K, L) = \mu_0 K/L^2$ is the gyroelectric ratio.

It is often assumed that the *magnetic* dipole moment of a symmetric-top molecule can be separated into the sum of an axial moment μ_K which is associated with the axial component of electronic orbital and spin angular momentum, and a moment of magnitude μ_R which is perpendicular to the symmetry axis and which has its origin in the gross rotational motion of the nuclei and electrons. According to this model,

$$\begin{aligned}\boldsymbol{\mu} = {} & \mu_K[\hat{\mathbf{L}} \cos\theta + \hat{\mathbf{M}} \sin\theta \cos\phi + \hat{\mathbf{N}} \sin\theta \sin\phi] \\ & + \mu_R[\hat{\mathbf{L}} \sin\theta - \hat{\mathbf{M}} \cos\theta \cos\phi - \hat{\mathbf{N}} \cos\theta \sin\phi]\end{aligned}$$

and $\bar{\boldsymbol{\mu}} = (\mu_K \cos\theta + \mu_R \sin\theta)\hat{\mathbf{L}}$. The moments μ_K and μ_R are usually written in the forms $\mu_K = g_K \beta K/\hbar$ and $\mu_R = g_R \beta_{\text{nuc}}(L^2 - K^2)^{1/2}/\hbar$, where $\beta = e\hbar/2m_e c$ and $\beta_{\text{nuc}} = e\hbar/2m_p c$ denote the Bohr and nuclear magnetons and where g_K and g_R are, respectively, the axial and rotational "g-factors." Since β is so much greater than β_{nuc}, it is an excellent approximation to set the average moment equal to $(g_K \beta K^2/L^2)\mathbf{L}$ whenever $K \neq 0$; when K is equal to zero we conclude that $\boldsymbol{\mu} = g_R \beta_{\text{nuc}} \mathbf{L}$. (The quantum analogs of these results are obtained by replacing the momenta K and L with $\hbar K$ and $\hbar[L(L + 1)]^{1/2}$, respectively.)

2.4. Equations of Change and Entropy Production

We introduce the symbol $n_\alpha\langle\psi\rangle_\alpha = \int d\bar{1}\, F_\alpha(\bar{1})\, \psi(\bar{1})$ for the ensemble average of a single-particle field $\psi(\bar{1}) = \psi(\mathbf{c}_1 , \mathscr{J}_1)$. Provided that ψ is independent of t and $\mathbf{x}$, it then can be proved that

$$\begin{aligned}&\partial_t(n_\alpha\langle\psi\rangle_\alpha) + \nabla \cdot [\mathbf{u}(n_\alpha\langle\psi\rangle_\alpha) + n_\alpha\langle \mathbf{C}\psi_\alpha\rangle] - n_\alpha \left\langle \frac{\partial}{\partial \mathbf{c}} \cdot (\mathbf{F}^{(e)}\psi) \right\rangle_\alpha - n_\alpha\langle[\psi, \mathscr{H}_\alpha]_{\mathbf{P.B.}}\rangle \\ &\quad = \partial_c(n_\alpha\langle\psi_\alpha\rangle) \qquad (20)\end{aligned}$$

where (by an appeal to bilateral normalization)

$$\partial_c(n_\alpha\langle\psi\rangle_\alpha) = \sum_\beta \iiiint d\bar{1}\, d\bar{2}\, d\bar{1}'\, d\bar{2}'\, w_{\alpha\beta}(\bar{1}'\bar{2}' \mid \bar{1}\bar{2})\, F_\alpha(\bar{1})\, F_\beta(\bar{2})[\psi_\alpha(\bar{1}') - \psi_\alpha(\bar{1})] \tag{21}$$

and

$$\begin{aligned}\sum_\alpha \partial_c(n_\alpha\langle\psi\rangle_\alpha) = \sum_\alpha \sum_\beta \iiiint d\bar{1}\, d\bar{2}\, d\bar{1}'\, d\bar{2}'\, w_{\alpha\beta}(\bar{1}'\bar{2}' \mid \bar{1}\bar{2})\, F_\alpha(\bar{1})\, F_\beta(\bar{2}) \\ \times \tfrac{1}{2}[\psi_\alpha(\bar{1}') + \psi_\beta(\bar{2}') - \psi_\alpha(\bar{1}) - \psi_\beta(\bar{2})]\end{aligned} \tag{22}$$

For example, with $\psi_\alpha = m_\alpha$ we obtain from (20)–(22) the component and summed continuity equations $\partial_t\rho_\alpha + \nabla \cdot (\rho_\alpha \mathbf{u}_\alpha) = 0$ and $\partial_t\rho + \nabla \cdot (\rho\mathbf{u}) = 0$ with $\rho_\alpha = n_\alpha\langle m_\alpha\rangle_\alpha$, $\rho_\alpha\mathbf{u}_\alpha = n_\alpha\langle m_\alpha\mathbf{c}\rangle_\alpha$, $\rho = \sum_\alpha \rho_\alpha$, and $\rho\mathbf{u} = \sum_\alpha \rho_\alpha\mathbf{u}_\alpha$. In an analogous fashion we deduce the component and summed momentum balance relationships

$$\partial_t(\rho_\alpha\mathbf{u}_\alpha) + \nabla \cdot [\rho_\alpha(\mathbf{u}\mathbf{u}_\alpha + \mathbf{u}_\alpha\mathbf{u} - \mathbf{u}\mathbf{u}) + \mathsf{p}_\alpha] - \rho_\alpha\mathbf{F}_\alpha^{(e)} = \sum_\beta \rho_\alpha\mathbf{F}_{\alpha\beta} \tag{23}$$

and

$$\rho\, d_t u = -\nabla \cdot \mathsf{p} + \rho\mathbf{F}^{(e)} \qquad (d_t = \partial_t + \mathbf{u} \cdot \nabla) \tag{24}$$

where $\mathsf{p}_\alpha = n_\alpha\langle m_\alpha CC\rangle_\alpha$, with $\mathbf{C} = \mathbf{c} - \mathbf{u}$, is the contribution of the species α to the pressure tensor $\mathsf{p} = \sum_\alpha \mathsf{p}_\alpha$ and where

$$\rho_\alpha\mathbf{F}_{\alpha\beta} = -\rho_\beta\mathbf{F}_{\beta\alpha} = \iiiint d\bar{1}\, d\bar{2}\, d\bar{1}'\, d\bar{2}'\, w_{\alpha\beta}(\bar{1}'\bar{2}' \mid \bar{1}\bar{2})\, F_\alpha(\bar{1})\, F_\beta(\bar{2})\, m_\alpha(\mathbf{c}_1' - \mathbf{c}_1) \tag{25}$$

is the interspecies frictional force. Finally, the equation of change for the "internal energy" $e = \rho^{-1} \sum_\alpha n_\alpha\langle\tfrac{1}{2}m_\alpha C^2 + \epsilon_\alpha\rangle_\alpha$ is found to be

$$\rho\, d_t e = -\nabla \cdot \mathbf{Q} - \mathsf{p} : \nabla\mathbf{u} - \sum_\alpha n_\alpha\mathbf{V}_\alpha \cdot \mathbf{F}_\alpha^{(e)} \tag{26}$$

where $\mathbf{V}_\alpha = \mathbf{u}_\alpha - \mathbf{u}$ is the diffusion velocity of species α and where $\mathbf{Q} = \sum_\alpha n_\alpha\langle\mathbf{C}(\tfrac{1}{2}m_\alpha C^2 + \epsilon_\alpha)\rangle_\alpha$ is the diffusive flux of energy.

It is usual to identify the entropy density of a dilute gas with the functional $s(t\mathbf{x}) = \rho^{-1}k \sum_\alpha n_\alpha\langle 1 - \log F_\alpha\rangle_\alpha$ of the singlet distribution functions. The variations of this density are governed by the equation $\rho\, d_t s = -\nabla \cdot \mathbf{J}_s + g_s$, where $\mathbf{J}_s = k \sum_\alpha n_\alpha\langle\mathbf{C}(1 - \log F_\alpha)\rangle_\alpha$ is the flux and

$$\begin{aligned}g_s &= k \sum_\alpha \int d\bar{1}\, [1 - \log F_\alpha(\bar{1})]\, \partial_c F_\alpha(\bar{1}) \\ &= -k \sum_\alpha \sum_\beta \iiiint d\bar{1}\, d\bar{2}\, d\bar{1}'\, d\bar{2}'\, w_{\alpha\beta}(\bar{1}\bar{2} \mid \bar{1}'\bar{2}') \log F_\alpha(\bar{1})[F_\alpha(\bar{1}')\, F_\beta(\bar{2}') - F_\alpha(\bar{1})\, F_\beta(\bar{2})] \\ &= -\tfrac{1}{2}k \sum_\alpha \sum_\beta \iiiint d\bar{1}\, d\bar{2}\, d\bar{1}'\, d\bar{2}'\, w_{\alpha\beta}(\bar{1}'\bar{2}' \mid \bar{1}\bar{2}) \\ &\quad \times \log\{F_\alpha(\bar{1}')\, F_\beta(\bar{2}')/F_\alpha(\bar{1})\, F_\beta(\bar{2})\}\, F_\alpha(\bar{1})\, F_\beta(\bar{2})\end{aligned}$$

the homogeneous rate of entropy production. To obtain the third line of this sequence from the second we have invoked the property of bilateral normalization and the fact that $w_{\alpha\beta}(\bar{1}\bar{2} \mid \bar{1}'\bar{2}') = w_{\beta\alpha}(\bar{2}\bar{1} \mid \bar{2}'\bar{1}')$. By adding the expression

$$0 = \tfrac{1}{2}k \sum_{\alpha} \sum_{\beta} \iiiint d\bar{1}\, d\bar{2}\, d\bar{1}'\, d\bar{2}'\, w_{\alpha\beta}(\bar{1}'\bar{2}' \mid \bar{1}\bar{2})[F_\alpha(\bar{1}')\, F_\beta(\bar{2}') - F_\alpha(\bar{1})\, F_\beta(\bar{2})]$$

to g_s we obtain

$$\begin{aligned} g_s = \tfrac{1}{2}k \sum_{\alpha} \sum_{\beta} \iiiint d\bar{1}\, d\bar{2}\, d\bar{1}'\, d\bar{2}'\, w_{\alpha\beta}(\bar{1}'\bar{2}' \mid \bar{1}\bar{2})\, F_\alpha(\bar{1})\, F_\beta(\bar{2}) \\ \times [\{F_\alpha(\bar{1}')\, F_\beta(\bar{2}')/F_\alpha(\bar{1})\, F_\beta(\bar{2})\} - 1 - \log\{F_\alpha(\bar{1}')\, F_\beta(\bar{2}')/F_\alpha(\bar{1})\, F_\beta(\bar{2})\}] \end{aligned}$$

Then, since $\eta(x) = x - 1 - \log x$ is greater than zero for $x > 0$, it follows that g_s must be nonnegative. Furthermore, since $\eta(x)$ vanishes if and only if $x = 1$, we conclude that the rate of entropy production is zero only when $F_\alpha(\bar{1}')\, F_\beta(\bar{2}') = F_\alpha(\bar{1})\, F_\beta(\bar{2})$ for every pair of states $(\bar{1}\bar{2})$ and $(\bar{1}'\bar{2}')$ for which $w_{\alpha\beta}(\bar{1}'\bar{2}' \mid \bar{1}\bar{2})$ is nonzero These equations can be satisfied only if the logarithm of the distribution function is a linear combination of the binary invariants, mass, momentum, and energy. The distribution function which satisfies these constraints is characteristic of a state of local equilibrium and can be written in the form

$$ {}^{\circ}F_\alpha(\bar{1}) = n_{\alpha 0}(m_\alpha/2\pi k T_0)^{3/2}\, z_\alpha^{-1} \exp\left\{-\frac{1}{kT_0}\left[\frac{1}{2}\, m_\alpha(\mathbf{c}_1 - \mathbf{u}_0)^2 + \epsilon_\alpha(1)\right]\right\} \tag{27}$$

where $z_\alpha(T_0) = \int d\mathscr{I}_1 \exp[-\epsilon_\alpha(\mathscr{I}_1)/kT_0]$ is the classical partition function associated with the internal degrees of freedom.

The values of the coefficients $n_{\alpha 0}$, T_0, and $\mathbf{u}_0$ are arbitrary. Without loss of generality we can set them equal to the local values assumed by the concentration, temperature, and fluid velocity, that is, to $n_\alpha(t\mathbf{x})$, $T(t\mathbf{x})$, and $\mathbf{u}(t\mathbf{x})$ respectively.

