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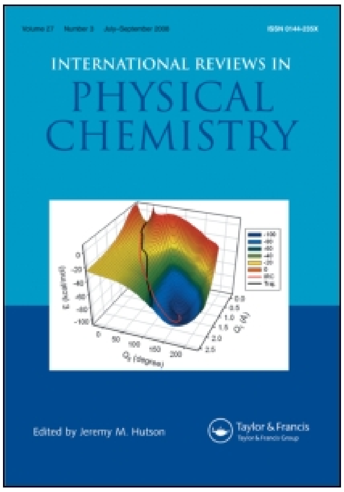

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Relaxation and transport of molecular systems in the gas phase

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Some of the properties of gas phase relaxation and transport are reviewed with an emphasis on those properties that are due entirely to the presence of internal states in real molecular systems. The theoretical formulations of such non-equilibrium effects is based on the quantum Boltzmann equation. The conditions for the validity and the properties of this equation are reviewed. This includes a general discussion of how the combination of free molecule motion and collisions is required for the approach to global equilibrium. It is shown how the free motion is equivalent to a phase randomization of the elements of the density operator that are off-diagonal in energy. Spin relaxation and the magnetic field dependence (Senftleben-Beenakker effects) of the viscosity for a gas of diatomics are used to illustrate these aspects of the approach to equilibrium.

1. Introduction

The description of the time dependence of a dilute gas is based on the Boltzmann equation [1]. Essentially the molecules of a dilute gas move freely most of the time, but every once in a while, two molecules meet in a binary collision. Since the molecules are almost always free, the bulk properties are well described by the average properties of a typical molecule. The classic work of Boltzmann considered only structureless (point) particles so this description was accomplished by a distribution function of position $\mathbf{r}$ and momentum $\mathbf{p}$, which varies with time as the gas evolves. It is this time variation that the Boltzmann equation describes by taking into account the two effects of free motion and binary collisions. Real molecules have internal states that need to be described by quantum mechanics so that a density operator is needed rather than a simple distribution function of $\mathbf{r}$ and $\mathbf{p}$, with an associated quantum form of the Boltzmann equation to describe the time variation of the density operator, again involving free motion and binary collisions. It is this quantum generalization of the Boltzmann equation and its application to a variety of chemical effects in relaxation and transport that is addressed in this paper. At normal temperatures it is usually unnecessary to worry about the quantum degeneracy effects associated with Fermi–Dirac and Bose–Einstein statistics, so these are ignored, the discussion being limited to Boltzmann statistics. This does not of course disallow the need for such symmetry considerations when determining the (intramolecular) internal states of a molecule, it only ignores intermolecular symmetry effects.

At higher densities, more than two molecules can be interacting so the Boltzmann equation has to be generalized in order to account for three and more particle collisions. There also arises the question whether the molecules are ever really 'free' or whether their motion between collisions should be modified to account for the (continuous but weak) interaction with other molecules in the gas. These questions are not addressed in this paper. The form of the classical dilute gas Boltzmann equation is well accepted in the literature, though there are differences of opinion about how, or even whether, it can be derived in a rigorous manner. For its quantum generalization, there has also been some argument about its detailed form. While these differing points of view are mentioned in this presentation, the author's bias of interpretation will predominate. In the subsequent presentation of the 'derivation' of the Boltzmann equation, the words 'derive' are always enclosed in quotes, to indicate this lack of rigour.

The relation between the exact evolution of the density operator (classical distribution function) as a rigorous consequence of the Schrödinger equation (Newton's equations), and the evolution predicted by the Boltzmann equation has a long history of conflicting opinion, in part responsible for Boltzmann's suicide. In particular, the Boltzmann equation describes an approach to equilibrium whereas the Schrödinger equation does not. Some discussion of this reversibility–irreversibility paradox is given, again with a bias for the author's point of view.

The paper begins with a short section on important aspects of notation and a review of the exact evolution of an N-molecule system with its constancy of the N-molecule entropy. Section 3 is devoted to the Boltzmann equation, starting with a subsection covering the concepts and approximations involved in its 'derivation'. While this involves formal manipulations, expressing the results in a matrix representation so that quantum calculations can be performed becomes nontrivial. Subsection 3.2 describes the detailed properties of the quantum Boltzmann collision term, specifically of the transition superoperator. This is fairly technical since it is necessary to carefully treat the energy differences (frequencies) between the different quantum states that enter before and after a collision. In many applications, the resulting expression simplifies significantly. Subsection 3.3 describes the simplest case, where the 1-molecule density operator is diagonal in the energy basis and the gas is in local thermal equilibrium, to connect to the set of kinetic equations describing the chemical kinetics of a set of bimolecular reactions. Generalization to include the analogue of thermal non-equilibrium and flow and/or diffusion phenomena (while retaining the requirements that the density operator be diagonal in energy and that the collisions are local) is the Wang-Chang–Uhlenbeck equation [2]. Aspects of the approach to equilibrium are discussed in subsection 3.4, emphasizing two limiting cases. For the Wang-Chang–Uhlenbeck case, Boltzmann's H-theorem shows how the local entropy increases until local thermodynamic equilibrium is reached, equivalently that the distribution is Boltzmann. But global equilibrium still requires an interplay between the motion of the molecules between collisions and the collision processes themselves. The second limiting case involves the approach to equilibrium of a density operator that is initially off-diagonal in energy. In this case the H-theorem has not been shown to be valid. It is shown how phase randomization can make the density operator diagonal in an energy representation so that the H-theorem becomes valid. This approach to equilibrium due to a combination of phase randomization and collisional motion is identical in principle to the combination of free flow and collisions responsible for the approach to equilibrium in an inhomogeneous gas. Subsection 3.4 ends with a short subsection contrasting the 1-molecule and N-molecule entropies.

To exemplify the utility of the quantum Boltzmann equation, two applications are reviewed in fair detail. Section 4 describes the relaxation of a spin where an intramolecular mechanism is dominant. While the spin–lattice and spin–spin relaxation times are usually emphasized, the kinetic approach also describes how the various spins evolve with time in their coupled motion. In this the density operator is off-diagonal in Zeeman energy so a quantum Boltzmann equation is required for the formulation of the spin kinetics. Section 5 describes the relation of the Boltzmann equation to the equations of hydrodynamics and treats the magnetic field dependence of the viscosity coefficients with certain simplifying approximations that have been used for an interpretation of experiment. In both applications it is the partial phase randomization of the Zeeman energies that are responsible for the detailed experimental observations of the dependence on the magnetic field. A short discussion section mentions some of the other applications of the quantum Boltzmann equation.

2. Notation and the exact *N*-molecule evolution

The whole gas is assumed to consist of N molecules in a volume W. As a mechanical system, the gas has energy eigenstates determined by its hamiltonian $H^{(N)}$, and any wavefunction Ψ of the system will evolve according to the Schrödinger equation

$$\mathrm{i}\hbar \frac{\partial \Psi}{\partial t} = H^{(N)} \Psi. \tag{1}$$

But the state of the gas can not be described by a single wavefunction, but rather by a density operator $\rho^{(N)}$ whose evolution is governed by the von Neumann [3], or quantum Liouville, equation

$$\begin{aligned} \mathrm{i}\hbar \frac{\partial \rho^{(N)}}{\partial t} &= [H^{(N)}, \rho^{(N)}]_- \\ &\equiv \hbar \mathscr{L}^{(N)} \rho^{(N)} = H^{(N)} \rho^{(N)} - \rho^{(N)} H^{(N)}. \end{aligned} \tag{2}$$

The notion of a superoperator as a linear transformation of operators, whose notation was introduced by Crawford [4], is an important concept for the efficient description of macroscopic kinetic phenomena. The first example of this kind of quantity is the Liouville superoperator $\mathscr{L}^{(N)}$ as the 'commutator of $H^{(N)}$ with'. In thermal equilibrium, the density operator is the time independent Boltzmann distribution

$$\rho^{(N)} = \frac{\exp(-H^{(N)}/k_\mathrm{B} T)}{N! Q_N} = \sum_j |j\rangle \frac{\exp(-E_j/k_\mathrm{B} T)}{N! Q_N} \langle j|, \tag{3}$$

involving the energy eigenstates $|j\rangle$ and eigenvalues E_j of $H^{(N)}$,

$$H^{(N)}|j\rangle = E_j|j\rangle, \tag{4}$$

and the canonical partition function $Q_N = \mathrm{Tr}_{1\ldots N} \exp(-H^{(N)}/k_\mathrm{B}T)/N!$.