2.5. Linearization of the Boltzmann Equation

We now write the distribution functions in the form $F_\alpha(\bar{1}) = {}^{\circ}F_\alpha(\bar{1})[1 + \Phi_\alpha(\bar{1})]$, where Φ_α is a measure of the system's displacement from the state described by the Maxwell–Boltzmann distribution ${}^{\circ}F_\alpha(\bar{1})$. Then, if the condition of the gas is sufficiently near to this local state of reference, we can neglect quadratic terms in Φ and conclude from (15) that

$$\partial_c F_\alpha(\bar{1}) \approx -\sum_{\beta} n_\alpha n_\beta \hat{\Gamma}_1^{(\alpha\beta)}(\Phi) \tag{28}$$

where the linear operators $\hat{\Gamma}^{(\alpha\beta)}$ are so defined that

$$\begin{aligned} n_\alpha n_\beta \hat{\Gamma}_1^{(\alpha\beta)}(\Theta) = \iiint d\bar{1}'\, d\bar{2}'\, d\bar{2}\, {}^{\circ}F_\alpha(\bar{1})\, {}^{\circ}F_\beta(\bar{2})\, w_{\alpha\beta}(\bar{1}\bar{2} \mid \bar{1}'\bar{2}') \\ \times [\Theta_\alpha(\bar{1}) + \Theta_\beta(\bar{2}) - \Theta_\alpha(\bar{1}') - \Theta_\beta(\bar{2}')] \end{aligned} \tag{29}$$

Properties of the Integral Operator $\hat{\Gamma}$. We begin our investigation of the operators $\hat{\Gamma}$ by restricting our attention to a single-component gas. As a first step in this direction we rewrite (29) in the familiar Fredholm form

$$n^2\hat{\Gamma}_1(\theta) = K^{(0)}(\bar{1})\,\theta(\bar{1}) + \int d\bar{2}\,K(\bar{1},\bar{2})\,\theta(\bar{2}) \tag{30}$$

Here the function $K^{(0)}$ and the kernel K are given by the formulas

$$K^{(0)}(\bar{1}) = \iiint d\bar{1}'\,d\bar{2}'\,d\bar{2}\;{}^\circ F(\bar{1})\,{}^\circ F(\bar{2})\,w(\bar{1}\bar{2}\mid\bar{1}'\bar{2}') \tag{31}$$

and

$$K(\bar{1},\bar{j}) = \iiint d\bar{1}'\,d\bar{2}'\,d\bar{2}\;{}^\circ F(\bar{1})\,{}^\circ F(\bar{2})\,w(\bar{1}\bar{2}\mid\bar{1}'\bar{2}')[\delta(\bar{2}-\bar{j}) - \delta(\bar{1}'-\bar{j}) - \delta(\bar{2}'-\bar{j})] \tag{32}$$

where $\delta(\bar{\imath}-\bar{j}) = \delta_3(\mathbf{c}_i - \mathbf{c}_j)\,\delta(\mathscr{J}_i - \mathscr{J}_j)$.

The adjoint of the (real) operator $\hat{\Gamma}$ is denoted by $\hat{\Gamma}^\dagger$ and defined so that $\int d\bar{1}\,\psi(\bar{1})\,\hat{\Gamma}_1(\phi) = \int d\bar{1}\,\phi(\bar{1})\,\hat{\Gamma}_1{}^\dagger(\psi)$ for all functions ψ and ϕ within the ranges of the two operators. By straightforward manipulations (and invoking bilateral normalization and energy and momentum conservation), one can prove the term-for-term equality of the two expressions

$$\begin{aligned} n^2\int d\bar{1}\,\psi(\bar{1})\,\hat{\Gamma}_1(\phi) &= \iiiint d\bar{1}\,d\bar{2}\,d\bar{1}'\,d\bar{2}'\;{}^\circ F(\bar{1})\,{}^\circ F(\bar{2})\,w(\bar{1}\bar{2}\mid\bar{1}'\bar{2}') \\ &\qquad\times \psi(\bar{1})[\phi(\bar{1}) + \phi(\bar{2}) - \phi(\bar{1}') - \phi(\bar{2}')] \\ &= \iiiint d\bar{1}\,d\bar{2}\,d\bar{1}'\,d\bar{2}'\;{}^\circ F(\bar{1})\,{}^\circ F(\bar{2})\,w(\bar{1}'\bar{2}'\mid\bar{1}\bar{2}) \\ &\qquad\times \phi(\bar{1})[\psi(\bar{1}) + \psi(\bar{2}) - \psi(\bar{1}') - \psi(\bar{2}')] \end{aligned}$$

and so establish that

$$\begin{aligned} n^2\hat{\Gamma}_1{}^\dagger(\phi) &= \iiint d\bar{1}'\,d\bar{2}'\,d\bar{2}\;{}^\circ F(\bar{1})\,{}^\circ F(\bar{2})\,w(\bar{1}'\bar{2}'\mid\bar{1}\bar{2})[\phi(\bar{1}) + \phi(\bar{2}) - \phi(\bar{1}') - \phi(\bar{2}')] \\ &= K^{(0)}(\bar{1})\,\phi(\bar{1}) + \int d\bar{2}\,K^\dagger(\bar{1},\bar{2})\,\phi(\bar{2}) \end{aligned} \tag{33}$$

where $K^\dagger$ differs from K of (32) in that $w(\bar{1}\bar{2}\mid\bar{1}'\bar{2}')$ is replaced with $w(\bar{1}'\bar{2}'\mid\bar{1}\bar{2})$.

We now wish to prove that $K^\dagger(\bar{1},\bar{2}) = K(\bar{2},\bar{1})$. From the definition (32)

$$\begin{aligned} K(\bar{j},\bar{1}) = &\iint d\bar{1}'\,d\bar{2}'\;{}^\circ F(\bar{1})\,{}^\circ F(\bar{j})\,w(\bar{j}\bar{1}\mid\bar{1}'\bar{2}') - \iint d\bar{2}'\,d\bar{2}\;{}^\circ F(\bar{j})\,{}^\circ F(\bar{2})\,w(\bar{j}\bar{2}\mid\bar{1}\bar{2}') \\ &- \iint d\bar{1}'\,d\bar{2}\;{}^\circ F(\bar{j})\,{}^\circ F(\bar{2})\,w(\bar{j}\bar{2}\mid\bar{1}'\bar{1}) \end{aligned}$$

and

$$\begin{aligned} K^\dagger(\bar{1},\bar{j}) = &\iint d\bar{1}'\,d\bar{2}'\;{}^\circ F(\bar{1})\,{}^\circ F(\bar{j})\,w(\bar{1}'\bar{2}'\mid\bar{1}\bar{j}) - \iint d\bar{2}'\,d\bar{2}\;{}^\circ F(\bar{1})\,{}^\circ F(\bar{2})\,w(\bar{j}\bar{2}'\mid 1\bar{2}) \\ &- \iint d\bar{1}'\,d\bar{2}\;{}^\circ F(\bar{1})\,{}^\circ F(\bar{2})\,w(\bar{1}'\bar{j}\mid\bar{1}\bar{2}) \end{aligned}$$

By invoking the properties of bilateral normalization and energy and momentum conservation [in the form ${}^\circ F(\bar{1})\,{}^\circ F(\bar{2})\,w(\bar{1}\bar{2} \mid \bar{1}'\bar{2}') = {}^\circ F(\bar{1}')\,{}^\circ F(\bar{2}')\,w(\bar{1}\bar{2} \mid \bar{1}'\bar{2}')$], one can establish the term-by-term equality of these two expressions and thereby achieve our objective.

Next we apply the parity operator to (29) and obtain

$$\begin{aligned}
\hat{P}\{n^2\hat{\Gamma}_1(\phi)\} &= \iiint d\bar{1}'\,d\bar{2}'\,d\bar{2}\;{}^\circ F(\hat{P}\bar{1})\,{}^\circ F(\bar{2})\,w(\hat{P}\bar{1}\;\bar{2} \mid \bar{1}'\bar{2}') \\
&\qquad \times [\phi(\hat{P}\bar{1}) + \phi(\bar{2}) - \phi(\bar{1}') - \phi(\bar{2}')] \\
&= \iiint d(\hat{P}\bar{1}')\,d(\hat{P}\bar{2}')\,d(\hat{P}\bar{2})\;{}^\circ F(\hat{P}\bar{1})\,{}^\circ F(\hat{P}\bar{2})\,w(\hat{P}\bar{1}\;\hat{P}\bar{2} \mid \hat{P}\bar{1}'\;\hat{P}\bar{2}') \\
&\qquad \times [\phi(\hat{P}\bar{1}) + \phi(\hat{P}\bar{2}) - \phi(\hat{P}\bar{1}') - \phi(\hat{P}\bar{2}')] \\
&= \iiint d\bar{1}'\,d\bar{2}'\,d\bar{2}\;{}^\circ F(\bar{1})\,{}^\circ F(\bar{2})\,w(\bar{1}\bar{2} \mid \bar{1}'\bar{2}') \\
&\qquad \times [\phi(\hat{P}\bar{1}) + \phi(\hat{P}\bar{2}) - \phi(\hat{P}\bar{1}') - \phi(\hat{P}\bar{2}')]
\end{aligned}$$

From this it follows that $\hat{P}$ and $\hat{\Gamma}$ commute, i.e., that $\hat{P}\hat{\Gamma} = \hat{\Gamma}\hat{P}$ or, more explicitly, $\hat{P}\{\hat{\Gamma}(\phi)\} = \hat{\Gamma}(\hat{P}\phi)$. An identical procedure can be used to prove that $\hat{\Gamma}$ commutes with the rotation operator $\hat{R}$. Furthermore, one can establish that $\hat{T}\hat{\Gamma} = \hat{\Gamma}^\dagger\hat{T}$ and so conclude that $\hat{T}$ and $\hat{\Gamma}$ commute if and only if $\hat{\Gamma}$ is self-adjoint, that is, if $\hat{\Gamma}^\dagger = \hat{\Gamma}$. It is not difficult to discover when this will be so, for there clearly exists a one-to-one correspondence between the adjointness of $\hat{\Gamma}$ and the symmetry of w. Furthermore an analogous relationship exists between the symmetry of w and that of the kernel K. When $\hat{T}\hat{P}\mathscr{J}_i = \mathscr{J}_i$, $\hat{\Gamma}$ is self-adjoint and w and K are symmetric. This is the case whenever the species are structureless or whenever the molecular interactions are such that no internal variables are collisionally altered. However, we generally can expect $\hat{\Gamma}$ to be self-adjoint only if the set $\mathscr{J}$ is limited to variables with positive $\hat{T}\hat{P}$ eigenvalues, e.g., true scalars such as L^2, p^2, and $(\mathbf{L} \cdot \mathbf{p})^2$.

When w is symmetric it is said that "detailed balancing" prevails, that the specific rate of each "elementary process" is precisely equal to that of its inverse. From the H-theorem we know already that this detailed balancing is not essential to the maintenance of dynamic equilibrium. Let us now suppose that one has selected a transition rate matrix w. Then, there may exist circumstances under which it is reasonable to replace this matrix with its symmetric part, i.e., to replace each element $w(\bar{1}\bar{2} \mid \bar{1}'\bar{2}')$ with the corresponding quantity

$$w^{(\mathrm{sym})}(\bar{1}\bar{2} \mid \bar{1}'\bar{2}') \equiv \tfrac{1}{2}[w(\bar{1}\bar{2} \mid \bar{1}'\bar{2}') + w(\bar{1}'\bar{2}' \mid \bar{1}\bar{2})] = w^{(\mathrm{sym})}(\bar{1}'\bar{2}' \mid \bar{1}\bar{2}) \tag{34}$$

To help in our search for conditions which might justify this replacement, we recall that $w(\bar{1}'\bar{2}' \mid \bar{1}\bar{2}) = w(\hat{T}\hat{P}\bar{1}\;\hat{T}\hat{P}\bar{2} \mid \hat{T}\hat{P}\bar{1}'\;\hat{T}\hat{P}\bar{2}')$, where $\hat{T}\hat{P}\mathbf{c} = \mathbf{c}$. Thus, $w^{(\mathrm{sym})}$ is the transition rate matrix appropriate to situations for which the states $(\mathbf{c}, \mathscr{J})$ and $(\mathbf{c}, \hat{T}\hat{P}\mathscr{J})$ can be assigned equal *a priori* probabilities. For example, under these circumstances the distribution function for a gas of symmetric-top molecules must be such that $F(\bar{1}) = F(t\mathbf{x}\mathbf{c}_1\mathbf{L}_1K_1)$ is equal to $F(t\mathbf{x}\mathbf{c}_1 - \mathbf{L}_1K_1)$, or equivalently, $F(\bar{1})$ must be an even function of $\mathbf{L}_1$.

There are significant differences between this "nonpolar" ensemble and the "isotropic" ensemble for which the appropriate transition-rate matrix is given by

$$w^{(\mathrm{iso})}(\overline{1}\overline{2} \mid \overline{1}'\overline{2}') = (4\pi)^{-2} \iiiint d\hat{L}_1\, d\hat{L}_2\, d\hat{L}_1'\, d\hat{L}_2'\, w(\overline{1}\overline{2} \mid \overline{1}'\overline{2}') \tag{35}$$

Here, for simplicity, we have assumed that $\hat{\mathbf{L}} = \mathbf{L}/L$ is the only dynamical variable with a negative $\hat{T}\hat{P}$ eigenvalue. Since $w(\overline{1}\overline{2} \mid \overline{1}'\overline{2}') = w(\hat{T}\hat{P}\overline{1}'\ \hat{T}\hat{P}\overline{2}' \mid \hat{T}\hat{P}\overline{1}\ \hat{T}\hat{P}\overline{2})$, it then follows that $w^{(\mathrm{iso})}(\overline{1}\overline{2} \mid \overline{1}'\overline{2}') = w^{(\mathrm{iso})}(\overline{1}'\overline{2}' \mid \overline{1}\overline{2})$, a condition which Watanabe$^{(11)}$ has termed "averaged balance."

By adopting the nonpolar ensemble, one forfeits all chance of accounting for phenomena which depend upon a preferential direction of molecular rotation. The nonpolar ensemble restricts the distribution function to a ray dependence upon the angular distribution of molecular spin. The isotropic ensemble admits no dependence whatsoever upon this variable. For example, the isotropic distribution function can depend upon $\mathbf{L}$ only through the rotational energy $\epsilon(\mathscr{J})$.

One may, of course, expand the "ignorable" set η to include variables from the set $\mathscr{J}$ in which he has no interest or which he has judged to be of less importance than others. The $\hat{\Gamma}$ operators associated with the diminished set of free-flight invariants will be self-adjoint if $\hat{T}\hat{P}\mathscr{J}_k = \mathscr{J}_k$ for every variable belonging to the set.

Symmetry Conditions and Bracket Integrals. There is considerable significance and several practical consequences of determining the set of operators which commute with $\hat{\Gamma}$. Thus, the Galilean (rotational) invariance of w ensures us that the eigenfunctions of $\hat{\Gamma}$ can be classified according to the irreducible representations of the group of rotations in three space. Furthermore, the commutability of $\hat{P}$ and $\hat{\Gamma}$ implies that these eigenfunctions also can be assigned definite parities. Finally, if $\hat{\Gamma}\hat{T} = \hat{T}\hat{\Gamma}$, the eigenfunctions of $\hat{\Gamma}$ can be selected to be eigenfunctions of the time-reversal operator as well.

The symmetry considerations have an important bearing upon the properties of the "bracket integrals,"

$$[\phi, \psi] = n^2(\phi, \hat{\Gamma}(\psi)) \equiv n^2 \int d\overline{1}\ \phi(\overline{1})\ \hat{\Gamma}_1(\psi) \tag{36}$$

to which the various transport and relaxation coefficients are related. In the theory of these coefficients one also encounters the related integrals $[\phi; \psi]$, which differ from the corresponding quantities $[\phi, \psi]$ in that the integrands $\phi(\overline{1})\, \hat{\Gamma}_1(\chi)$ of (36) are replaced with $\phi(\overline{1}) \cdot \hat{\Gamma}(\chi)$. Integrals of this second variety are defined only for pairs of functions ϕ and χ both of which are tensors of the same rank. The symbol $\phi \cdot \hat{\Gamma}(\chi)$ is understood to mean the appropriate scalar product, with tensor contractions formed in accordance with the "nesting convention" of Chapman and Cowling, e.g., $\boldsymbol{\phi} \cdot \hat{\Gamma}(\boldsymbol{\psi}) = \sum_i \phi_i \hat{\Gamma}(\psi_i)$, $\boldsymbol{\phi} \cdot \hat{\Gamma}(\boldsymbol{\psi}) = \sum_i \sum_j \phi_{ij} \hat{\Gamma}(\psi_{ji})$, etc.

As consequences of the properties of w it can be proved that:

(a) $[\phi; \phi^\dagger] \geqslant 0$ for all functions ϕ. The equality obtains if and only if ϕ is a binary invariant. The symbol $\phi^\dagger$ here denotes the tensor with components $(\phi^\dagger)_{ij\ldots\mathrm{nm}} = \phi_{\mathrm{nm}\ldots ji}$.

And for tensor *components* ϕ and ψ

(b) $[\phi, \psi] = 0$ if the parities of ϕ and ψ differ.

(c) $[\phi, \psi] = 0$ if ϕ and ψ are components of tensors which transform as basis elements belonging to different irreducible representations of the rotation group.

(d) $[\phi, \chi] = T_\phi T_\psi [\chi, \phi]$ where T_χ is the time-reversal eigenvalue of χ. Furthermore, if $\hat{\Gamma}$ is self-adjoint (as it is for structureless molecules), then $[\phi, \psi] = [\psi, \phi]$ and so this integral is different from zero only if $T_\phi = T_\psi$.

(e) $[\phi, \chi] = \mathscr{I}_\phi \mathscr{I}_\psi [\psi, \phi]$, where $\mathscr{I}_\phi$ and $\mathscr{I}_\psi$ are the time-reversal eigenvalues of $\hat{\Gamma}(\phi)$ and $\hat{\Gamma}(\psi)$, respectively.

(f) $[\phi, \psi] = 0$ if either or both of ϕ and ψ is a binary invariant.

In several of these statements it is implied that one is dealing exclusively with eigenfunctions of $\hat{T}$ and/or of $\hat{P}$. This is always possible to arrange, since an arbitrary function F can be uniquely decomposed into the sum of two functions $\frac{1}{2}(1 + \hat{P})F$ and $\frac{1}{2}(1 - \hat{P})F$, which are eigenfunctions of $\hat{P}$ with eigenvalues $+1$ and -1, respectively. An analogous argument applies to the operator $\hat{T}$.

As an illustration, let us suppose that $\mathscr{J} = \mathbf{L}$. Then, for each choice of positive integers j_1 and j_2 one can construct the set of $2J + 1$ functions

$$S_{j_1 j_2 JM}(\hat{\mathbf{c}}, \hat{\mathbf{L}}) = \sum_{m_1} \sum_{m_2} \langle j_1 j_2 m_1 m_2 \mid JM \rangle \, Y_{j_1}^{m_1}(\hat{\mathbf{c}}) \, Y_{j_2}^{m_2}(\hat{\mathbf{L}})$$

which satisfy the orthogonality conditions

$$\iint d^2\hat{c} \, d^2\hat{L} \, S^*_{j_1 j_2 JM}(\hat{\mathbf{c}}, \hat{\mathbf{L}}) \, S_{j_1' j_2' J' M'}(\hat{\mathbf{c}}, \hat{\mathbf{L}}) = \delta_{JJ'} \, \delta_{MM'} \, \delta_{j_1 j_1'} \, \delta_{j_2 j_2'}$$

Here J can be any integer within the interval $(j_1 + j_2, |j_1 - j_2|)$, M any integer within $(J, -J)$, and $\langle j_1 j_2 m_1 m_2 \mid JM \rangle$ is the familiar vector coupling coefficient (see, for example, Edmonds$^{(12)}$). The parity of $S_{j_1 j_2 JM}$ is $(-1)^{j_1}$; its time-reversal eigenvalue is $(-1)^{j_1 + j_2}$.

Let us define the action of the rotation $\hat{R}$ upon the function $\psi(\mathbf{c}, \mathbf{L})$ to be $\hat{R}\psi(\mathbf{c}, \mathbf{L}) = \psi(\mathbf{c}', \mathbf{L}')$, where $(\mathbf{c}, \mathbf{L})$ and $(\mathbf{c}', \mathbf{L}')$, respectively, are the velocities and angular momenta measured in the original and rotated frames. Thus, $\mathbf{c}' = \mathsf{M}(\alpha\beta\gamma)\mathbf{c}$, where the elements of the orthogonal matrix M are dependent upon the values of the Euler angles α, β, and γ used to parametrize the rotation. The functions $S_{j_1 j_2 JM}$ transform in the manner

$$\hat{R} S_{j_1 j_2 JM}(\hat{\mathbf{c}}, \hat{\mathbf{L}}) = S_{j_1 j_2 JM}(\hat{\mathbf{c}}', \hat{\mathbf{L}}') = \sum_{M'} D^J_{M'M}(\alpha\beta\gamma) \, S_{j_1 j_2 JM'}(\hat{\mathbf{c}}, \hat{\mathbf{L}})$$

and so form a basis for the $(2J + 1)$-dimensional irreducible representation D^J of the rotation group. The specific properties of the representation coefficients $D^J_{M'M}$

are of no particular interest to us here. What is important is the fact that we can select the eigenfunctions of $\hat{\Gamma}$ ($\hat{\Gamma}S_{..\gamma} = \gamma S_{..\gamma}$) to have the form

$$S_{j_1JM\gamma}(\mathbf{c}, \mathbf{L}) = \sum_{j_2} a_{j_1j_2J\gamma}(c, L)\, S_{j_1j_2JM}(\hat{\mathbf{c}}, \hat{\mathbf{L}})$$

The parity of this function is $(-1)^{j_1}$ but it is not an eigenfunction of $\hat{T}$.

In general, $\hat{\Gamma}$ will not be self-adjoint, and so eigenfunctions of this operator belonging to different eigenvalues are not orthogonal, that is, the integral

$$\begin{aligned}[S_{j_1JM\gamma}\,;\, S_{j_1'J'M'\gamma'}] &= \iint d^3c\, d^3L\, L^{-1} S^*_{j_1JM\gamma}(\mathbf{c}, \mathbf{L})\, \hat{\Gamma}_1(S_{j_1'J'M'\gamma'}) \\ &= \gamma' \left\{ \int_0^\infty dc\, c^2 \int_0^\infty dL\, L \sum_{j_2} a^*_{j_1j_2J\gamma}(c, L)\, a_{j_1j_2J\gamma'}(c, L) \right\} \delta_{JJ'}\, \delta_{MM'}\, \delta_{j_1j_1'}\end{aligned}$$

will not vanish for $\gamma \neq \gamma'$. It is obvious how these considerations and conclusions would be modified if one were to introduce the (statistical) approximation of a nonpolar or isotropic ensemble.

Generalization to Gas Mixture. To extend our considerations to a gas mixture, we interpret $n_\alpha n_\beta \hat{\Gamma}^{(\alpha\beta)}$ to be the ($\alpha\beta$)-component of an operator $n^2\hat{\Gamma}$ and identify ϕ_α with the α-component of a "composition vector." The inner product of two composition vectors, Φ and Ψ, is defined in obvious analogy with (36) by the "brace integral"

$$\{\Phi, \Psi\} \equiv (\Phi, n^2\hat{\Gamma}(\Psi)) \equiv \sum_\alpha \sum_\beta n_\alpha n_\beta \int d\bar{1}\, \phi_\alpha(\bar{1})\, \hat{\Gamma}_1^{(\alpha\beta)}(\Psi_\alpha) \tag{37}$$

We then introduce the adjoint of $\hat{\Gamma}$ through the relationship $(\Phi, \hat{\Gamma}(\Psi)) = (\Psi, \hat{\Gamma}^\dagger(\Phi))$. This operator is found to differ from $\hat{\Gamma}$ of (29) in that the functions $w_{\alpha\beta}(\overline{12} \mid \overline{1}'\overline{2}')$ are everywhere replaced with the corresponding functions $w_{\alpha\beta}(\overline{1}'\overline{2}' \mid \overline{12})$. If there is an inverse to each collisional event, then these two functions are equal and $\hat{\Gamma}$ is self-adjoint.

By a straightforward extension of our previous considerations, one verifies that the brace integrals satisfy all of the conditions (a)–(f).

3. DEDUCTION OF THE BOLTZMANN EQUATION FROM THE LIOUVILLE EQUATION

Now that the phenomenological theory of the Boltzmann equation has been developed in considerable detail we address ourselves to the task of deriving this equation from something more fundamental. Although the approach we adopt is also applicable to the derivation of other kinetic equations (less restricted by the densities for which they are valid or subject to stochastic approximations less severe than that of molecular chaos), our considerations here shall be confined to the Boltzmann equation. To minimize notational complexity, we confine our attention to a single-component gas. (The generalization to a gas mixture offers no new conceptual or theoretical difficulties.) We denote by $f^{(N)}$ the generic density function on the space of the conjugate variables appropriate to a gas of N identical polyatomic molecules. Since there are no sources or sinks of members of the ensemble representative of this system, $f^{(N)}$ satisfies the continuity (Liouville) equation

$$\partial_t f^{(N)} + [f^{(N)}, H^{(N)}] = 0 \tag{38}$$

where

$$[\Phi, H^{(N)}] = \sum_{i=1}^{N} \sum_{\beta=1}^{\nu} \left(\frac{\partial \Phi}{\partial q_{i\beta}} \frac{\partial H^{(N)}}{\partial p_{i\beta}} - \frac{\partial \Phi}{\partial p_{i\beta}} \frac{\partial H^{(N)}}{\partial q_{i\beta}} \right) \tag{39}$$

is the Poisson bracket of Φ and of the Hamiltonian function $H^{(N)}$ for the N-particle system. Here $q_{i\beta}$ and $p_{i\beta}$ denote the conjugate coordinate and momentum associated with the β degree of freedom of molecule i.

We assume $H^{(N)}$ to be the sum $\sum_i H_i^{(1)} + \sum_i \sum_{j>i} V_{ij}$ of single-particle functions $H_i^{(1)}$ and of pair interactions V_{ij}. Consequently, the set of reduced distribution functions

$$f^{(n)} = [N!/(N-n)!] \int dX_{n+1} \cdots \int dX_N \, f^{(N)} \tag{40}$$

are governed by the BBGKY hierarchy of coupled equations,

$$\partial_t f^{(n)} + [f^{(n)}, H^{(n)}] = \sum_{i=1}^{n} \sum_{\beta=1}^{\nu} \int dX_{n+1} \left\{ \frac{\partial}{\partial p_{i\beta}} \left(f^{(n+1)} \frac{\partial V_{i,n+1}}{\partial q_{i\beta}} \right) - \frac{\partial}{\partial q_{i\beta}} \left(f^{(n+1)} \frac{\partial V_{i,n+1}}{\partial p_{i\beta}} \right) \right\} \tag{41}$$

In (40) and (41) the symbol dX_i ($\equiv \prod_\beta dq_{i\beta}\, dp_{i\beta}$) denotes the differential element in the ν-dimensional phase space of molecule i. Although it is reasonable to assume that the pair potential V_{ij} is independent of the particle momenta, $\mathbf{p}_i = m\mathbf{c}_i$ and $\mathbf{p}_j = m\mathbf{c}_j$, we do not exclude the possibility of dependence upon the momenta conjugate to the internal coordinates. This permits more flexibility in the choice of the variables I_i. For example, let us suppose that the interaction appropriate to two rigid rotors can be expressed fully in terms of $\mathbf{x}_{ij}$ ($\equiv \mathbf{x}_i - \mathbf{x}_j$) and the unit vectors $\mathbf{e}_i$ and $\mathbf{e}_j$ directed along the molecular symmetry axes. One can then choose for internal coordinates the polar spherical angles (θ_i and ϕ_i) of $\mathbf{e}_i$; the associated pair of conjugate momenta are p_{θ_i} and p_{ϕ_i}. The function V_{ij} clearly is independent of these momenta. However, one might prefer a description in terms of the action-angle variables of the rotors. The generalized momenta are then L_i and L_{iz}, the magnitude and z-projection of the rotational angular momentum $\mathbf{L}_i$. The coordinate conjugate to L_{iz} is the angle which locates the position of the line of nodes in the plane perpendicular to the space-fixed z axis. The conjugate of $L_i = |\mathbf{L}_i|$ is the angle between the lines of nodes and $\mathbf{e}_i$. With this choice of coordinates $\mathbf{e}_i$, and hence V_{ij}, is a function of L_{iz}/L_i as well as of both angular variables.