The expectation value for an N molecule physical observable $A^{(N)}$ is determined as the trace $\mathrm{Tr}_{1\ldots N}$ over the states of the N molecules,

$$\langle A \rangle = \mathrm{Tr}_{1\ldots N} A^{(N)} \rho^{(N)}, \tag{5}$$

whose time dependence follows from the von Neumman equation,

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle A \rangle = \frac{-\mathrm{i}}{\hbar} \mathrm{Tr}_{1\ldots N} A^{(N)} [H^{(N)}, \rho^{(N)}]_- . \tag{6}$$

The identity operator $1^{(N)}$ is a particularly important observable, which determines the normalization of $\rho^{(N)}$, in particular

$$\mathrm{Tr}_{1\ldots N} 1^{(N)} \rho^{(N)} = 1. \tag{7}$$

A different kind of quantity of importance for macroscopic behaviour is the entropy

$$S^{(N)} = - k_\mathrm{B} \mathrm{Tr}_{1\ldots N} \rho^{(N)} \ln(N! \rho^{(N)}). \tag{8}$$

It is an important aspect of mechanical motion that this entropy does not change with time,

$$\begin{aligned}\frac{\mathrm{d}S^{(N)}}{\mathrm{d}t} &= - k_{\mathrm{B}} \mathrm{Tr}_{1\ldots N} \frac{\partial \rho^{(N)} \ln (N! \rho^{(N)})}{\partial t} \\ &= - \frac{k_{\mathrm{B}}}{i\hbar} \mathrm{Tr}_{1\ldots N} [\ln (N! \rho^{(N)}) + 1] [H^{(N)}, \rho^{(N)}]_{-} \\ &= - \frac{k_{\mathrm{B}}}{\mathrm{i}\hbar} \mathrm{Tr}_{1\ldots N} [H^{(N)}, \rho^{(N)} \ln (N! \rho^{(N)}) + \rho^{(N)}]_{-} = 0. \end{aligned} \tag{9}$$

For most chemical systems, the hamiltonian is well approximated as a sum of 1-particle (kinetic) and pair–particle (potential) terms,

$$H^{(N)} = \sum_{j} K_j + \sum_{j< l} V_{jl}. \tag{10}$$

For a structureless molecule, K_1 is just the translational kinetic energy $\mathbf{p}_1^2/m$, but for real molecules this can include the rotation, vibration and electronic hamiltonians. It can also include the Zeeman hamiltonian describing how the spins are affected by an external magnetic field. The intermolecular potential V_{12} is in general anisotropic and responsible for chemical reactions. For the evolution of density operators, each of these terms in the hamiltonian has a corresponding superoperator, namely

$$\begin{aligned} \mathscr{K}_j A &\equiv \hbar^{-1} [K_j, A]_{-} \\ \mathscr{V}_{jl} A &\equiv \hbar^{-1} [V_{jl}, A]_{-}. \end{aligned} \tag{11}$$

In a dilute gas, the physical observables are only 1-particle observables, typically $A^{(N)} = \Sigma_j A_j$, and only the 1-molecule reduced density operator

$$\rho_1^{(1)} \equiv N \mathrm{Tr}_{2\ldots N} \rho^{(N)} \tag{12}$$

is needed in order to follow the behaviour of A, since

$$\langle A \rangle = \sum_j \mathrm{Tr}_{1\ldots N} A_j \rho^{(N)} = \mathrm{Tr}_1 A_1 \rho_1^{(1)}. \tag{13}$$

It follows that it is the evolution of the simpler quantity $\rho_1^{(1)}$, in contrast to $\rho^{(N)}$, that is needed for the description of the time dependence of such physical observables. From the von Neumann equation, this evolution is determined by

$$\mathrm{i} \frac{\partial \rho_1^{(1)}}{\partial t} = K_1^{(1)} \rho_1^{(1)} + \mathrm{Tr}_2 \mathscr{V}_{12} \rho_{12}^{(2)}. \tag{14}$$

Here $\rho_{12}^{(2)}$ is the pair density operator, the second in the hierarchy of density operators

$$\rho_{1\ldots n}^{(n)} \equiv N(N-1)\ldots(N-n+1) \mathrm{Tr}_{n+1\ldots N} \rho^{(N)}. \tag{15}$$

Equation (14) is just the first member of the quantum form of the BBGKY hierarchy, whose nth member is

$$\mathrm{i} \frac{\partial \rho_{1\ldots n}^{(n)}}{\partial t} = \mathscr{L}_{1\ldots n}^{(n)} \rho_{1\ldots n}^{(n)} + \mathrm{Tr}_{n+1} \mathscr{V}_{1\ldots n+1}^{(n+1)}, \rho_{1\ldots n}^{(n+1)}. \tag{16}$$

This is named after its many discoveries: Bogoliubov [5], Born and Green [6], Kirkwood [7] and Yvon [8]. These equations depend on reduced density operators of higher and higher order, so can not be solved by themselves. Thus they are in that sense, just a formalism, but these equations serve as a structure for making approximations for finding a closed equation for the evolution of $\rho_1^{(1)}$. Such an approximation is the Boltzmann equation.

3. Boltzmann equation

3.1. '*Derivation*'

In a dilute gas, the molecules move independently most of the time and undergo binary collisions every once in a while. For this picture to be valid, the intermolecular potential must be short ranged. This implies that charged particles with their long-ranged coulomb interaction must be treated in a different manner, and will not be treated in this presentation. The motion of a typical molecule is described exactly by the first BBGKY equation (14). Clearly the independent (free) motion is described by the $\mathscr{H}_1$ term, so that collisions are associated with the trace term. But to get an equation that can be solved, it is necessary to approximate the trace term in such a way that it can be evaluated entirely in terms of the singlet density operator $\rho_1^{(1)}$. This is the essence of the Boltzmann equation.

The trace term in equation (14) involves the interaction V_{12} between two particles. The particles get into such an interaction by coming together from being freely moving in an independent manner before the interaction (collision) plays a significant role. Thus, if one takes the pair of particles back in time to when the particles are non-interacting, the pair density operator should factor into a product of singlets. Formally this is

$$\lim_{t\to-\infty} \rho_{(12)}^{(2)}(t) \to \rho_1^{(1)}(t)\,\rho_2^{(1)}(t). \tag{17}$$

Immediately there are a number of conceptual questions that arise. An obvious first comment is that the factorization has been done in the past rather than the future. This bias reflects our perception of nature, namely the world evolves from the past to the future, so this choice of past times amounts to inserting an 'arrow of time' into the evolution of the mechanical system. There has been a great deal of discussion of this point, a classic being the Ehrenfests' article [9] in 1912. Translations of this with their respective commentary are by T. Ehrenfest [10] and in Appendix 1 of ter Haar's book [11]. An explicit elaboration of taking the opposite time limit has been given by Cohen and Berlin [12].

A more subtle aspect is the exact scale of time for the limit. As motivated by the discussion, the factorization is to occur before the collision begins. Thus the time-scale is at most of the order of nanoseconds for a typical gas under standard conditions of room temperature and atmospheric pressure, namely a time large compared to the typical time of duration of a collision τ_c and short to a typical mean free time between collisions, τ_f. This means that from the time of interaction, the factorization time is to be only of the order of nanoseconds in the past. There seems to be disagreement in the literature on this point, and often an exact mathematical limit (that is, to a real time limit of $-\infty$ rather than to a limit of $\approx -\tau_f$) seems to have been interpreted. But for obtaining a closed equation for $\rho^{(1)}(t)$, it is necessary to relate the pair density operator $\rho^{(2)}(t)$ at time t to the singlet *at the same time*. This has been accomplished by contrasting the (binary) collision motion with non-interacting motion, thus, for a time t in the midst of a collision.

$$\left.\begin{aligned}\rho^{(2)}(t) &= \exp[-\mathrm{i}\mathscr{L}_{12}^{(2)}(t-t_0)]\,\rho^{(2)}(t_0) = \exp[-\mathrm{i}\mathscr{L}_{12}^{(2)}(t-t_0)]\,\rho_1^{(1)}(t_0)\,\rho_2^{(1)}(t_0)\\ &= \exp[-\mathrm{i}\mathscr{L}_{12}^{(2)}(t-t_0)]\exp[-\mathrm{i}(\mathscr{K}_1^{(1)}+\mathscr{K}_2^{(1)})(t_0-t)]\,\rho_1^{(1)}(t)\,\rho_2^{(1)}(t),\end{aligned}\right\} \tag{18}$$

with now the limit $t - t_0 \gg \tau_c$ taken so that it is infinite on the collision time scale. The limit of the combination of evolution superoperators is the Møller superoperator,

$$\Omega_{\mathscr{L}} \equiv \lim_{t\to\infty} \exp(-\mathrm{i}\mathscr{L}^{(2)}_{12}\, t)\exp(\mathrm{i}\mathscr{K}^{(2)}_{12}\, t), \tag{19}$$

whose mathematically rigorous definition has been given by Jauch *et al.* [13]. Inserting this result into the first BBGKY equation (14) gives the quantum Boltzmann equation

$$\mathrm{i}\frac{\partial \rho^{(1)}_1(t)}{\partial t} = \mathscr{K}^{(1)}_1 \rho^{(1)}_1(t) + \mathrm{Tr}_2 \mathscr{V}_{12}\, \Omega_{\mathscr{L}12}\, \rho^{(1)}_1(t)\, \rho^{(1)}_2(t). \tag{20}$$