For a system with a Hamiltonian of the form we have assumed the macroscopic properties of interest can be computed from a knowledge of the singlet and pair distribution functions, $f^{(1)}$ and $f^{(2)}$. In fact, at the low densities which are of specific concern to us here the singlet distribution function alone is of importance. Now, a moment's reflection should serve to recall that implicit in much of what we said and did in the previous section was the assumption that the concentrations measured by the Boltzmann distribution functions f_α and F_α did not include molecules which were in the midst of collisional encounters. Thus, we identified f_α with the concentration of α-species molecules which were, in some vaguely defined sense, isolated from other molecules. This suggests that it is not the usual singlet distribution of statistical mechanics which we can expect to satisfy the Boltzmann equation, but rather a function such as

$$\tilde{f}^{(1)}(1) = N \int dX_2 \cdots \int dX_N \left(\prod_{j=2}^{N} \zeta_{j,1} \right) f^{(N)} \tag{42}$$

where the function $\zeta_{j,i}$ assumes the value zero whenever the center of mass of j lies within a convex region $\sigma_{i,j} = \sigma(\{q_i\,, p_i\}; \{q_j\,, p_j\})$ surrounding molecule i and is otherwise equal to unity. This new function can be expressed in terms of the set $\{f^{(n)}\}$ as follows[4]:

$$\begin{aligned} \tilde{f}^{(1)}(1) &= f^{(1)}(1) - \int_{\sigma_{1,2}} dX_2 f^{(2)}(12) + \tfrac{1}{2} \int_{\sigma_{1,2}} dX_2 \int_{\sigma_{1,3}} dX_3 f^{(3)}(123) - \cdots \\ &= \sum_{n \geqslant 0} [(-1)^n/n!] \int_{\sigma_{1,2}} dX_2 \cdots \int_{\sigma_{1,n+1}} dX_{n+1} f^{(n+1)} \end{aligned} \tag{43}$$

Although this would appear to be an infinite series, it does in fact truncate after a finite number of terms. Thus, for any realistic choice of the intermolecular forces only a limited number of molecules can be fitted within the region σ. The physical interpretation of the series is clear: the first term is just the molecule density, the second term subtracts from this the number of paired molecules, the third corrects for the counting of pairs which are imbedded within molecular trios, etc. As the density tends to zero any difference between $\tilde{f}^{(1)}$ and $f^{(1)}$ can be attributed exclusively to the formation of bound pairs, trimers, and the like. Although it is not essential, we henceforth assume that no such aggregates exist.

The equation of change for $\tilde{f}^{(1)}$ can be obtained directly from the definition (42) or by summing the sequence of equations (41) as indicated by (43). The former procedure is more direct. We multiply (38) by $(N\Xi_1)$, with $\Xi_1 = \prod_{j \geqslant 2} \zeta_{j,1}$, and integrate to obtain

$$\begin{aligned} \partial_t \tilde{f}^{(1)} &+ N \int dX_2 \cdots \int dX_N\, \Xi_1 \left[f^{(N)}, \sum_{1}^{N} H_i^{(1)} \right] \\ &= -N \int dX_2 \cdots \int dX_N\, \Xi_1 \left[f^{(N)}, \sum_{j>i}\sum V_{ij} \right] \end{aligned}$$

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[4] Distribution functions of this sort have been used previously by Grad[13] and O'Toole and Dahler.[14] The present development closely resembles the treatment by the latter of the Boltzmann equation for structureless species.

This can be reduced to the form

$$\begin{aligned}\partial_t \tilde{f}^{(1)}(1) + [\tilde{f}^{(1)}(1), H_1^{(1)}] - \int dX_2\, \tilde{f}^{(2)}(12)[\zeta_{2,1}\,, H_1^{(1)} + H_2^{(1)}]\\ = -N \int dX_2 \cdots \int dX_N\, \Xi_1[f^{(N)}, V] \end{aligned} \tag{44}$$

with $V = \sum\sum_{j>i} V_{ij}$ and where

$$\begin{aligned}\tilde{f}^{(2)}(12) &= [N!/(N-2)!] \int dX_3 \cdots \int dX_N \left(\prod_{j=3}^{N} \zeta_{3,1}\right) f^{(N)}\\ &= f^{(2)}(12) - \int_{\sigma_{1,3}} dX_3\, f^{(3)}(123) + \cdots \end{aligned} \tag{45}$$

is the pair density conditioned by the requirement that no particle lie within the region $\sigma_{1,j}$ about molecule 1.

Let us assume that the linear dimensions of the region σ exceed the range of the intermolecular forces, or equivalently, that $\zeta_{j,1} V_{j1} = 0$ for all states of the two molecules 1 and j. As a consequence of this assumption (or restriction), the right-hand side of (44) vanishes (it is equal to the rate of change of the number of molecules in the set 2, 3,..., N, caused by their mutual interactions) and we obtain

$$\partial_t \tilde{f}^{(1)}(1) + [\tilde{f}^{(1)}(1), H_1^{(1)}] = \partial_c \tilde{f}^{(1)}(1) \tag{46}$$

with

$$\partial_c \tilde{f}^{(1)}(1) = \int dX_2\, \tilde{f}^{(2)}(12)\, \dot{\zeta}_{2,1}$$

and where $\dot{\zeta}_{2,1} = [\zeta_{2,1}\,, H_1^{(1)} + H_2^{(1)}]$. The right-hand side of (46) is the net rate of flow across the boundaries of σ, that is, the net rate at which molecules "break free" (at the surface of σ) into the state 1.

The space of the center-of-mass variable $\mathbf{x}_2$ can be spanned by a sequence of surfaces which are geometrically similar to the surface of $\sigma_{1,2}$ and scaled by a parameter ρ (for more details, see Curtiss and Dahler$^{(15)}$). Thus, the location of the center of mass of molecule 2, relative to that of molecule 1, can be given in terms of ρ and the surface normal $\mathbf{k}$, with ρ specifying the convex surface on which the mass center lies and $\mathbf{k}$ giving its position on this surface. When $\rho = 1$ the center of mass of 2 lies on the surface of $\sigma_{1,2}$ and therefore $\zeta_{2,1} = \eta(\rho - 1)$, where η is the unit step function. It follows that $\dot{\zeta}_{2,1} = \delta(\rho - 1)\dot{\rho}$. In terms of these coordinates $d^3x_2 = \rho^2 h\, d\rho\, d^2S$, where d^2S is the differential surface element of $\sigma_{1,2}$ and $\rho h = \mathbf{x}_{21} \cdot \mathbf{k}$. Thus,

$$\partial_c \tilde{f}(1) = \int d2 \int d^2S\, \dot{\rho} h \tilde{f}^{(2)}(12) \tag{47}$$

Furthermore, $\dot{\rho} h$ can be identified as the normal component $\mathbf{k} \cdot \mathbf{g}$ of the velocity $\mathbf{g}$ of the center of mass of molecule 2 relative to the point of contact on $\sigma_{1,2}$. For present purposes we restrict our attention to the very simplest case and select for σ a sphere whose radius is equal to the range R of the intermolecular forces. It then follows that $d^2S = R^2\, d^2\hat{n}$, $\rho h = x_{21}$, $\dot{\rho} h = \hat{\mathbf{n}} \cdot \mathbf{c}_{21}$, and

$$\partial_c \tilde{f}(1) = R^2 \int d2 \int d^2\hat{n}\, (\hat{\mathbf{n}} \cdot \mathbf{c}_{21})[\tilde{f}^{(2)}(12)]_{x_{21}=R} \tag{48}$$

where $\hat{\mathbf{n}} = \mathbf{x}_{21}/\mathrm{x}_{21}$ and $\mathbf{c}_{21} = \mathbf{c}_2 - \mathbf{c}_1$.

It should be noted that both (41) and (46) can be interpreted as continuity equations in the appropriate phase spaces. Thus, the BBGKY hierarchy (41) can be cast into the form

$$\partial_t f^{(n)} + \sum_{i=1}^{n} \sum_{\beta=1}^{\nu} \left\{ \frac{\partial}{\partial q_{i\beta}} (\bar{\dot{q}}_{i\beta} f^{(n)}) + \frac{\partial}{\partial p_{i\beta}} (\bar{\dot{p}}_{i\beta} f^{(n)}) \right\} = 0$$

where the "velocities" $\bar{\dot{q}}_{i\beta}$ and $\bar{\dot{p}}_{i\beta}$ are the values of $\dot{q}_{i\beta}$ and $\dot{p}_{i\beta}$ averaged in an n-particle aggregate, that is,

$$f^{(n)} \bar{\dot{q}}_{i\beta} = f^{(n)} \frac{\partial H^{(n)}}{\partial p_{i\beta}} + \int dX_{n+1} f^{(n+1)} \frac{\partial V_{i,n+1}}{\partial p_{i\beta}}$$

and

$$f^{(n)} \bar{\dot{p}}_{i\beta} = -f^{(n)} \frac{\partial H^{(n)}}{\partial q_{i\beta}} - \int dX_{n+1} f^{(n+1)} \frac{\partial V_{i,n+1}}{\partial q_{i\beta}}$$

Equation (46) has a similar interpretation, but since $\tilde{f}(1)$ is the distribution function for "isolated" molecules,

$$\bar{\dot{q}}_{i\beta} = \partial H^{(1)}/\partial p_{i\beta} \qquad \text{and} \qquad \bar{\dot{p}}_{i\beta} = -\partial H^{(1)}/\partial q_{i\beta}$$

in this case. Furthermore, since the number of isolated molecules is not a constant, we must include source and sink terms. These, taken together, give the net rate at which molecules flow inward across the surface σ, namely, $\int d2 \int d^2S\, (\mathbf{k} \cdot \mathbf{g}) \tilde{f}^{(2)}$. This result is in accord with (47).

To this point all is rigorous, but to complete the reduction to the Boltzmann equation, one must introduce approximations which, however well founded, do not fall into the category of mathematical identities. To provide motivation for these approximations, we shall rely upon Bogoliubov's description of the approach to equilibrium.(16) Although many others contributed to the development of the concept, it was he who stressed the importance of recognizing that equilibration takes place in three stages, each of which is characterized by its own time scale. These three scales are associated with the duration of a collision, the interval between successive collisions, and a macroscopic (hydrodynamic) interval. The gist of the argument is that when the values of these three relaxation times are well separated, the only pertinent variables which survive from one stage to the next are those whose values were unaltered by the relaxation process which took place during the previous stage. Hence, each stage is characterized by a "contraction" in the number of variables neded to describe the state of the gas. In the final, hydrodynamic stage the macroscopic variables (concentrations, fluid velocity, temperature) alone determine this state.

According to Bogoliubov, an initial state described by the distribution $f^{(N)}(t = 0)$ first passes through a period of "chaotization" which is completed in a span of time comparable to the duration of a single molecular collision. Within this brief interval all of the distributions functions $f^{(n)}$ which appear in the BBGKY sequence (41) are assumed to reduce to functionals of the singlet distribution function $f^{(1)}$ and to develop a dependence upon time which is exclusively that implied by these functional relationships. The rationale for this assertion is based upon the fact that all of the operators $[,H^{(n)}]$ except $[,H^{(1)}]$ depend upon the intermolecular forces and that these forces change substantially during the course of a collisional encounter. Therefore, of all the $f^{(n)}$ only $f^{(1)}$ can be expected to remain unchanged during the period of chaotization. This argument requires a slight modification in the case of polyatomic species, since the angles and phases associated with the internal degrees of freedom may change by significant amounts during an interval of time on the order of t_f, the lapse between two successive molecular collisions. To be consistent, we should expect that during the "kinetic stage" which follows the period of chaotization the singlet distribution functions will depend only upon invariants of the free-flight motion. We have discussed these in detail previously. The equation which governs the "contracted" singlet function can be gotten by averaging the first of the BBGKY equations over all the rapidly varying angle variables. Because of the kinetic-stage functional dependence of $f^{(n)}$ (and $f^{(2)}$ in particular) upon $f^{(1)}$, we can expect to be able to write a closed equation for the singlet function. This functional relationship is embodied in the assumption of molecular chaos which we discuss somewhat later.

During the kinetic stage there is relaxation to a state of local equilibrium which is determined by the local values of the macroscopic fields. Further relaxation to a state of final equilibrium is governed by the equations of fluid dynamics. In this final stage the singlet distribution function will have a small nonequilibrium distortion due to gradients of the macroscopic variables. Indeed, this distortion is uniquely determined by the macroscopic state of the gas. The corresponding singlet distribution function is called the "normal" solution of the kinetic equation. The significance of the macroscopic variables is that they correspond to average values of summational invariants. These quantities, in sum for the colliding particles, are not altered by collision, and so their average values change only on the hydrodynamic scale of time.

Let us now apply these conjectures concerning the approach to equilibrium to the further reduction of the kinetic equation (48). On the hemisphere $\hat{\mathbf{n}} \cdot \mathbf{c}_{21} < 0$ the centers of the two molecules are approaching one another, that is, the molecules are about to become engaged in a mutual collision. On the hemisphere $\hat{\mathbf{n}} \cdot \mathbf{c}_{21} > 0$ the particles are moving away from one another on postcollisional trajectories. Thus, we can rewrite (48) in the form

$$\begin{aligned}
\partial_c \tilde{f}^{(1)}(1) &= R^2 \int d2 \int d^2\hat{n}\, [\gamma(\hat{\mathbf{n}} \cdot \mathbf{c}_{21})\, \tilde{f}^{(2)}(\mathbf{x}_1\mathbf{c}_1 I_1\,;\, \mathbf{x}_1 + R\hat{\mathbf{n}}\,\mathbf{c}_2 I_2)_{\text{post}} \\
&\qquad - \gamma(-\hat{\mathbf{n}} \cdot \mathbf{c}_{21})\, \tilde{f}^{(2)}(\mathbf{x}_1\mathbf{c}_1 I_1\,;\, \mathbf{x}_1 + R\hat{\mathbf{n}}\,\mathbf{c}_2 I_2)_{\text{pre}}] \\
&= R^2 \int d2 \int d^2\hat{n}\, \gamma(\hat{\mathbf{n}} \cdot \mathbf{c}_{21})[\tilde{f}^{(2)}(\mathbf{x}_1\mathbf{c}_1 I_1\,;\, \mathbf{x}_1 + R\hat{\mathbf{n}}\,\mathbf{c}_2 I_2)_{\text{post}} \\
&\qquad - \tilde{f}^{(2)}(\mathbf{x}_1\mathbf{c}_1 I_1\,;\, \mathbf{x}_1 - R\hat{\mathbf{n}}\,\mathbf{c}_2 I_2)_{\text{pre}}]
\end{aligned} \tag{49}$$

where $\gamma(x) = x\eta(x)$ and where the subscripts "pre" and "post" indicate that the arguments of the distribution functions correspond to pre- and postcollisional states, respectively. We now select a polar axis in the direction of $\hat{\mathbf{c}} = \mathbf{c}_{21}/c_{21}$ and denote by θ and ϕ the polar spherical coordinates of the unit vector $\hat{\mathbf{n}}$. It then follows that $\hat{\mathbf{n}} \cdot \mathbf{c}_{21} = c \cos\theta$, $d^2\hat{n} = \sin\theta \, d\theta \, d\phi$, and $\hat{\mathbf{n}} \cdot \mathbf{c}_{21} R^2 \, d^2\hat{n} = R^2 c \cos\theta \sin\theta \, d\theta \, d\phi = c \, d\mathbf{b}$, where $b = R\sin\theta$ is the magnitude and $d\mathbf{b} = b \, db \, d\phi$ the differential element of the impact parameter $\mathbf{b} = R(\boldsymbol{\delta} - \hat{\mathbf{c}}\hat{\mathbf{c}}) \cdot \hat{n}$. Therefore, (49) becomes

$$\partial_c \tilde{f}^{(1)}(1) = \int d2 \int d\mathbf{b} \, c[\tilde{f}^{(2)}(\mathbf{x}_1\mathbf{c}_1 I_1 \, ; \, \mathbf{x}_1 + R\hat{\mathbf{n}} \, \mathbf{c}_2 I_2 \, ; \, t)_{\text{post}} \\ - \tilde{f}^{(2)}(\mathbf{x}_1\mathbf{c}_1 I_1 \, ; \, \mathbf{x}_1 - R\hat{\mathbf{n}} \, \mathbf{c}_2 I_2 \, ; \, t)_{\text{pre}}] \tag{50}$$

with $R\hat{\mathbf{n}} = \mathbf{b} + \hat{\mathbf{c}}(R^2 - b^2)^{1/2}$.

Until now all has been rigorous, but now we introduce the first of the three approximations which will transform the identity (50) into the Boltzmann equation. Specifically, we assume that the "completed" collisions to which the first term of (50) refers are isolated binary events. According to this approximation, each postcollisional state $(\mathbf{x}_1\mathbf{c}_1 I_1 \, ; \, \mathbf{x}_1 + R\hat{\mathbf{n}} \, \mathbf{c}_2 I_2)$, $\hat{\mathbf{n}} \cdot \mathbf{c}_{21} > 0$, appearing in (50) is to be identified with the termination of a binary collision which began at $t - t_c$ with the two molecules in the state $(\mathbf{x}_1{}^\star\mathbf{c}_1{}^\star I_1{}^\star; \, \mathbf{x}_1 + R\hat{\mathbf{n}}^\star \, \mathbf{c}_2 I_2{}^\star)$. (This "starred" state is precisely the same as that defined in the preceding section.) This approximation, which is virtually exact for short-range repulsive interactions, permits us to replace $\tilde{f}^{(2)}(\mathbf{x}_1\mathbf{c}_1 I_1 \, ; \, \mathbf{x}_1 + R\hat{\mathbf{n}} \, \mathbf{c}_2 I_2 \, ; \, t)_{\text{post}}$ of (50) with $\tilde{f}^{(2)}(\mathbf{x}_1{}^\star\mathbf{c}_1{}^\star I_1{}^\star; \, \mathbf{x}_1{}^\star + R\hat{\mathbf{n}}^\star \, \mathbf{c}_2{}^\star I_2{}^\star; \, t - t_c)_{\text{pre}}$.

The second and most crucial approximation is that of "molecular chaos." In particular, we assume that for precollisional states the pair density factors into the product of the corresponding singlet distribution functions, that is, $\tilde{f}^{(2)}(12)_{\text{pre}} = \tilde{f}^{(1)}(1)\tilde{f}^{(1)}(2)$. This is the functional relationship between the pair and singlet distribution functions which is appropriate to a dilute gas.

Our final assumption has to do with "coarse graining" in time and space and, in particular, with the variations of $\tilde{f}^{(1)}$ which occur during intervals of the order t_c and over distances of the order of R or $| \mathbf{x}_1{}^\star - \mathbf{x}_1 | \approx c_{21} t_c$. We recognize these to be precisely the variations of which the Boltzmann distribution function of Section 2 was independent. Therefore, we neglect them here and obtain from (50)

$$\partial_c \tilde{f}^{(1)}(t\mathbf{x}1) \approx \int d2 \int d\mathbf{b} \, c[\tilde{f}^{(1)}(t - t_c \, , \mathbf{x}^\star 1^\star) \tilde{f}^{(1)}(t - t_c \, , \mathbf{x}^\star + R\hat{\mathbf{n}}^\star 2^\star) \\ - \tilde{f}^{(1)}(t, \mathbf{x}1) \tilde{f}^{(1)}(t, \mathbf{x} - R\hat{\mathbf{n}}2)] \\ \approx \int d2 \int d\mathbf{b} \, c[\tilde{f}^{(1)}(t\mathbf{x}1^\star) \tilde{f}^{(1)}(t\mathbf{x}2^\star) - \tilde{f}^{(1)}(t\mathbf{x}1) \tilde{f}^{(1)}(t\mathbf{x}2)] \tag{51}$$

or

$$\partial_c f^{(1)}(1) \approx \iiint d1' \, d2' \, d2 \left[\int d\mathbf{b} \, c \, \delta(1' - 1^\star) \, \delta(2' - 2^\star) \right] \\ \times [f^{(1)}(1') f^{(1)}(2') - f^{(1)}(1) f^{(1)}(2)] \\ \approx \iiint d1' \, d2' \, d2 \, w(12 \mid 1'2')[f^{(1)}(1') f^{(1)}(2') - f^{(1)}(1) f^{(1)}(2)] \tag{52}$$

where $w(12 \mid 1'2')$ is the transition rate defined by (12) of Section 2. Finally, by averaging over the rapidly changing angle variables η_1, we obtain (15) and (16) of the preceding section.

To arrive at (51), which is formally identical to the Boltzmann equation (4), we have ignored the effects of three-body collisions and assumed a lack of statistical correlations prior to collision. Furthermore, since we have neglected variations of $f^{(1)}$ over times comparable to the duration of a collision and over distances of the order of R or $c_{21}t_c$, this function can indeed be identified with the density f which occurs in the Boltzmann equation. These approximations and the arguments of Section 2 concerning the replacement of $f_\alpha(1)$ with $F_\alpha(\bar{1})$ are consistent with Bogoliubov's description of the "kinetic stage" in the approach to equilibrium.

3.1. Approximate Theory for Impulsive Interactions

The derivation of the Boltzmann equation which we have just presented is quite general and relies exclusively upon approximations which are statistical in nature, that is, the theory incorporates a rigorous treatment of the binary scattering process. However, this leaves us in a posture which, to say the very least, is a bit absurd, for we are unaware of a single instance of inelastic scattering (we reject the rough-sphere model because of its lack of realism) for which the differential cross sections and/or transition rates are actually available. To be sure, there do exist perturbation procedures which appear capable of generating useful approximations to these quantities but, at the time of this writing, no calculations of transport coefficients (except rotational and vibrational relaxation times) based upon these techniques have been reported. Indeed, the only cases for which extensive calculations have been performed are those where the inelastic scattering events were treated as if the colliding molecules were hard, nondeformable convex objects.(2,8,15) The approximations involved in these calculations are of a rather special sort. Thus, a collision between two rigid nonspherical objects may be "simple" in the sense that the entire event consists of a single impulsive encounter, or it may be complex "chattering" event consisting of a sequence of highly correlated impulses. Since collisions of the latter variety are so very difficult to analyze, it is the natural approximation simply to ignore their existence. (The positivist's point of view is to interpret this neglect of chattering events as a refinement of the collision model.) The probability of occurrence of a chattering collision is dependent upon the degree of eccentricity of the nonspherical interactions and upon the values of various kinematic parameters such as moments of inertia and characteristic frequencies of vibrational modes. The neglect of chatter will, of course, be a less severe approximation for some values of these variables than for others.

Although the assumption of impulsive molecular interactions is certainly somewhat less than realistic, there is little reason to suspect that it will lead to grossly inaccurate conclusions about fluids composed of relatively small, weakly polar molecules. This is particularly true at temperatures for which the value of kT greatly exceeds the strength of the actual attractive interactions. But even if one is prepared to accept the assumption, he still finds himself confronted with formidible computational complexities. Because of these difficulties, only a very limited number of rigid models have been studied in the past. However, recent advances(17) now make it possible to compute with comparative ease the bracket and brace integrals for a great variety of nonspherical species. We are presently engaged in exploiting this fact and in generating transport coefficients for molecules of several shapes.

The Boltzmann equations which were derived earlier in this section are appropriate for a theory based upon an exact treatment of chattering collisions. One has only to select the diameter ($2R$) of the "collision sphere" to be larger than the greatest linear dimension of either of the participating rigid bodies. However, we intend to neglect chatter, and so it is better to adopt a different approach: instead of defining the beginning and end of an event in terms of the penetration of the collision sphere, we formulate the theory in terms of the beginning and end of the very brief ($t_c = 0^+$) "contacts" between the surfaces of the two rigid bodies. Thus, in place of (50) we begin with the corresponding identity

$$\begin{aligned}\partial_c \tilde{f}^{(1)}(1) &= \int d2 \int d^2S\, (\mathbf{k}\cdot\mathbf{g})\, \tilde{f}^{(2)}(\mathbf{x}\; 1; \mathbf{x} + \boldsymbol{\zeta}_1 - \boldsymbol{\zeta}_2\; 2; t)\\ &= \int d2 \int d^2S\, [\gamma(\mathbf{k}\cdot\mathbf{g})\, f^{(2)}(\mathbf{x}\; 1^\star; \mathbf{x} + \boldsymbol{\zeta}_1 - \boldsymbol{\zeta}_2\; 2^\star; t - 0^+)_{\text{pre}}\\ &\qquad - \gamma(-\mathbf{k}\cdot\mathbf{g})\, \tilde{f}^{(2)}(\mathbf{x}\; 1; \mathbf{x} + \boldsymbol{\zeta}_1 - \boldsymbol{\zeta}_2\; 2; t)_{\text{pre}}]\end{aligned} \tag{53}$$

which first was derived by Curtiss and Dahler(15) and which one can also obtain directly from (47). Here $d^2S = d^2k\, S(\mathbf{k}, \boldsymbol{\beta}_1, \boldsymbol{\beta}_2)$ denotes the differential element of the surface which is generated by the center of mass of molecule 2 as it slides over molecules 1 in such a way that the orientations $\boldsymbol{\beta}_1$ and $\boldsymbol{\beta}_2$ of both remain fixed. The vector $\mathbf{k}$ is the outward-directed unit normal to the surface of molecule 1 at the point of its common tangency (and contact) with molecule 2.

The symbol $\boldsymbol{\zeta}_i$ indicates the vector extending from the center of mass of molecule i to this point of contact, and $\mathbf{g} = \mathbf{c}_{21} + (\mathsf{I}_2^{-1}\cdot\mathbf{L}_2)\times\boldsymbol{\zeta}_2 - (\mathsf{I}_1^{-1}\cdot\mathbf{L}_1)\times\boldsymbol{\zeta}_1$ is the relative velocity at impact of the points of contact on the surfaces of the two bodies; $\mathsf{I}_i = \mathsf{I}(\beta_i)$ is the inertial tensor of molecule i. Since the collisional impulses are of infinitesimal duration, the positions and orientations of the bodies are unaltered by these events. If the surfaces of the molecules are smooth, impact reverses the algebraic sign of $\mathbf{k}\cdot\mathbf{g}$, that is, $\mathbf{k}\cdot\mathbf{g} = -\mathbf{k}\cdot\mathbf{g}^\star$. This results in the changes of molecular velocities and angular momenta given by the formulas $\mathbf{c}_i^\star - \mathbf{c}_i = \mathbf{k}_i K/m$ and $\mathbf{L}_i^\star - \mathbf{L}_i = \boldsymbol{\zeta}_i \times \mathbf{k}_i K$, with $\mathbf{k}_1 = \mathbf{k}$, $\mathbf{k}_2 = -\mathbf{k}$, and

$$K = m(\mathbf{k}\cdot\mathbf{g})[1 + \tfrac{1}{2}m\{\mathsf{I}_1^{-1} : (\boldsymbol{\zeta}_1\times\mathbf{k})(\boldsymbol{\zeta}_1\times\mathbf{k}) + \mathsf{I}_2^{-1} : (\boldsymbol{\zeta}_2\times\mathbf{k})(\boldsymbol{\zeta}_2\times\mathbf{k})\}]^{-1}$$

To obtain the second form of (53), we have separated the first into pre- and postcollisional contributions and replaced each state in the second of these categories with the unique precollisional state which was its (immediate) precursor.