Again several comments need to be made. (i) The above assumes only *binary* collisions, namely that the possible interaction with other molecules besides the colliding pair can be ignored during a collision. That is the reason for being able to use the pair evolution superoperator $\exp[-\mathrm{i}\mathscr{L}^{(2)}(t - t_0)]$. (ii) The contrasting evolutions of pair collision versus free motion essentially acts to correct the free motion of a pair into collisional motion. There is also the contrast between the finite time for the factorization before a collision occurs and the infinite time difference required for the formal existence of the Møller superoperator. (iii) This combination of approximations is generally known as Boltzmann's 'Stosszahlansatz'. (iv) There is no rigour in the above 'derivation'. The arguments presented above are the same as I used [14] in 1960 and I consider that they follow the same philosophy of approach as Boltzmann [1] used in his derivation of the classical Boltzmann equation. Waldmann [15, 16] obtained a related result by looking at the changes occurring to a physical observable due to collisions. Yvon [17] related the pair density operator to a product of the singlets, but did not pursue the result to get a Boltzmann equation. There have been a number of 're-derivations' of this equation and some arguments about its form and validity. (v) Before the work of Waldmann and myself, the only quantum form for the Boltzmann equation for handling internal states was the Wang-Chang–Uhlenbeck equation [2], which consists of a set of coupled equations, one for each molecular energy state. What that missed and equation (20) contains, is the allowance of superpositions of molecular energy states, which requires the full density operator for its treatment, rather than just having a set of probabilities. The essential difference between the work of Waldmann and myself, besides the detailed method of derivation, was as to how far one takes these superpositions into account. In both of these 'derivations', the aim was only to include degenerate states, whereas it was only later [18] that the full role of superposition was realized and put into perspective. It is not clear as to how much agreement there is in the literature on the validity of this latter perspective. Some of the interpretations discussed later depend on this general perspective of the role of superpositions.

An alternative 'deviation' of the Boltzmann equation has been presented by Boercker and Dufty [19]. This involves a factorization assumption at the three particle level rather than at the two particle level discussed above. Their factorization depends on the form of the interaction term of the second BBGKY equation. Specifically, the trace over the third particle is approximated as

$$\mathrm{Tr}_3[\mathscr{V}_{13} + \mathscr{V}_{23}]\,\rho^{(3)}_{123} \approx \mathrm{Tr}_3\left[\mathscr{V}_{13}\,\rho^{(2)}_{13}\,\rho^{(1)}_2 + \mathscr{V}_{23}\,\rho^{(2)}_{23}\,\rho^{(1)}_1\right]. \tag{21}$$

The rationale for this factorization is presumably that, if molecules 1 and 3 are interacting, via $\mathscr{V}_{13}$, then the states of these two particles are dependent upon one another while, if only binary collisions are to occur, particle 2 must be independent of the colliding pair. A similar argument applies to the term involving $\mathscr{V}_{23}$. The trace over particle 3 now involves exactly the combination of terms that appears in the right hand side of the first BBGKY equation (14). Thus the trace over particle 3 can be eliminated on the right hand side of equation (21) to give

$$\begin{aligned}\mathrm{Tr}_3[\mathscr{V}_{13}+\mathscr{V}_{23}]\,\rho_{123}^{(3)}(t) &\approx \left[\mathrm{i}\frac{\partial \rho_1^{(1)}(t)}{\partial t}-\mathscr{K}_1^{(1)}\rho_1^{(1)}(t)\right]\rho_2^{(1)}(t)+\left[\mathrm{i}\frac{\partial \rho_2^{(1)}(t)}{\partial t}-\mathscr{K}_2^{(1)}\rho_2^{(1)}(t)\right]\rho_1^{(1)}(t)\\ &= \mathrm{i}\frac{\partial \rho_1^{(1)}(t)\,\rho_2^{(1)}(t)}{\partial t}-\mathscr{K}_{12}^{(2)}\rho_1^{(1)}(t)\,\rho_2^{(1)}(t)\\ &= \mathrm{i}\exp(-\mathrm{i}\mathscr{K}_{12}^{(2)}t)\frac{\partial}{\partial t}[\exp(\mathrm{i}\mathscr{K}_{12}^{(2)}t)\,\rho_1^{(1)}(t)\,\rho_2^{(1)}(t)] \qquad (22)\end{aligned}$$

an expression involving only the singlet density operator and thus allowing a closure of the BBGKY hierarchy. A formal time integral of the second BBGKY equation (16), with the above binary collision approximation for its trace term and some simplification, including an integration by parts,

$$\begin{aligned}\rho_{12}^{(2)}(t) &= \exp(-\mathrm{i}\mathscr{L}_{12}^{(2)}s)\,\rho_{12}^{(2)}(t-s)-\mathrm{i}\mathrm{Tr}_3\int_{t-s}^{t}\mathrm{d}t'\exp(-\mathrm{i}\mathscr{L}_{12}^{(2)}(t-t'))[\mathscr{V}_{13}+\mathscr{V}_{23}]\,\rho_{123}^{(3)}(t')\\ &\approx \exp(-\mathrm{i}\mathscr{L}_{12}^{(2)}s)\,\rho_{12}^{(2)}(t-s)+\int_{t-s}^{t}\mathrm{d}t'\exp(-\mathrm{i}\mathscr{L}_{12}^{(2)}(t-t'))\\ &\quad\times\exp(-\mathrm{i}\mathscr{K}_{12}^{(2)}t')\frac{\partial}{\partial t'}[\exp(\mathrm{i}\mathscr{K}_{12}^{(2)}t')\,\rho_1^{(1)}(t)\,\varepsilon_2^{(1)}(t')]\\ &= \rho_1^{(1)}(t)\,\rho_2^{(1)}(t)+\exp(-\mathrm{i}\mathscr{L}_{12}^{(2)}s)\,[\rho_{12}^{(2)}(t-s)-\rho_1^{(1)}(t-s)\,\rho_2^{(1)}(t-s)]\\ &\quad-\int_{t-s}^{t}\mathrm{d}t'\frac{\partial}{\partial t'}[\exp(-\mathscr{L}_{12}^{(2)}(t-t'))\exp(-\mathrm{i}\mathscr{K}_{12}^{(2)}(t'-t))]\\ &\quad\times\exp(\mathrm{i}\mathscr{K}_{12}^{(2)}(t'-t))\,\rho_1^{(1)}(t')\,\rho_2^{(1)}(t'), \qquad (23)\end{aligned}$$

relates the pair density operator at time t to the singlet density operator at earlier times t'. Insertion of this result into the first BBGKY equation (14) and making three further approximations gives the Boltzmann equation. This starts with the result of insertion

$$\begin{aligned}\mathrm{i}\frac{\partial \rho_1^{(1)}(t)}{\partial t} &= \mathscr{K}_1^{(1)}\rho_1^{(1)}(t)+\mathrm{Tr}_2\,\mathscr{V}_{12}\exp(-\mathrm{i}\mathscr{L}_{12}^{(2)}s)\,[\rho_{12}^{(2)}(t-s)-\rho_1^{(1)}(t-s)\,\rho_2^{(1)}(t-s)]\\ &\quad+\mathrm{Tr}_2\,\mathscr{V}_{12}\,\rho_1^{(1)}(t)\,\rho_2^{(1)}(t)\\ &\quad-\mathrm{Tr}_2\,\mathscr{V}_{12}\int_{t-s}^{t}\frac{\partial}{\partial t'}[\exp(-\mathrm{i}\mathscr{L}_{12}^{(2)}(t-t'))\exp(-\mathrm{i}\mathscr{K}_{12}^{(2)}(t'-t))]\\ &\quad\times\exp(\mathrm{i}\mathscr{K}_{12}^{(2)}(t'-t))\,\rho_1^{(1)}(t')\,\rho_2^{(1)}(t'). \qquad (24)\end{aligned}$$