As before, we obtain the Boltzmann equation by replacing each of the pair densities $\tilde{f}_{\text{pre}}^{(2)}$ in (53) with the corresponding product of singlet distribution functions. This is a less acceptable approximation here than it was previously, for some of the states appearing in (53) can only occur as members of a chattering sequence. By following this factorization with a coarse-graining of $\tilde{f}^{(1)}$, we obtain

$$\begin{aligned}\partial_c f^{(1)}(1) &= \int d2 \int d^2S\, [\gamma(\mathbf{k}\cdot\mathbf{g})\, f^{(1)}(1^\star)\, f^{(1)}(2^\star) - \gamma(-\mathbf{k}\cdot\mathbf{g})\, f^{(1)}(1)\, f^{(1)}(2)] \\ &= \iiint d1'\, d2'\, d2\, [w(12 \mid 1'2')\, f^{(1)}(1')\, f^{(2)}(2') - w(1'2' \mid 12)\, f^{(1)}(1)\, f^{(1)}(2)]\end{aligned} \tag{54}$$

with

$$w(12 \mid 1'2') = \int d^2S\, \gamma(\mathbf{k}\cdot\mathbf{g})\, \delta(1' - 1^\star)\, \delta(2' - 2^\star) \tag{55}$$

and

$$w(1'2' \mid 12) = \int d^2S\, \gamma(-\mathbf{k}\cdot\mathbf{g})\, \delta(1' - 1^\star)\, \delta(2' - 2^\star) \tag{56}$$

To prove the time-reversal property $w(1'2' \mid 12) = w(\hat{T}1\ \hat{T}2 \mid \hat{T}1'\ \hat{T}2')$, we write (55) in the more explicit form

$$\begin{aligned}&w(\mathbf{c}_1\mathbf{L}_1\boldsymbol{\beta}_1\,;\, \mathbf{c}_2\mathbf{L}_2\boldsymbol{\beta}_2 \mid \mathbf{c}_1'\mathbf{L}_1'\boldsymbol{\beta}_1';\, \mathbf{c}_2'\mathbf{L}_2'\boldsymbol{\beta}_2') \\ &\quad = \int d^2S\, \gamma[\mathbf{k}\cdot(\mathbf{c}_{21} + \boldsymbol{\omega}_2 \times \boldsymbol{\zeta}_2 - \boldsymbol{\omega}_1 \times \boldsymbol{\zeta}_1)]\, \delta(\boldsymbol{\beta}_1 - \boldsymbol{\beta}_1') \\ &\qquad \times \delta(\boldsymbol{\beta}_2 - \boldsymbol{\beta}_2')\, \delta_3(\mathbf{G} - \mathbf{G}')(\mathbf{c}^\star - \mathbf{c}')\, \delta_3(\mathbf{L}_1{}^\star - \mathbf{L}_1')\, \delta_3(\mathbf{L}_2{}^\star - \mathbf{L}_2')\end{aligned} \tag{57}$$

where $\boldsymbol{\omega}_i \equiv \mathsf{I}_i^{-1}\cdot\mathbf{L}_i$. The formula for $w(\mathbf{c}_1'\mathbf{L}_1'\boldsymbol{\beta}_1';\, \mathbf{c}_2'\mathbf{L}_2'\boldsymbol{\beta}_2' \mid \mathbf{c}_1\mathbf{L}_1\boldsymbol{\beta}_1\,;\, \mathbf{c}_2\mathbf{L}_2\boldsymbol{\beta}_2)$ differs only in the algebraic sign of the argument of γ. In (57) we now replace each velocity and angular momentum with its negative, that is, with its image under time reversal. The argument of γ is then replaced with its negative and a term like $\delta_3(\mathbf{L}_1{}^\star - \mathbf{L}_1')$ becomes $\delta_3(\tilde{\mathbf{L}}_1{}^\star - (-\mathbf{L}_1'))$, with $\tilde{\mathbf{L}}_1{}^\star = \tilde{\mathbf{L}}_1(-\mathbf{c}_1, -\mathbf{c}_2, -\mathbf{L}_1, -\mathbf{L}_2, \boldsymbol{\beta}_1, \boldsymbol{\beta}_2, \mathbf{k}) = -\mathbf{L}_1{}^\star$, where the last equality is a consequence of dynamic reversibility. Consequently, $\delta_3(\mathbf{L}_1{}^\star - \mathbf{L}_1') \to \delta_3(-\mathbf{L}_1{}^\star - (-\mathbf{L}_1')) = \delta_3(\mathbf{L}_1{}^\star - \mathbf{L}_1')$ and the theorem to be proved has been established.

As a result of time-reversal invariance, we can prove the property of bilateral normalization and so reduce (54) to the standard form (52). To this same approximation, the differential cross section is given by the formula

$$\sigma(\mathbf{c}'I_1'I_2' \to \mathbf{c}I_1I_2) = (c/c'^2) \int d^2k\, S(\mathbf{k}, \boldsymbol{\beta}_1, \boldsymbol{\beta}_2)\, \gamma(\mathbf{k}\cdot\mathbf{g})\, \delta_2(\hat{\mathbf{c}}' - \hat{\mathbf{c}}^\star)\, \delta(I_1' - I_1{}^\star)\, \delta(I_2' - I_2{}^\star) \tag{58}$$

Although a far from trivial task, the evaluation of the transition rates and cross section defined by (55) and (58) is certainly within the realm of possibility. Indeed, for the special case of loaded spheres this already has been accomplished.$^{(18)}$

To complete the approximate theory for impulsive interactions, one can, as before, perform the contraction $f(1) \to F(\bar{1})$ and introduce integral operators $\hat{\Gamma}$ and the related Fredholm kernels K. These quantities, as well as the transition rate (55) and the cross section (58), exhibit the same symmetry properties as do the corresponding quantities associated with the exact treatment of the collisional events.

We speak of inverse collisions if, for each event $(1'2'\mathbf{b}') \rightarrow (12\mathbf{b})$, there exist impact parameters $\mathbf{b}_1$ and $\mathbf{b}_1'$ such that the "inverse" event $(12\mathbf{b}_1) \rightarrow (1'2'\mathbf{b}_1')$ is dynamically possible. One can prove without difficulty that the transition rate matrix w is symmetric for interactions which admit inverse collisions. However, it is only for loaded spheres$^{(19)}$ (with soft or rigid interactions) that the existence of inelastic inverse collisions actually has been established. Interactions which admit "pseudoinverse" collisions are much more common. The pseudoinverse of $(1'2'\mathbf{b}') \rightarrow (12\mathbf{b})$ is the event $(\hat{1}\hat{2}\mathbf{b}_1) \rightarrow (\hat{1}'\hat{2}'\mathbf{b}_1')$, where the states i and $\hat{i}$ differ only in the algebraic signs of the angular momentum $\mathbf{L}_i$. Pseudoinverse events are known to exist for the rough-sphere and loaded-spherocylinder models. They also occur for all rigid and convex, smooth bodies and for their soft-potential analogs.$^{(20)}$ In the cases just mentioned it is more natural to describe the collision events, both direct and inverse (or pseudoinverse), in terms of $\mathbf{k}$, the direction of the common normal to the molecular "surfaces" (contours of constant interaction energy$^{(20)}$) at their point of mutual contact, than in terms of the impact parameter $\mathbf{b}$.

4. CONCLUDING REMARKS

Throughout this paper we have dealt exclusively with classical mechanics, but there is no difficulty whatsoever in transcribing the phenomenological theory of Section 2 into the language of quantum mechanics. In place of the variables $I_i = (q_i p_i)$ we introduce $\nu = (\zeta_i L_i M_i)$, where L_i and M_i, respectively, are the quantum numbers associated with internal angular momentum and its projection and where ζ_i is the set of whatever additional quantum numbers are needed to fully specify the state of an individual molecule. The kinetic equations for the distribution functions $f_\alpha(t\mathbf{x}\mathbf{c}\nu)$ are given by (4) and (8) of Section 2 provided that one replaces the integration $\int di\,(\cdots) \equiv \iint d^3c_i\, dI_i\,(\cdots)$ with the corresponding operation $\sum_{\nu_i} \int d^3c_i(\cdots)$ and the cross section $\sigma_{\alpha\beta}(\mathbf{c}'I_1'I_2' \rightarrow \mathbf{c}I_1I_2)$ with $\sigma_{\alpha\beta}(\mathbf{c}'\nu_1'\nu_2' \rightarrow \mathbf{c}\nu_1\nu_2)$.

To obtain the isotropic approximation, we assume that the distribution functions are independent of the projection quantum numbers and so replace $f_\alpha(t\mathbf{x}\mathbf{c}\nu)$ with its "average," $\omega^{-1}F_\alpha(t\mathbf{x}\mathbf{c}\mathscr{J})$, where $\omega = 2L + 1$ is the degeneracy of the molecular state with rotational quantum number L and where $\mathscr{J} = (\zeta L)$. The kinetic equations then become

$$\begin{aligned}(\partial_t + \mathbf{c}_1 \cdot \nabla + \cdots)\, F_\alpha(\mathbf{c}_1\mathscr{J}_1) &= \sum_{\beta} \sum_{\mathscr{J}_1'} \sum_{\mathscr{J}_2'} \sum_{\mathscr{J}_2} \int d^2\hat{c}' \int d^3c_2\, c\sigma_{\alpha\beta}(\mathbf{c}\mathscr{J}_1\mathscr{J}_2 \rightarrow \mathbf{c}'\mathscr{J}_1'\mathscr{J}_2') \\ &\quad \times [(\omega_1'\omega_2'/\omega_1\omega_2)\, F_\alpha(\mathbf{c}_1'\mathscr{J}_1')\, F_\beta(\mathbf{c}_2'\mathscr{J}_2') - F_\alpha(\mathbf{c}_1\mathscr{J}_1)\, F_\beta(\mathbf{c}_2\mathscr{J}_2)] \qquad (59)\end{aligned}$$

where the degeneracy-averaged cross sections

$$\sigma_{\alpha\beta}(\mathbf{c}\mathscr{J}_1\mathscr{J}_2 \rightarrow \mathbf{c}'\mathscr{J}_1'\mathscr{J}_2') = (1/\omega_1\omega_1) \sum_{M_1M_2M_1'M_2'}\!\!\cdots\!\sum \sigma_{\alpha\beta}(\mathbf{c}\nu_1\nu_2 \rightarrow \mathbf{c}'\nu_1'\nu_2')$$

satisfy the condition of averaged balance,

$$\omega_1'\omega_2'c'^2\sigma_{\alpha\beta}(\mathbf{c}'\mathscr{J}_1'\mathscr{J}_2' \rightarrow \mathbf{c}\mathscr{J}_1\mathscr{J}_2) = \omega_1\omega_2c^2\sigma_{\alpha\beta}(\mathbf{c}\mathscr{J}_1\mathscr{J}_2 \rightarrow \mathbf{c}'\mathscr{J}_1'\mathscr{J}_2')$$

If we assume the distribution to be nonpolar, then $f_\alpha(t\mathbf{x}\mathbf{c}\nu) \to \frac{1}{2}\tilde{F}_\alpha(t\mathbf{x}\mathbf{c}\mathscr{J}\lambda)$, where $\lambda = |M|$ is the magnitude of the projection quantum number. In place of (59) one then obtains kinetic equations which contain the average of the cross section over both algebraic signs of the projection quantum numbers.

The linear integral operators associated with the isotropic and nonpolar approximations are both self-adjoint, but the operator associated with the unaveraged cross sections will not, in general, exhibit this property. The sets of kinetic equations which correspond to these three cases are all of the form first proposed by Wang Chang and Uhlenbeck.(6) They argued that molecules in different states of excitation could be treated as distinct chemical species and that the kinetic theory for a polyatomic gas should not, therefore, differ significantly from that for a gas mixture of structureless species which undergo binary reactions $a_i + b_j = a_{i'} + b_{j'}$. There was some criticism of the Wang Chang and Uhlenbeck equations by those who thought that kinetic equations of the form (4) could be derived from a "master equation" of the form (1) only if the principle of detailed balance were applicable. However, we have seen that time-reversal invariance (bilateral normalization) alone is sufficient for this purpose. A more serious and lasting defect of the Wang Chang and Uhlenbeck equations was discovered by those who attempted to derive them directly from the Schroedinger equation.(3,4,12) The origin of this defect is the natural spatial degeneracy of the internal eigenstates of rotating molecules. To illustrate the problem, let us suppose that at one instant the microstate of the system could be described as a collection of wave packets, each representative of a molecule in some definite internal state and with a prescribed momentum. Each time two of these molecules collide, scattered waves emanate from the point of their impact. These waves eventually become spatially resolved into distinct packets—an elastic component which recedes from the point of impact at the same speed as before collision, and various inelastic components whose speeds generally differ from the precollision values and depend specifically upon the postcollisional states of the two molecules. The time required for this resolution to occur is dependent upon the width of the initial packet and, more particularly, upon the group velocities associated with the different components of the scattered wave. If the resolution is complete before either of the scattered particles suffers its next collision, then the situation is relatively uncomplicated. However, the group velocities associated with the several components of a degenerate postcollisional eigenstate are all the same and so, in this case, the free streaming of the particles does not result in spatial resolution of the components. The phase relationships among the components remain unchanged until the next collision. Thus, it is very reasonable to expect that the correct quantum-mechanical kinetic equations will involve the phases as well as the moduli of the scattering amplitudes. Since the (quantum) cross sections which appear in the Wang Chang and Uhlenbeck equations depend only upon the latter, we should not be surprised to find that they are of limited validity.