The first approximation involves eliminating the first trace term : since the particles are interacting, via $\mathscr{V}_{12}$ at time t, then at time $t-s$, the particles are independent, so that $\rho_{12}^{(2)}$ should factor at this time and the different term vanish. Secondly, over most of the integration range, t' corresponds to a time before the collision between particles 1 and 2 has begun. This allows the 'time-shift' approximation

$$\exp(\mathrm{i}\mathscr{K}_{12}^{(2)}(t'-t))\,\rho_1^{(1)}(t')\,\rho_2^{(1)}(t') \approx \rho_1^{(1)}(t)\,\rho_2^{(1)}(t) \qquad (25)$$

to be made. Essentially this assumes that the two particles are evolving freely at this pre-collision time. As a result, the integration over t' can be explicitly carried out, with the result

$$\mathrm{i}\frac{\partial \rho_1^{(1)}(t)}{\partial t} = \mathscr{H}_1^{(1)}\rho_1^{(1)}(t) + \mathrm{Tr}_2\,\mathscr{V}_{12}\exp(-\mathrm{i}\mathscr{L}_{12}^{(2)}s)\exp(\mathrm{i}\mathscr{H}_{12}^{(2)}s)\,\rho_1^{(1)}(t)\,\rho_2^{(1)}(t). \qquad (26)$$

The last approximation is to recognize that for $s \to \infty$, the combination of evolution operators is the Møller superoperator $\Omega_{\mathscr{L}_{12}}$, see equation (19), and thus this equation becomes the Boltzmann equation (20). This approach by Boercker and Dufty thus gives an alternate motivation for what goes into the rationale of the Boltzmann equation. It also leads to a different form for the pair density operator, whose explicit form has been investigated [20]. Klimontovich [21] also 'derived' the Boltzmann equation by a method which is almost identical to that of Boercker and Dufty [19], phrasing the approximations in terms of (classical) correlation functions rather than reduced distribution functions. A fairly detailed analysis and comparison of these forms for the binary collision approximation closures of the BBGKY hierarchy has recently been given [22].

As stated above, there has been many attempts to rigorously derive the Boltzmann equation. To the author's knowledge, the most recent of these is by Lanford [23]. After considerable effort, he is able to justify that the Boltzmann equation is valid for times up to a fraction of the mean free time. Clearly this is insufficient to justify the standard usage made of the Boltzmann equation, namely to describe how a gas evolves over a macroscopic time-scale. This inability to mathematically assess the relationship between the evolution predicted by the Boltzmann equation and the exact evolution predicted by the von Neumann equation makes it difficult to know how to generalize the Boltzmann equation to more general situations such as the behaviour at higher density.

There have been many efforts to generalize the Boltzmann equation to higher order in density, in particular to include three and more particle collisions. Bogoliubov's approach [5] has been followed by many workers, in particular by Choh and Uhlenbeck [24] and Cohen [25]. Green [26], Klimontovich [21] and the author [27] each has pursued his own method. Some comparison of these works have been made [22, 28]. These generalizations are not discussed further in this paper. A different aspect is whether bound states of the molecules are present with the inherent question of chemical recombination and decay. A formulation of kinetic theory that can handle the latter has been given [29], while aspects of the role of bound states on gas transport coefficients is actively being pursued. Rainwater [30] has formulated a theory that combines several different density effects. His work provides the currently best fit to the experimental low density dependence of gas transport coefficients, but it has not been derived from a single unified starting point. Attempts to incorporate all aspects into one concerted theory is in progress, see in particular the thesis by Wei [31].

A particularly useful reference point is the reduction of the quantum Boltzmann to a set of bimolecular reactions describing the occupation of the various internal states of the molecules in the gas. This is a special case of the Wang-Chang–Uhlenbeck equation [2]. As part of this reduction, an explicit connection is made between the abstract manner in which collisions enter into the Boltzmann equation and standardly defined differential cross-sections and rate constants. To accomplish this reduction, it is necessary to examine in detail the properties of the transition superoperator

$\mathscr{T} \equiv \mathscr{V}\Omega_{\mathscr{L}}$. This is somewhat technical but these general properties are important for understanding the connections between different applications of the Boltzmann equation. The properties of the transition superoperator expressed here are drawn from [18, 32].

3.2. *Detailed properties of the transition superoperator* $\mathscr{T} = \mathscr{V}\Omega_{\mathscr{L}}$

The Møller superoperator is defined as the limit, equation (19), of the product of two evolution superoperators, contrasting free and interacting motion. Formally this limit only exists [13] when acting on trace class operators, essentially representing states that die off rapidly at large distances. For chemical applications, it is common to think of wavefunctions with a definite energy, or transitions with a definite frequency (energy difference). For that purpose it is necessary to extend the range of definition of the Møller superoperator. This is standardly done by adding a convergence factor dependent on a small positive number ε which can be set to zero after the limit sensitive computations have been completed. A useful procedure for accomplishing this is to start with the differential form for the product of the evolution superoperators

$$\frac{\partial}{\partial t}\exp(-\mathrm{i}\mathscr{L}t)\exp(\mathrm{i}\mathscr{K}t) = -\mathrm{i}\exp(-\mathrm{i}\mathscr{L}t)\mathscr{V}\exp(\mathrm{i}\mathscr{K}t), \tag{27}$$

which can be integrated to give the integral form

$$\exp(-\mathrm{i}\mathscr{L}t)\exp(\mathrm{i}\mathscr{K}t) = 1 - \mathrm{i}\int_0^t \mathrm{d}t'\exp(-\mathrm{i}\mathscr{L}t')\mathscr{V}\exp(\mathrm{i}\mathscr{K}t'). \tag{28}$$

For notational simplicity the particle labelling has been dropped even though binary collisions are being emphasized. As well, since collisions really only involve the relative motion, it is convenient to consider the energy parameters mentioned in this subsection as being only for the relative motion (that includes the internal state energy). The limit $t \to \infty$ of this gives an alternate form for the Møller superoperator, but inserting a convergence factor and taking the limit gives an extended form for the Møller superoperator that can be applied to non-trace class operators

$$\Omega_{\mathscr{L}\varepsilon} = 1 - \mathrm{i}\int_0^\infty \mathrm{d}t'\exp(-\varepsilon t')\exp(-\mathrm{i}\mathscr{L}t')\mathscr{V}\exp(\mathrm{i}\mathscr{K}t'). \tag{29}$$

Of particular, and general, interest is the transition operator $|Ej\rangle\langle E'j'|$ between the two eigenstates of the *non-interacting* pair hamiltonian K. These states are labelled here by their energies, E or E' and generic indices j and j' for particular elements of the degenerate levels. This operator is an eigenoperator of the free motion superoperator

$$\mathscr{K}|Ej\rangle\langle E'j'| = \omega_{EE'}|Ej\rangle\langle E'j'| \tag{30}$$

with eigen*frequency* $\omega_{EE'} \equiv (E - E')/\hbar$. The effect of the extended Møller superoperator on this operator can be expressed in a resolvent (Green's function) form

$$\begin{aligned}\Omega_{\mathscr{L}\varepsilon}|Ej\rangle\langle E'j'| &= |Ej\rangle\langle E'j'| - \mathrm{i}\int_0^\infty \mathrm{d}t'\exp(-\varepsilon t')\exp(-\mathrm{i}\mathscr{L}t') \\ &\quad\times\exp(\mathrm{i}\omega_{EE'}t')|Ej\rangle\langle E'j'| \\ &= \left[1 + \frac{1}{\omega_{EE'} + \mathrm{i}\varepsilon - \mathscr{L}}\mathscr{V}\right]|Ej\rangle\langle E'j'| \equiv \Omega_{\mathscr{L}}(\omega_{EE'} + \mathrm{i}\varepsilon)|Ej\rangle\langle E'j'|. \end{aligned} \tag{31}$$

The superoperator within square brackets is just the generalization to superoperators, of the Lippmann–Schwinger equation of scattering theory [33, 34]. There has been some argument [35–37] about the difference between the abstract Møller superoperator $\Omega_{\mathcal{L}}$ and the resolvent form of equation (31). The latter form depends not only on the convergence parameter ε, but also on the detailed form of the operator on which it acts, which determines the frequency that enters into the resolvent. This particular relation arises because of the convergence requirement that the particles become free in the distant past. The same type of resolvent arises in other theories of the time dependence of physical phenomena, specifically from a Fourier time transform of the full evolution superoperator, but the usages and how they arise must be carefully taken into account so as not to confuse the conceptual implications of each approach for the description of the dynamical behaviour of a physical system.

The Møller superoperator transforms non-interacting motion of an operator into interacting motion. The corresponding transformation for a wavefunction is the Møller operator Ω. Jauch *et al.* [13] have rigorously shown that the Møller superoperator can be expressed in terms of the Møller operator when acting on a trace class operator A in terms of the Møller operator Ω, according to

$$\Omega_{\mathcal{L}} A = \Omega A \Omega^{\dagger}. \tag{32}$$

Essentially both the ket and bra states of the operator are separately transformed. This has been the method [14, 17, 18] used to relate collisions in a density operator formalism to the usual wavefunction picture. A more direct relation which emphasizes the properties of the transition superoperator $\mathcal{T}$, is to use Fano's approach [38]. This first requires identifying the frequency parametrized transition superoperator

$$\mathcal{T}(z) \equiv \mathcal{V}\Omega_{\mathcal{L}}(z) = \mathcal{V} + \mathcal{V}\frac{1}{z-\mathcal{L}}\mathcal{V}. \tag{33}$$

This is identical in structure (for two particles) to the memory kernel that Fano introduced for his analysis of the pressure broadening of spectral lines. Fano introduced a star notation to designate that the starred operator becomes a superoperator, by which it is to act before all operators to the right of it, for example, $A^*B \equiv BA$ implies that A^* is a superoperator that changes the operator B into the operator BA. Any commutator can thus be treated as a combination of two operations, in particular $\hbar\mathcal{V} = V - V^*$ and $\hbar\mathcal{L} = H - H^*$. On choosing the contour C' in the complex plane as the line $-\infty < \mathcal{R}z' < \infty$ with $\mathcal{I}z > \mathcal{I}z' > 0$, Fano showed that the Liouville resolvent can be written in terms of hamiltonian resolvents (note that $\hbar$'s have been introduced to preserve dimensions and in such a way that the notation is simplest)

$$\frac{1}{z-\hbar\mathcal{L}} = \frac{1}{2\pi \mathrm{i}}\int_{C'} \frac{\mathrm{d}z'}{(z'-H)(z'-z-H^*)}. \tag{34}$$

On inserting this relation into equation (33), and performing a number of simplifying computations, including contour evaluations where they can be explicitly done, see [37, 38], the transition superoperator can be written

$$\begin{aligned}\hbar\mathcal{T}(z/\hbar) &= T(z+K^*) - T^*(K-z)\\ &\quad + \frac{1}{2\pi \mathrm{i}}\int_{C'} \mathrm{d}z'\left[\frac{1}{z'-K} - \frac{1}{z'-z-K^*}\right] T(z')T^*(z'-z)\left[\frac{1}{z'-K} - \frac{1}{z'-z-K^*}\right].\end{aligned} \tag{35}$$

Here the transition operator is defined as

$$T(z) \equiv V + V\frac{1}{z - H}V. \tag{36}$$

For use in the Boltzmann equation, this parametrized transition superoperator arises only when the real part $\mathscr{R}z$ of the parameter z is consistent with the operator on which it acts, compare equation (31). In particular, the combination of resolvents acting on a typical energy parametrized operator is (setting $z = E - E' + \mathrm{i}\varepsilon$ and $z' = x' + \mathrm{i}\eta$ with the subsequent notion of the limit $\varepsilon \to 0$)

$$\begin{aligned}\left[\frac{1}{x' - K + \mathrm{i}\eta} - \frac{1}{x' + \mathrm{i}\eta - E + E' - \mathrm{i}\varepsilon - K^*}\right]&|Ej\rangle\langle E'j'| \\ = \left[\frac{1}{x' - E + \mathrm{i}\eta} - \frac{1}{x' - E - \mathrm{i}(\varepsilon - \eta)}\right]&|Ej\rangle\langle E'j'| \underset{\varepsilon \to 0}{\to} -2\pi\mathrm{i}\delta(x' - E)|Ej\rangle\langle E'j'|.\end{aligned} \tag{37}$$

This has the effect of simplifying the expression for $\mathscr{T}(z/\hbar)$ to

$$\begin{aligned}\hbar\mathscr{T}(\omega_{EE'})|Ej\rangle\langle E'j'| &= T(E)|Ej\rangle\langle E'j'| - |E_j\rangle\langle E'j'|T^\dagger(E') \\ &\quad - \left[\frac{1}{E - K + \mathrm{i}(\varepsilon - \eta)} - \frac{1}{E' - K^* - \mathrm{i}\eta}\right]T(E)|Ej\rangle\langle E'j'|\,T^\dagger(E').\end{aligned} \tag{38}$$

Here the parametrization of the transition operator T with a real energy E is understood as the limit $\lim_{\varepsilon \to 0} T(E + \mathrm{i}\varepsilon)$, and the adjoint $T^\dagger$ has to approach the real axis from below rather than above. Similarly the frequency parametrized collision superoperator is understood as the limit $\lim_{\varepsilon \to 0} \mathscr{T}(\omega_{EE'} + \mathrm{i}\hbar\varepsilon)$. Specifically of importance, and not often emphasized in the literature, is the consequence that the energy parameter of the transition operator is exactly the energy of the eigenstate of K on which it acts, and similarly for the adjoint quantities. If a matrix element of the transition superoperator is calculated, the energy dependences are explicitly displayed

$$\begin{aligned}&\langle E''j''|\hbar\mathscr{T}(\omega_{EE'})(|E_j\rangle\langle E'j'|)|E'''j'''\rangle \\ &\quad = \langle E''j''|T(E)|E_j\rangle\,\delta(E' - E''')\,\delta_{j'j'''} - \delta(E'' - E)\,\delta_{j''j}\langle E'j'|T^\dagger(E')|E'''j''\rangle \\ &\qquad - \left[\frac{1}{E - E'' + \mathrm{i}(\varepsilon - \eta)} - \frac{1}{E' - E''' - \mathrm{i}\eta}\right]\langle E''j''|T(E)|E_j\rangle\langle E'j'|T^\dagger(E')|E'''(j''').\end{aligned} \tag{39}$$

Finally, if one restricts the collisions to be 'on-the-frequency-shell', namely that $E'' - E''' = E - E'$, then the above combination of resolvents reduces to an energy delta function $-2\pi\mathrm{i}\delta(E'' - E)$ and all transition operators are evaluated 'on-the-energy-shell'. It is only under such restricted conditions that a transition operator matrix element is equivalent to an energy parametrized scattering operator, $S(E)$, matrix element on the discrete index

$$S_{j''j}(E) = \delta_{j''j} - 2\pi\mathrm{i}\langle Ej''|T(E)|Ej\rangle. \tag{40}$$

Note that $S(E)$ is defined only on-the-energy-shell, but for such cases the transition superoperator can be written in the simpler form

$$\begin{aligned}&\langle E''j''|\hbar\mathscr{T}(\omega_{EE'})(|Ej\rangle\langle E'j'|)|(E'' - E + E')j'''\rangle \\ &\qquad = \frac{1}{-2\pi\mathrm{i}}\delta(E'' - E)[S_{j''j}(E)\,S_{j'j'''}(E') - \delta_{j''j}\delta_{j'j'''}].\end{aligned} \tag{41}$$

It is this form of the collision superoperator that has been used for computations in many applications of the Boltzmann equation, in particular in much of the work on pressure broadening [39]. While standard methods of calculating the effects of collisions only discuss the S matrix, or equivalently the on-the-energy-shell T matrix, it is seen that this is only valid for use in the collision term of the Boltzmann equation under restrictive conditions or as an approximation.

3.3. *Wang-Chang–Uhlenbeck equation*

In general the density operator for a molecule in the gas, here labelled as molecule 1, has an expansion in eigenstates of $H_1^{(1)}$ according to

$$\rho_1^{(1)} = \sum_{j_1 j_1'} \int\int \mathrm{d}\mathbf{p}_1\, \mathrm{d}\mathbf{p}_1' |\mathbf{p}_1 j_1\rangle \rho^{(1)}_{\mathbf{p}_1 j_1, \mathbf{p}_1' j_1'} \langle \mathbf{p}_1' j_1'|, \tag{42}$$

involving the momenta $\mathbf{p}_1$, $\mathbf{p}_1'$ of the ket and bra states and the molecular internal states j_1 and j_1'. If the gas is homogeneous, then the momentum dependence is diagonal. Furthermore, if the state is determined completely by the concentration $c_j(\mathbf{p}_1)$ of molecules in state j_1 with momentum $\mathbf{p}_1$, then the expansion coefficient of the density operator reduces to

$$\rho^{(1)}_{\mathbf{p}_1 j_1, \mathbf{p}_1', j_1'} = h^3\, c_j(\mathbf{p}_1)\, \delta(\mathbf{p}_1 - \mathbf{p}_1')\, \delta_{j_1 j_1'}. \tag{43}$$

In the Boltzmann equation, the collision term involves the product of such singlet density operators and can be written in terms of the relative momentum $\mathbf{p} = (m_1 \mathbf{p}_2 - m_2 \mathbf{p}_1)/(m_1 + m_2)$ and centre of mass momentum $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$ as

$$\rho_1^{(1)} \rho_2^{(1)} = h^6 \sum_{j_1 j_2} \int\int \mathrm{d}\mathbf{P}\mathrm{d}\mathbf{p} |\mathbf{P}\rangle |\mathbf{p}j\rangle c_{j_1}(\mathbf{p}_1)\, c_{j_2}(\mathbf{p}_2) \langle \mathbf{p}j| \langle \mathbf{P}|, \tag{44}$$

with $j \equiv j_1 j_2$ a composite index for the internal states of the pair of molecules and allowance made for the molecules to be different with differing masses m_1 and m_2. The energy of *relative* motion (including internal states) is then $E_j = \mathbf{p}^2/2\mu + \varepsilon_j$, μ being the reduced mass. It is this relative energy that enters into the parametrization of the transition operator, while the centre of mass momentum is unaffected by the collision dynamics.