The generalization of the Boltzmann equation derived by Waldmann(3) and Snider(4) is free from this criticism. According to their more rigorous theory, the distribution function $f_\alpha(t\mathbf{x}\mathbf{c}\mathscr{J}M)$ must be replaced with a matrix $f_\alpha(t\mathbf{x}\mathbf{c}\mathscr{J})_{MM'}$. If one assumes this matrix to be diagonal, that is, if $f_\alpha(t\mathbf{x}\mathbf{c}\mathscr{J})_{MM'} \approx f_\alpha(t\mathbf{x}\mathbf{c}\mathscr{J}M)\,\delta_{MM'}$, then the equations of Waldmann and Snider reduce to those of Wang Chang and Uhlenbeck. Although there surely are some situations for which this approximation is inadequate (particularly as regards spin relaxation and diffusion), it seems overwhelmingly likely that it will have a negligible effect upon the numerical values of the usual transport coefficients and relaxation times.

APPENDIX: THE "NORMAL SOLUTION" OF THE BOLTZMANN EQUATION

One among the many uses to which the Boltzmann equations can be put is that of providing theoretical estimates of phenomenological coefficients such as those of viscosity, diffusion, and thermal conductivity. Here we outline the procedure for accomplishing this objective. The approach we shall use is an adaptation of one to which we were introduced by Professor Duane Condiff of the Carnegie-Mellon University.[22] With no significant loss of generality we may assume the molecules to be diamagnetic and that **F** (≡ **H**) is a static magnetic field. The Boltzmann equation (19) then can be written in the form

$$\left[\partial_t + \mathbf{c}_1 \cdot \frac{\partial}{\partial \mathbf{x}} + F_\alpha^{(e)} \cdot \frac{\partial}{\partial \mathbf{c}_1} + \bar{\boldsymbol{\mu}}_{\alpha 1} \times \mathbf{H} \cdot \frac{\partial}{\partial \mathbf{L}_1}\right] F_\alpha(\bar{1}) = \sum_\beta \,[F_\alpha \mid F_\beta]_1 \tag{A.1}$$

with

$$\begin{aligned}[\Phi_\alpha \mid \Psi_\beta] &= \int \cdots \int d^3c_1{}'\, d^3c_2{}'\, d^3c_2\, d\mathscr{J}_1{}'\, d\mathscr{J}_2{}'\, d\mathscr{J}_2\, w_{\alpha\beta}(\bar{1}\bar{2} \mid \bar{1}'\bar{2}') \\ &\quad \times [\Phi_\alpha(\bar{1}')\, \Psi_\beta(\bar{2}') - \Phi_\alpha(\bar{1})\, \Psi_\beta(\bar{2})] \\ &= \int \cdots \int d^2\hat{c}'\, d^3c_2\, d\mathscr{J}_2\, d\mathscr{J}_1{}'\, d\mathscr{J}_2{}'\, c_{21}\sigma_{\alpha\beta}(\mathbf{c}, \tilde{\mathscr{J}}_1\tilde{\mathscr{J}}_2 \to \mathbf{c}', \tilde{\mathscr{J}}_1{}'\tilde{\mathscr{J}}_2{}') \\ &\quad \times [\Phi_\alpha(\bar{1}')\, \Psi_\beta(\bar{2}') - \Phi_\alpha(\bar{1})\, \Psi_\beta(\bar{2})]\end{aligned} \tag{A.2}$$

and where $\tilde{\mathscr{J}}_i = \hat{T}\hat{P}\mathscr{J}_i$. Some solutions of these equations exhibit properties which are characteristic of one or another of the stages involved in Bogoliubov's description of the approach to equilibrium. To demonstrate this, we examine the Boltzmann equations from the point of view of dimensional analysis. We begin by identifying several characteristic parameters of the fluid:

c_γ, a speed, $(k\bar{T}/m_\gamma)^{1/2}$, associated with the species γ and with a reference temperature $\bar{T}$;

$c_{\beta\alpha}$, a speed, $(k\bar{T}/\mu_{\alpha\beta})^{1/2}$, associated with the relative motion of species α and β

$\bar{n}_\gamma$, a mean concentration for species γ;

$\lambda_f = 1/\bar{n}R^2$; a free path length associated with the mean concentration n (assuming the ranges of all molecular interactions to be about the same)

l, a representative "macroscopic" length, e.g., size of apparatus or $P/|\nabla P|$ where P denotes some macroscopic field;

τ, a characteristic interval of time;

and then define the dimensionless quantites

$$\mathbf{x}^* = \mathbf{x}/l; \qquad t^* = t/\tau; \qquad \mathbf{c}_1{}^* = \mathbf{c}_1/c_\alpha\,; \qquad c_{21}^* = c_{21}/c_{\beta\alpha}\,; \qquad \mathbf{L}_1{}^* = L_1/\hbar$$

$$\boldsymbol{\mu}_{\alpha 1}^* = \bar{\boldsymbol{\mu}}_{\alpha 1}/\beta_{\mathrm{nuc}}\,; \qquad \sigma_{\alpha\beta}^* = (v_\alpha v_\beta/R^2)\,\sigma_{\alpha\beta}\,; \qquad \mathscr{F}_\alpha(\bar{1}) = (c_\alpha{}^3 v_\alpha/\bar{n}_\alpha)\,F_\alpha(\bar{1})$$

where $v_\alpha = \int d\mathscr{J}_\alpha = v_\alpha \int d\mathscr{J}_\alpha{}^*$.

Since there is no "natural" unit of time (except for the periods of the timelike variables η, and we have "discarded" these), τ must be constructed from the other quantities which are at our disposal. There are three possibilities, R/c_α, λ_f/c_α, and l/c_α, with corresponding orders of magnitude of 10^{-11} sec, 10^{-9} sec, and 10^{-6} sec or greater. The approximations used in the derivation clearly imply that the Boltzmann equations are inapplicable to the shortest of these three scales of time, that is, to times of the order of the duration of Bogoliubov's "initial period." If we select τ equal to the kinetic time scale, $\tau_{\mathrm{kin}} = \lambda_f/c_\alpha$, (A.1) then becomes

$$\begin{aligned} &\partial_{t^*}\mathscr{F}_\alpha(\bar{1}) + \epsilon\left(\mathbf{c}_1{}^* \cdot \frac{\partial}{\partial \mathbf{x}^*} + \mathbf{F}_\alpha^{(e)*} \cdot \frac{\partial}{\partial \mathbf{c}_1{}^*}\right)\mathscr{F}_\alpha \\ &\qquad = -\theta\boldsymbol{\mu}_{\alpha 1}^* \times \hat{\mathbf{H}} \cdot \frac{\partial}{\partial \mathbf{L}_1{}^*}\,\mathscr{F}_\alpha(1) + \sum_\beta\,[\mathscr{F}_\alpha \mid \mathscr{F}_\beta]_1^* \end{aligned} \tag{A.3}$$

with $\epsilon = \lambda_f/l$,

$$\begin{aligned} [\phi_\alpha \mid \psi_\beta]_1^* = \frac{\bar{n}_\beta}{n}\left(1 + \frac{m_\alpha}{m_\beta}\right)^{1/2} \int \cdots \int d^2\hat{c}'\, d^3c_2{}^*\, d\mathscr{J}_2{}^*\, d\mathscr{J}_1'{}^*\, d\mathscr{J}_2'{}^*\, c_{21}^*\sigma_{\alpha\beta}^* \\ \times\,[\phi_\alpha(\bar{1}')\,\psi_\beta(\bar{2}') - \phi_\alpha(\bar{1})\,\psi_\beta(\bar{2})] \end{aligned} \tag{A.4}$$

and where $\mathbf{F}_\alpha^{(e)*} = l\mathbf{F}_\alpha^{(e)}/c_\alpha{}^2 \approx lm_\alpha\mathbf{F}_\alpha^{(e)}/k\bar{T}$ is the energy, in units of the thermal mean, which is required to displace a molecule through a distance l against the field of force $\mathbf{F}_\alpha^{(e)}$. We shall assume that $\mathbf{F}_\alpha^{(e)*}$ is of the order unity. Finally, $\theta = \omega_H/\omega_c$ is the ratio of the (proton) Larmor frequency, $\omega_H = eH/2m_pc$, to the collision frequency, $\omega_c = 1/\tau_{\mathrm{kin}}$.

With τ chosen equal to $\tau_{\mathrm{hy}} = l/c_\alpha$ we obtain in place of (A.3) the equations

$$\begin{aligned} &\epsilon\left(\partial_{t^*} + c_1{}^* \cdot \frac{\partial}{\partial \mathbf{x}^*} + \mathbf{F}_\alpha^{(e)*} \cdot \frac{\partial}{\partial \mathbf{c}_1{}^*}\right)\mathscr{F}_\alpha(1) \\ &\qquad = -\theta\boldsymbol{\mu}_{\alpha 1}^* \times \hat{\mathbf{H}} \cdot \frac{\partial}{\partial \mathbf{L}_1{}^*}\,\mathscr{F}_\alpha(1) + \sum_\beta\,[\mathscr{F}_\alpha \mid \mathscr{F}_\beta]_1^* \end{aligned} \tag{A.5}$$

In both cases it is reasonable to expand the dimensionless distribution functions in the perturbation series

$$\mathscr{F}_\alpha = \mathscr{F}_\alpha^{[0]} + \epsilon\mathscr{F}_\alpha^{[1]} + \epsilon^2\mathscr{F}_\alpha^{[2]} + \cdots$$

where the value of $\epsilon = \lambda_f/l$ can vary from as much as 10^{-3} to as little as 10^{-7} or even less.

The dimensional analysis serves to establish the relative magnitudes of the various terms which contribute to the Boltzmann equations. On the scale of time to which the equations (A.3) are appropriate, spatial variations of the singlet distribution functions can be ignored compared to variations with time. Consequently, in first approximation, the Boltzmann equations reduce to equations descriptive of the rate at which collisions are effective in establishing local Maxwell–Boltzmann distributions. Interactions with the magnetic field will contribute to this process only if $\theta = \omega_H/\omega_c$ is of the order of unity.

In contrast to these homogeneous relaxation phenomena, variations of the distribution functions recorded on the hydrodynamic scale of time $[t/\tau_{\text{hy}} = O(1)]$ are to be described in terms of the flows of energy, momentum, and mass which occur in response to imposed gradients of temperature, velocity, and concentration. The influence of the magnetic field will be significant only if it is so intense or if the gas pressure is so low that $\theta \equiv \omega_H/\omega_c = O(1)$.

Now that the relative magnitudes of the terms have been established we can dispense with the dimensionless quantities and write in place of (A.3) and (A.5)

$$\partial_t F_\alpha(1) + \epsilon \left(\mathbf{c}_1 \cdot \frac{\partial}{\partial \mathbf{x}} + \mathbf{F}_\alpha^{(e)} \cdot \frac{\partial}{\partial \mathbf{c}_1}\right) F_\alpha(1) = -\theta \bar{\boldsymbol{\mu}}_{\alpha 1} \times \mathbf{H} \cdot \frac{\partial}{\partial \mathbf{L}_1} F_\alpha(1) + \sum_\beta [F_\alpha \mid F_\beta]_1 \tag{A.3$'$}$$

and

$$\epsilon \left(\partial_t + \mathbf{c}_1 \cdot \frac{\partial}{\partial \mathbf{x}} + \mathbf{F}_\alpha^{(e)} \cdot \frac{\partial}{\partial \mathbf{c}_1}\right) F_\alpha(1) = -\theta \bar{\boldsymbol{\mu}}_{\alpha 1} \times \mathbf{H} \cdot \frac{\partial}{\partial \mathbf{L}_1} F_\alpha(1) + \sum_\beta [F_\alpha \mid F_\beta]_1 \tag{A.5$'$}$$

respectively. In these equations ϵ (and θ) serves simply as a "marker" which is to be set equal to unity after the perturbation expansion

$$F_\alpha = F_\alpha^{[0]} + \epsilon F_\alpha^{[1]} + \epsilon^2 F_\alpha^{[2]} + \cdots$$

has been used to order the successively smaller contributions to the distribution function. In what follows our concern will reside exclusively with the hydrodynamic scale of time and with the corresponding "normal solution" of the Boltzmann equation. It is consistent with Bogoliubov's hypothesis (and with all else we have stated in connection with this stage in the evolution of the system) to assume that during the hydrodynamic stage the time dependence of the functions F_α is governed exclusively by the time dependence of the temperature, fluid velocity, and species concentrations, and that the equations of motion of each of these variables ρ is expandable in a series $\partial_t \rho = \partial_0 \rho + \epsilon \partial_1 \rho + \epsilon^2 \partial_2 \rho + \cdots$. We later verify that the functions $\partial_k \rho$ are determined uniquely by the criteria that the equations for the functions $F_\alpha^{(k)}$ be soluble. The solution of the Boltzmann equation generated by this prescription is the normal solution of Chapman and Enskog.