As the density operator for relative motion, see equation (44), is diagonal in energy, all terms have zero frequency from the point of view of the collision superoperator. The Boltzmann collision term includes a trace over the states of the second molecule, which includes an integration over its *final* momentum $\mathbf{p}_2'$. Since the momentum $\mathbf{p}_1'$ of the first molecule is fixed, the integration over $\mathbf{p}_2'$ is equivalent to an integration over the centre of mass momentum $\mathbf{P}$. The resulting collision term of the Boltzmann equation (20) is, after some calculation

$$\begin{aligned}
&\langle \mathbf{p}_1 j_1 | \mathrm{Tr}_2\, \mathscr{T}_{12}\, \rho_1^{(1)} \rho_2^{(1)} | \mathbf{p}_1' j_1' \rangle \\
&\quad = \delta(\mathbf{p}_1 - \mathbf{p}_1') \frac{h^6}{\hbar} \sum_{j_2} \int \mathrm{d}\mathbf{p}_2 \langle \mathbf{p} j_1 j_2 | T(E')\, c_{j_1'}(\mathbf{p}_1) - c_{j_1}(\mathbf{p}_1)\, T^\dagger(E) | \mathbf{p} j_1' j_2 \rangle c_{j_2}(\mathbf{p}_2) \\
&\qquad + \delta(\mathbf{p}_1 - \mathbf{p}_1') \sum_{j_2 j_1'' j_2''} \frac{h^6}{\hbar} \int\int \mathrm{d}\mathbf{p}_2\, \mathrm{d}\mathbf{p}'' \langle \mathbf{p} j_1\, j_2 | T(E'') | \mathbf{p}'' j_1''\, j_2'' \rangle \langle \mathbf{p}'' j_1'' j_2'' | T^\dagger(E'') | \mathbf{p} j_1' j_2 \rangle \\
&\qquad \times \left[\frac{1}{E'' - E' - \mathrm{i}\eta} - \frac{1}{E'' - E + \mathrm{i}(\varepsilon - \eta)} \right] c_{j_1''}(\mathbf{p}_1'')\, c_{j_2''}(\mathbf{p}_2'').
\end{aligned} \tag{45}$$

It is because of the conservation of centre of mass momentum that the collision term is diagonal in momentum. From a different point of view, a homogeneous system remains homogeneous. The difference between E and E' is entirely due to molecule 1 being in either state j_1 or j_1'. But it is noticed that, even though the density operators in the collision term (before the collision) are diagonal in internal state and energy, the result of the collision can be non-diagonal in internal state and energy. This is a particular example of how collisions can couple different frequency components of the density operator.

A special case is the diagonal-in-internal-state part of the collision term. This has a simpler structure since this implies that $E' = E$, with the consequence that the term in the square bracket reduces to $2\pi i\delta(E - E'')$. As well, the first term involving the difference in the transition operator and its adjoint is simplified through the optical theorem

$$\begin{aligned}\langle \mathbf{p}j|T - T^\dagger|\mathbf{p}j\rangle &= 2\pi i\langle \mathbf{p}j|T\delta(E - K)\,T^\dagger|\mathbf{p}j\rangle \\ &= -\,2\pi i\sum_{j''}\int d\mathbf{p}''\,\delta(E - E'')|\langle \mathbf{p}_j|T|\mathbf{p}''j''\rangle|^2 \\ &= \frac{-\,ip}{(2\pi)^3\hbar^2\mu}\sum_{j''}\int d\hat{\mathbf{p}}''\,\sigma_{\mathbf{p}j\to\mathbf{p}''j''}. \end{aligned} \qquad (46)$$

It is to be understood in the above that, if not otherwise indicated, the energy for which T is to be evaluated is the eigenenergy of the non-interacting hamiltonian K on which it acts. Here $\sigma_{\mathbf{p}''j''\to\mathbf{p}j}$ is the differential cross-section and $\hat{\mathbf{p}}''$ is the unit vector associated with $\mathbf{p}''$. Since the cross-section involves the absolute square of a T matrix element, the cross-section has the symmetry

$$(2\pi)^4\hbar^2\mu\mu''|\langle \mathbf{p}j|T|\mathbf{p}''j''\rangle|^2 = \frac{p''}{p}\sigma_{\mathbf{p}''j''\to\mathbf{p}j} = \frac{p}{p''}\sigma_{\mathbf{p}j\to\mathbf{p}''j''}. \qquad (47)$$

If the discussion is limited to the diagonal-in-internal-state part of the density operator, equivalently to the concentrations of the different internal states, the Boltzmann equation reduces to

$$\begin{aligned}\frac{\partial c_{j_1}(\mathbf{p}_1)}{\partial t} = \sum_{j_2 j_1'' j_2''}\iiint d\mathbf{p}_2\,d\mathbf{p}_1''\,d\mathbf{p}_2''\,\delta(E - E'')\,\delta(\mathbf{p}_1'' + \mathbf{p}_2'' - \mathbf{p}_1 - \mathbf{p}_2)\frac{p''}{\mu\mu''p}\sigma_{\mathbf{p}''j''\to\mathbf{p}j} \\ \times[c_{j_1''}(\mathbf{p}_1'')\,c_{j_2''}(\mathbf{p}_2'') - c_{j_1}(\mathbf{p}_1)\,c_{j_2}(\mathbf{p}_2)]. \end{aligned} \qquad (48)$$

This has used the cross-section symmetry (47). Clearly energy and linear momentum are conserved in the collision process. This equation can be looked upon as a set of second order chemical reactions for species distinguished from each other by their internal state label j and momentum $\mathbf{p}$. If the momentum dependence is further assumed to be in equilibrium (Maxwellian), then on integrating over $\mathbf{p}_1$, this equation becomes

$$\frac{\partial c_{j_1}}{\partial t} = \sum_{j_2 j_1'' j_2''}[k_{j''\to j}c_{j_1''}c_{j_2''} - k_{j\to j''}c_{j_1}c_{j_2}] \qquad (49)$$

which is recognized as a standard set of bimolecular chemical reactions with rate constants determined by

$$\begin{aligned}k_{j''\to j} &= (2\pi)^4\hbar^2\mu\iint|\langle \mathbf{p}j|T|\mathbf{p}''j''\rangle|^2\frac{p\exp(-p''^2/2\mu''k_B T)}{(2\pi\mu''k_B T)^{3/2}}d\hat{\mathbf{p}}\,d\mathbf{p}'' \\ &= \left(\frac{8k_B T}{\pi\mu''}\right)^{1/2}\frac{1}{(k_B T)^2}\iiint\overline{\sigma_{\mathbf{p}''j''\to\mathbf{p}j}}\exp(-E_{tr}''/kT)\,E_{tr}''\,dE_{tr}'', \end{aligned} \qquad (50)$$

where E_{tr} is the translational energy and

$$\overline{\sigma_{p''j'\to pj}} \equiv \frac{1}{4\pi}\iint \sigma_{\mathbf{p}''j'\to\mathbf{p}j}\,\mathrm{d}\hat{\mathbf{p}}\,\mathrm{d}\hat{\mathbf{p}}'' \tag{51}$$

is the angle averaged collision cross-section. It also follows immediately from the transition operator form for the rate constant, together with energy conservation, that the forward and reverse rate constants satisfy the chemical equilibrium condition

$$\mu^{3/2}\exp\left(-\varepsilon_{j'}/k_{\mathrm{B}}T\right)k_{j'\to j} = \mu^{3/2}\exp\left(-\varepsilon_{j}/k_{\mathrm{B}}T\right)k_{j\to j'}. \tag{52}$$

But it is noted that these reaction rate equations are only strictly valid if the gas is homogeneous and the density operator restricted to being diagonal in internal states. Also of note is that the internal state label here denotes individual states, in particular degenerate states have not been lumped together. Degeneracy factors were a problem in some of the earlier work where the difference between individual states and degenerate sets, in particular rotational j states, was not properly taken into account.

In an inhomogeneous gas, the classical distribution function $f(\mathbf{r}, \mathbf{p}, t)$ is position dependent. In quantum mechanics this position dependence is associated with an off-diagonal momentum dependence of the density operator. Rather than keeping track of off-diagonal elements of the density operator, it is more convenient to express the position dependence in a classical manner. A standard method of accomplishing this is via the Wigner function [40]

$$f_{jj'}(\mathbf{r}, \mathbf{p}) = \frac{1}{h^3}\int \mathrm{d}\mathbf{q}\exp\left(\mathrm{i}\mathbf{q}\cdot\mathbf{r}/\hbar\right)\langle \mathbf{p}+\frac{1}{2}\mathbf{q}j\,|\rho^{(1)}|\,\mathbf{p}-\frac{1}{2}\mathbf{q}j'\rangle. \tag{53}$$

To include internal states, $f_{jj'}(\mathbf{r}, \mathbf{p})$ is here both a density operator in internal states and a Wigner function for the translational motion. The Wang-Chang–Uhlenbeck equation [2] is the Boltzmann equation (2) expressed in terms of the Wigner function but restricted, first to being diagonal in internal states, and second, that the collisions are local, specifically that a collision occurs at one point in space, thus

$$\begin{aligned}\frac{\partial f_j(\mathbf{r}, \mathbf{p}_1)}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\nabla f_j(\mathbf{r}, \mathbf{p}_1) = \sum_{j_2 j_1' j_2'}\iiint \mathrm{d}\mathbf{p}_2\,\mathrm{d}\mathbf{p}_1''\mathrm{d}\mathbf{p}_2''\,\delta(E-E'')\,\delta(\mathbf{p}_1''+\mathbf{p}_2''-\mathbf{p}_1-\mathbf{p}_2)\\ \times\frac{p''}{\mu\mu''p}\sigma_{\mathbf{p}''j'\to\mathbf{p}j}[f_{j_1'}(\mathbf{r}, \mathbf{p}_1'')f_{j_2'}(\mathbf{r}, \mathbf{p}_2'')-f_{j_1}(\mathbf{r}, \mathbf{p}_1)f_{j_2}(\mathbf{r}, \mathbf{p}_2)].\end{aligned} \tag{54}$$

This is an approximation and implies that a separation between macroscopic (fluid flow, temperature differences, etc.) and microscopic (molecular dynamics of collision processes) motion can be made. A collision occurs within a distance of a few angstroms whereas gas inhomogeneity is typically on the scale of millimetres. This assumption of the collision being local was also inherently made in the original Boltzmann equation [1]. To clearly understand what is involved in making this separation of distance scale, it is necessary to analyse the effects of non-diagonalities in momentum. This is a lengthy process that is not covered here. An efficient aid to carrying out this analysis is the parametrization introduced by Baerwinkel and Grossmann [41]. This parametrization has been used to examine corrections to the collisional locality [42], which are responsible for a major contribution to the density dependence of gas transport coefficients [30, 43, 44]. With more accurate experimental methods and greater interest in engineering applications, the understanding and prediction of such density dependence has become of renewed interest.

3.4. *Approach to equilibrium*

Boltzmann's 'H-theorem' is equivalent to showing that the collision term increases the entropy. But it was inherently assumed by Boltzmann that collisions are local, a constraint on the more general form of the collision term which must be generalized to being on-the-frequency-shell [18]. But even within the initial constraint of local collisions, this implies that this is only a local approach to equilibrium, that is to a local Boltzmann distribution with a local temperature, density and mean (stream) velocity. But complete equilibrium requires a globally uniform temperature, density and stream velocity. This occurs only through an interplay between collisional and streaming motion. While this approach to global equilibrium is reviewed only for a simple case, it is also expressed in terms of diagonal and non-diagonal elements of the density operator to illustrate how these approach equilibrium. This is analogous to the approach to equilibrium (in a homogeneous system) which is responsible for the pressure broadening of spectral lines, spin relaxation and a number of other effects involving internal states. The inhomogeneous and homogeneous cases are discussed in turn. The following section discusses some aspects of the reversibility–irreversibility paradox, namely the difference between the invariance of the N-molecule entropy, equation (9), and the increasing 1-molecule entropy.

3.4.1. *Decay to equilibrium in a spatially inhomogeneous system*

For a one molecule density operator, the entropy is

$$S = - k_{\mathrm{B}} \mathrm{Tr}_1 \, \rho_1^{(1)} \ln (\rho_1^{(1)}/e). \tag{55}$$

The factor of e here and $N!$ in equation (8) are required for consistency with the factorization

$$\rho^{(N)} \approx \prod_j (\rho_j^{(1)}/N) \tag{56}$$

(associated with the independence of the molecules in a low density gas, and taking into account the normalizations of the different density operators) and to agree at equilibrium with the standard expression for the entropy from the method of partition functions.

For simplicity of presentation, the detailed discussion of the approach to global equilibrium is restricted to using the Wang-Chang–Uhlenbeck equation, whose collision term is spatially local and whose Wigner function is diagonal in internal energy, with only comments made about the general case. Expressed in terms of the Wigner function, with internal states, and neglecting quantum corrections, the entropy can be related, $S = \int s(\mathbf{r})\, \mathrm{d}\mathbf{r}$, to an entropy density

$$s(\mathbf{r}) = - k_{\mathrm{B}} \sum_j \int \mathrm{d}\mathbf{p}_1 f_j(\mathbf{r}, \mathbf{p}_1) \ln (f_j(\mathbf{r}, \mathbf{p}_1)/e). \tag{57}$$

The equation of change for this entropy density is

$$\begin{aligned} &\frac{\partial s(\mathbf{r})}{\partial t} + \nabla \cdot \sum_j \int \frac{\mathbf{p}}{m} f_j(\mathbf{r}, \mathbf{p}) \ln \left(\frac{f_j(\mathbf{r}, \mathbf{p})}{e} \right) \mathrm{d}\mathbf{p} \equiv \sigma_s \\ &= - k_{\mathrm{B}} \sum_{j_1 j_2 j_1' j_2'} \iiiint \mathrm{d}\mathbf{p}_1 \, \mathrm{d}\mathbf{p}_2 \, \mathrm{d}\mathbf{p}_1' \, \mathrm{d}\mathbf{p}_2' \, \delta(E - E') \, \delta(\mathbf{p}_1' + \mathbf{p}_2' - \mathbf{p}_1 - \mathbf{p}_2) \\ &\times \frac{p'}{\mu \mu' p} \sigma_{\mathbf{p}' j' \to \mathbf{p} j} \ln \left(\frac{f_{j_1}(\mathbf{r}, \mathbf{p}_1)}{e} \right) [f_{j_1'}(\mathbf{r}, \mathbf{p}_1') f_{j_2'}(\mathbf{r}, \mathbf{p}_2') - f_{j_1}(\mathbf{r}, \mathbf{p}_1) f_{j_2}(\mathbf{r}, \mathbf{p}_2)]. \end{aligned} \tag{58}$$

The divergence term describes how the entropy flows from one position to another, specifically the entropy flux is

$$\mathbf{J}_s = - k_{\mathrm{B}} \sum_j \int \frac{\mathbf{p}}{m} f_j(\mathbf{r},\mathbf{p}) \ln\left(\frac{f_j(\mathbf{r},\mathbf{p})}{e}\right) \mathrm{d}\mathbf{p}. \tag{59}$$

By symmetry, first between molecules 1 and 2, and second between the primed states and the unprimed, noting the cross-section symmetry of equation (47), the collision contribution can be written as

$$\begin{aligned}\sigma_s = & -\frac{1}{4}k_{\mathrm{B}} \sum_{j_1 j_2 j_1' j_2'} \iiiint \mathrm{d}\mathbf{p}_1\,\mathrm{d}\mathbf{p}_2\,\mathrm{d}\mathbf{p}_1'\,\mathrm{d}_2'\,\delta(E-E')\,\delta(\mathbf{p}_1'+\mathbf{p}_2'-\mathbf{p}_1-\mathbf{p}_2)\\ & \times \frac{p'}{\mu\mu' p}\sigma_{\mathbf{p}'j'\to\mathbf{p}j} \ln\left(\frac{f_{j_1}(\mathbf{r},\mathbf{p}_1) f_{j_2}(\mathbf{r},\mathbf{p}_2)}{f_{j_1'}(\mathbf{r},\mathbf{p}_1') f_{j_2'}(\mathbf{r},\mathbf{p}_2')}\right)[f_{j_1'}(\mathbf{r},\mathbf{p}_1') f_{j_2'}(\mathbf{r},\mathbf{p}_2') - f_{j_1}(\mathbf{r},\mathbf{p}_1) f_{j_2}(\mathbf{r},\mathbf{p}_2)]\\ & \geqslant 0.\end{aligned} \tag{60}$$