It is readily verified that the functions $F_\alpha^{(0)}$ satisfy the set of nonlinear equations

$$0 = \sum_\beta [F_\alpha^{[0]} \mid F_\beta^{[0]}]_1 - \bar{\boldsymbol{\mu}}_{\alpha 1} \times \mathbf{H} \cdot \frac{\partial}{\partial \mathbf{L}_1} F_\alpha^{[0]}(1)$$

and that the solutions of these equations are the Maxwell–Boltzmann functions ${}^\circ F_\alpha$ of (27). If we then select the values of the coefficients $n_{\alpha 0}$, T_0, and $\mathbf{u}_0$ to coincide with those of the local concentrations, temperature, and fluid velocity, the distortions $F_\alpha^{(k)} \equiv {}^\circ F_\alpha \phi_\alpha^{(k)}$, $k > 0$, must satisfy the subsidiary conditions

$$\begin{gathered}\int d\bar{1}\, F_\alpha^{[k]}(\bar{1}) = 0, \qquad \sum_\alpha \int d\bar{1}\, F_\alpha^{[k]}(\bar{1})\, m_\alpha \mathbf{C}_1 = 0 \\ \sum_\alpha \int d\bar{1}\, F_\alpha^{[k]}(\bar{1})[\tfrac{1}{2} m_\alpha C_1^2 + \epsilon_\alpha(\mathscr{J}_1)] = 0\end{gathered} \tag{A.6}$$

and the sequence of linear, inhomogeneous, integrodifferential equations

$$\tilde{\partial}_0\, {}^\circ F_\alpha(\bar{1}) = -\hat{\Omega}_{\alpha 1}(\Phi^{[1]}) \tag{A.7}$$

$$\tilde{\partial}_0\, {}^\circ F_\alpha^{[1]}(\bar{1}) + \partial_1\, {}^\circ F_\alpha(\bar{1}) - \sum_\beta [F_\alpha^{[1]} \mid F_\beta^{[1]}]_1 = -\hat{\Omega}_{\alpha 1}(\Phi^{[2]}) \tag{A.8}$$

$$\vdots$$

with

$$\begin{gathered}\tilde{\partial}_0 = \partial_0 + \mathbf{c}_1 \cdot \frac{\partial}{\partial \mathbf{x}} + \mathbf{F}_\alpha^{(e)} \cdot \frac{\partial}{\partial \mathbf{c}_1} \\ \hat{\Omega}_{\alpha 1}(\Psi) \equiv \left\{ \bar{\boldsymbol{\mu}}_{\alpha 1} \times \mathbf{H} \cdot \frac{\partial}{\partial \mathbf{L}_1} \Psi \right\} {}^\circ F_\alpha(\bar{1}) + \sum_\beta n_\alpha n_\beta \hat{\Gamma}_1^{(\alpha\beta)}(\Psi)\end{gathered} \tag{A.9}$$

and where $\hat{\Gamma}^{(\alpha\beta)}$ is defined by Eq. (29) of the text.

In order for solutions to exist, the inhomogeneous portions (left-hand members) of these equations must be orthogonal to all solutions of the associated homogeneous adjoint equations, $\hat{\Omega}_{\alpha 1}^{\dagger}(\chi) = 0$. Since the latter consists of 1, $m_\alpha \mathbf{c}_1$, and $\frac{1}{2} m_\alpha C_1^2 + \epsilon_\alpha(1)$, (A.7) will be soluble if and only if

$$\int d\bar{1}\, [\tilde{\partial}_0\, {}^\circ F_\alpha(\bar{1})] = 0$$

and

$$\sum_\alpha \int d\bar{1}\, m_\alpha \mathbf{C}_1 [\tilde{\partial}_0\, {}^\circ F_\alpha(\bar{1})] = \sum_\alpha \int d\bar{1}\, [\tfrac{1}{2} m_\alpha C_1^2 + \epsilon_\alpha(1)][\tilde{\partial}_0\, {}^\circ F_\alpha(\bar{1})] = 0$$

These conditions determine $\partial_0 T$, $\partial_0 n_\alpha$, and $\partial_0 \mathbf{u}$ uniquely and permit us to express $\tilde{\partial}_0\, {}^\circ F_\alpha$ in the explicit form

$$\begin{aligned}{}^\circ F_\alpha(\bar{1}) \Big[&\frac{n}{n_\alpha} \left(\frac{2kT}{m_\alpha} \right)^{1/2} \mathbf{W}_1 \cdot \mathbf{d}_\alpha + \left(\frac{2kT}{m_\alpha} \right)^{1/2} \mathbf{W}_1 \{ W_1^2 + \epsilon_\alpha^*(1) - \tfrac{5}{2} - \bar{\epsilon}_\alpha^* \} \cdot \nabla(\ln T) \\ &+ \left\{ 2\mathbf{W}_1 \mathbf{W}_1 - \boldsymbol{\delta} \left(\frac{p}{Tc_v} [W_1^2 + \epsilon_\alpha^*(1) - \tfrac{3}{2} - \bar{\epsilon}_\alpha^*] + 1 \right) \right\} : \nabla \mathbf{u} \Big]\end{aligned} \tag{A.10}$$

where $\mathbf{W}_1 = (m_\alpha/2kT)^{1/2}\,\mathbf{C}_1$, $\epsilon_\alpha{}^*(1) = \epsilon_\alpha(1)/kT$, and $c_V = \frac{3}{2}nk + \sum_\beta n_\beta \hat{c}_\beta$. Finally, $\bar{\epsilon}_\alpha{}^* = \bar{\epsilon}_\alpha/kT$ and $\hat{c}_\alpha \equiv d\bar{\epsilon}_\alpha/dT$ are defined in terms of the mean internal energies, $\bar{\epsilon}_\alpha(T) = Z_\alpha^{-1}\int d\mathscr{J}\,\epsilon_\alpha(\mathscr{J})\exp[-\epsilon_\alpha(\mathscr{J})/kT]$, and

$$\mathbf{d}_\alpha = \nabla x_\alpha + (x_\alpha - w_\alpha)\,\nabla \ln p - p^{-1}w_\alpha\left(\rho\mathbf{F}_\alpha^{(e)} - \sum_\beta \rho_\beta \mathbf{F}_\beta^{(e)}\right)$$

with $x_\alpha = n_\alpha/n$, $w_\alpha = \rho_\alpha/\rho$, and $p = nkT$.

Similar considerations apply to the functions $\partial_k T$, $\partial_k n_\alpha$, $\partial_k \mathbf{u}$ for $k > 0$ and so to the construction of the inhomogeneous portions of the equations for the higher-order distortions $\Phi_\alpha^{[k]}$.

Since $\hat{\Omega}$ is linear, the functions $\Phi_\alpha^{[1]}$ must be of the form

$$\Phi_\alpha^{[1]}(\bar{1}) = -(2kT)^{1/2}\,\mathbf{A}_\alpha \cdot \frac{\nabla T}{T} - \mathsf{B}_\alpha : \overset{\circ}{\overline{\overline{\nabla \mathbf{u}}}} - D_\alpha \nabla \cdot \mathbf{u} + n \sum_\beta \mathbf{C}_\alpha^{(\beta)} \cdot \mathbf{d}_\beta \quad \text{(A.11)}$$

where B_α is a symmetric and traceless second-rank tensor and where $\mathbf{A}_\alpha$, B_α, $\mathbf{C}_\alpha^{(\beta)}$, and D_α depend upon the dynamical variables $\mathbf{W}$ and $\mathscr{J}$ of a molecule of the species α. It can be verified that these functions satisfy the equations

$$m_\alpha^{-1/2}\ {}^\circ F_\alpha(1)[\mathbf{W}_1(\mathbf{W}_1{}^2 + \epsilon_\alpha{}^*(\bar{1}) - \tfrac{5}{2} - \bar{\epsilon}_\alpha{}^*)] = \hat{\Omega}_{\alpha 1}(\mathbf{A}) \quad \text{(A.12)}$$

$${}^\circ F_\alpha(\bar{1})[\overset{\circ}{\overline{\overline{2\mathbf{W}_1\mathbf{W}_1}}}] = \hat{\Omega}_{\alpha 1}(\mathsf{B}) \quad \text{(A.13)}$$

$${}^\circ F_\alpha(\bar{1})\{\tfrac{2}{3}(1+\chi)^{-1}\,\chi(W_1{}^2 - \tfrac{3}{2}) - [\epsilon_\alpha{}^*(1) - \bar{\epsilon}_\alpha{}^*]\} = \hat{\Omega}_{\alpha 1}(D) \quad \text{(A.14)}$$

$${}^\circ F_\alpha(\bar{1})[n_\alpha^{-1}(2kT/m_\alpha)^{1/2}\,\mathbf{W}_1(\delta_{\alpha\lambda} - \delta_{\alpha\kappa})] = \hat{\Omega}_{\alpha 1}(\mathbf{C}^{(\kappa)} - \mathbf{C}^{(\lambda)}) \quad \text{(A.15)}$$

with $\chi = \sum n_\beta \hat{c}_\beta/(3nk/2)$.

In the absence of the magnetic field the solutions of these equations are related to the coefficients of diffusion, thermal diffusion, thermal conductivity, and shear and bulk viscosity by formulas given in Appendix E of the paper by Condiff *et al.*(8a) The modifications arising from the influence of the magnetic field have been discussed elsewhere.(9,23)

Throughout much of this paper the external field dependence of the collision matrices and cross sections have been ignored, either implicitly or explicitly. Among the consequences of the applied field $\mathbf{F}$ are the dipolar energy shifts, $\epsilon_\alpha \to \epsilon_\alpha - \bar{\boldsymbol{\mu}}_\alpha \cdot \mathbf{F}$, and the corresponding replacement of the factor $\delta(E - E')$, which occurs in $w_{\alpha\beta}$, with $\delta\{(E - E') - [\bar{\boldsymbol{\mu}}_\alpha(1) + \bar{\boldsymbol{\mu}}_\beta(2) - \bar{\boldsymbol{\mu}}_\alpha(1') - \bar{\boldsymbol{\mu}}_\beta(2')] \cdot \mathbf{F}\}$. Furthermore, the differential cross sections may themselves depend explicitly upon the strength of the external field. To first approximation the field alters the transition rates by an amount proportional to $\boldsymbol{\mu} \cdot \mathbf{F}/kT$. In most cases this affects the values of the transport coefficients far less than do the field-dependent "streaming terms" occuring on the left-hand side of the Boltzmann equation. (This is principally a consequence of the fact that $t_f \gg t_c$.) The earlier parts of this appendix are based upon the implicit assumption that this is the case.

There are, however, situations where it is important to take the level shifts into account, at least partially. For example, in the theory of spin relaxation and diffusion one is interested in the displacement of the magnetization from its equilibrium value, but is not concerned with field dependence of the diffusion coefficient or spin relaxation times. Under circumstances such as these it is convenient to express the distribution function in the manner $F_\alpha = {}^\circ F_\alpha{}^{\mathbf{F}}(1 + \phi_\alpha)$, where ${}^\circ F_\alpha{}^{\mathbf{F}} \sim \exp[-\beta(\frac{1}{2}m_\alpha C^2 + \epsilon_\alpha - \bar{\boldsymbol{\mu}}_\alpha \cdot \mathbf{F})]$ is the local Maxwell–Boltzmann distribution appropriate to a system immersed in a static field **F**. The integrand of the Boltzmann collision term then can be written

$$\begin{aligned} &w_{\alpha\beta}^{\mathbf{F}}[F_\alpha(\bar{1}')\, F_\beta(\bar{2}') - F_\alpha(\bar{1})\, F_\beta(\bar{2})] \\ &\quad = w_{\alpha\beta}^{F}[{}^\circ F_\alpha{}^{\mathbf{F}}(\bar{1}')\, {}^\circ F_\beta{}^{\mathbf{F}}(2') - {}^\circ F_\alpha{}^{\mathbf{F}}(\bar{1})\, {}^\circ F_\beta{}^{\mathbf{F}}(\bar{2})] \\ &\qquad + w_{\alpha\beta}^{\mathbf{F}}\, {}^\circ F_\alpha{}^{\mathbf{F}}(\bar{1})\, {}^\circ F_\beta{}^{\mathbf{F}}(\bar{2})[\phi_\alpha(\bar{1}') + \phi_\beta(\bar{2}') - \phi_\alpha(\bar{1}) - \phi_\beta(\bar{2})] + O(\phi^2) \end{aligned}$$

with $w_{\alpha\beta}^{\mathbf{F}} = w_{\alpha\beta}^{\mathbf{F}}(\bar{1}\bar{2} \mid \bar{1}'\bar{2}')$. The first term is zero. The second is first order in the deviations from equilibrium. If our interest is confined to deviations which are of first order *either* in **F** or gradients of the macroscopic fields, that is, if we choose to ignore first- and higher-order field contributions to the dissipative coefficients, then we can replace $w_{\alpha\beta}^{\mathbf{F}}$ with $w_{\alpha\beta} \equiv (w_{\alpha\beta}^{\mathbf{F}})_{\mathbf{F}=\mathbf{0}}$ and ${}^\circ F_\alpha{}^{\mathbf{F}}$ with ${}^\circ F_\alpha \equiv ({}^\circ F_\alpha{}^{\mathbf{F}})_{\mathbf{F}=\mathbf{0}}$. Thus, a first-order theory of this sort can be based upon the expression $F_\alpha = {}^\circ F_\alpha{}^{\mathbf{F}}(1 + \phi_\alpha)$ and the approximation

$$w_{\alpha\beta}^{\mathbf{F}}[F_\alpha(\bar{1}')\, F_\beta(\bar{2}') - F_\alpha(\bar{1})\, F_\beta(\bar{2})] \approx w_{\alpha\beta}\, {}^\circ F_\alpha(\bar{1})\, {}^\circ F_\beta(\bar{2})[\phi_\alpha(\bar{1}') + \phi_\beta(\bar{2}') - \phi_\alpha(\bar{1}) - \phi_\beta(\bar{2})] \tag{A.16}$$

The application of this approximation to spin and thermal relaxation will be presented elsewhere.

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