The form of the combination of Wigner functions has the structure $(y-x)\ln(x/y) \leqslant 0$, which shows the collisional entropy change to be positive unless

$$\ln(f_{j_1'}(\mathbf{r},\mathbf{p}_1')) + \ln(f_{j_2'}(\mathbf{r},\mathbf{p}_2')) = \ln(f_{j_1}(\mathbf{r},\mathbf{p}_1)) + \ln(f_{j_2}(\mathbf{r},\mathbf{p}_2)), \tag{61}$$

which can only be satisfied if $\ln(f_j(\mathbf{r},\mathbf{p}))$ is a summational invariant, specifically is linear in mass, momentum and energy. This can be written as

$$f_j(\mathbf{r},\mathbf{p}) = \frac{n\Lambda^3}{q_{\mathrm{int}}}\exp[-(\mathbf{p}-m\mathbf{v}_0)^2/2mk_{\mathrm{B}}T]\exp(-\varepsilon_j/k_{\mathrm{B}}T), \tag{62}$$

where $\Lambda \equiv h/(2\pi m k_{\mathrm{B}} T)^{1/2}$ is the thermal deBroglie wavelength and $q_{\mathrm{int}} \equiv \Sigma_j \exp(-\varepsilon_j/k_{\mathrm{B}}T)$ is the internal state partition function. The number density n, temperature T and stream velocity $\mathbf{v}_0$ are all functions of the local position $\mathbf{r}$ and time t. It is because the collisions are treated as being local that they drive the Wigner function to a Boltzmann distribution. But just because the Wigner function is locally Boltzmann, the entropy density is not necessarily constant. Rewriting equation (58) in the form of a general equation of change

$$\frac{\partial s(\mathbf{r})}{\partial t} + \nabla\cdot\mathbf{J}_s = \sigma_s, \tag{63}$$

gives a description of how the entropy density changes due to the entropy flux $\mathbf{J}_s$ and entropy production σ_s. The flux is usually [45] subdivided into convective and conductive contributions but such detail is avoided in this presentation.

Corresponding to a local Boltzmann distribution for the Wigner function, the collision term in the Wang-Chang–Uhlenbeck equation vanishes, to be left with

$$\begin{aligned}&\frac{\partial f_j(\mathbf{r},\mathbf{p}_1)}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\nabla f_j(\mathbf{r},\mathbf{p}_1)\\ &= \left[\frac{\partial \ln n}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\nabla\ln n + \left(\frac{(\mathbf{p}-m\mathbf{v}_0)^2}{2mk_{\mathrm{B}}T} - \frac{3}{2} + \frac{\varepsilon_j - \langle\varepsilon\rangle}{k_{\mathrm{B}}T}\right)\left(\frac{\partial \ln T}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\nabla\ln T\right)\right.\\ &\qquad \left. + \left(\frac{\partial \mathbf{v}_0}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\nabla\mathbf{v}_0\right)\cdot\frac{\mathbf{p}_1 - m\mathbf{v}_0}{k_{\mathrm{B}}T}\right] f_j(\mathbf{r},\mathbf{p}_1).\end{aligned} \tag{64}$$

Thus any position dependence of the density, stream velocity and temperature will cause the Wigner function to change. For example, if only the density is treated as being non-uniform, then by formal integration

$$f_j(\mathbf{r}, \mathbf{p}_1, t) = n\left(\mathbf{r} + \frac{\mathbf{p} - m\mathbf{v}_0}{m} t, 0\right) f_j(\mathbf{r}, \mathbf{p}_1, 0) \tag{65}$$

shows how the distribution function changes with time from an initial state at $t = 0$, becoming in general a non-Maxwellian momentum distribution. The global approach to equilibrium is thus seen as a combination of the collisions driving the distribution function to a local Boltzmann distribution, while the free motion terms mix the local Boltzmann distributions to drive the distribution away from being Boltzmann. In this simplified discussion, no account is made of the relative sizes of different cross-sections so no assessment can be made as to whether one particular non-equilibrium mode reaches equilibrium before another. For example, usually the efficiency for changes in vibrational state is much slower than for rotational states and this is of importance in describing the detailed mechanism by which relaxation to global equilibrium occurs.

Finally it is useful to discuss the approach to equilibrium in an inhomogeneous system in density matrix form using the momentum representation rather than in terms of the Wigner function. To simplify the collisional structure, it is assumed that most of the molecules are in homogeneous equilibrium, so that as far as a collision is concerned, only one of the colliding pair is out of equilibrium at a time, with the consequence that the collision term can be linearized. On linearization, the collision term can be written in terms of a set of relaxation times. For further simplification, the presence of internal states is ignored.

The density operator in momentum representation can be recovered from the Wigner function by the inverse Fourier transform

$$\langle \mathbf{p}j | \rho^{(1)} | \mathbf{p}' j' \rangle = \int \mathrm{d}\mathbf{r} \exp\left(\mathrm{i}(\mathbf{p}' - \mathbf{p}) \cdot \mathbf{r} / \hbar\right) f_{jj'}\left(\mathbf{r}, \frac{1}{2}(\mathbf{p} + \mathbf{p}')\right). \tag{66}$$

Under the simplifications posed above, the linearized Wang-Chang–Uhlenbeck equation without internal states (identical to a linearization of the original Boltzmann equation but for a real (quantum) cross-section) reduces to the set of linear equations

$$\begin{aligned} \frac{\partial \langle \mathbf{p} | \rho^{(1)} | \mathbf{p}' \rangle}{\partial t} = & -\frac{\mathrm{i}}{\hbar}\left(\frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}'^2}{2m}\right) \langle \mathbf{p} | \rho^{(1)} | \mathbf{p}' \rangle - \frac{1}{\tau_{\mathbf{pp}'}} \langle \mathbf{p} | \rho^{(1)} | \mathbf{p}' \rangle \\ & + \int \mathrm{d}\mathbf{p}'' K\left(\frac{\mathbf{p} + \mathbf{p}'}{2}, \mathbf{p}''\right) \left\langle \mathbf{p}'' + \frac{\mathbf{p} - \mathbf{p}'}{2} \middle| \rho^{(1)} \middle| \mathbf{p}'' - \frac{\mathbf{p} - \mathbf{p}}{2} \right\rangle. \end{aligned} \tag{67}$$

These are partially uncoupled, in that terms with different momentum off-diagonalities are uncoupled from each other. The relaxation time $\tau_{\mathbf{pp}'}$ and the integral kernel K (...) can be expressed in terms of collision cross-sections. What is of note is the structure of this equation, namely the evolution is governed by a frequency for the dynamical (free) motion and a relaxation due to collisions so that the magnitude of the off-diagonal element of the density operator is governed by a combination of free and collisional motion. In the Wigner representation the free motion is expressed as a position dependence while the collisions change only the momentum dependence. This same structure is also valid after linearization for the more general Boltzmann equation but with a possibly complex relaxation time. For the decay of internal motion there is a similar behaviour, as is now discussed.

3.4.2. *Decay to equilibrium of the internal states*

The object of this subsection is to illustrate the dynamics of internal state behaviour according to the Boltzmann equation. Of particular interest are the properties of the collision term. To keep the presentation short, several simplifying assumptions are made. These are: (i) the gas is homogeneous and the momentum distribution Maxwellian; (ii) the gas is a mixture in which only one species has internal states and this species has a very small concentration so that all collisions involving internal state changes can be treated as between an inert molecule and a molecule of the species with internal states, with the consequence that the Boltzmann equation is reduced to being linear in the internal state density operator.

A typical internal state density matrix element $\varrho_{jj'}$ is associated with the singlet density operator $\rho^{(1)}$ according to

$$\langle \mathbf{p}j|\rho^{(1)}|\mathbf{p}'j'\rangle = h^3 \varrho_{jj'} \frac{\exp(-p^2/2mk_B T)}{(2\pi m k_B)^{3/2}} \delta(\mathbf{p}-\mathbf{p}'), \tag{68}$$

compared with equation (43). The Boltzmann equation is then equivalent to

$$\frac{\partial \varrho_{jj'}}{\partial t} = -\mathrm{i}\left(\frac{\varepsilon_j - \varepsilon_{j'}}{\hbar}\right)\varrho_{jj'} - \sum_{j''j'''} R_{jj';j''j'''}\varrho_{j''j'''}, \tag{69}$$

where the relaxation matrix R is

$$\begin{aligned} R_{jj';j''j'''} = {}& \frac{(2\pi)^3 \mathrm{i} n\hbar^2}{(2\pi\mu k_B T)^{3/2}} \int \mathrm{d}\mathbf{p}\, [\langle \mathbf{p}j|T(E'')|\mathbf{p}j''\rangle \delta_{j'j'''} \\ & - \delta_{jj''}\langle \mathbf{p}j'''|T^\dagger(E''')|\mathbf{p}j'\rangle] \exp(-\mathbf{p}^2/2\mu k_B T) \\ & + \frac{(2\pi)^3 \mathrm{i} n\hbar^2}{(2\pi\mu k_B T)^{3/2}} \int\!\!\int \mathrm{d}\mathbf{p}\,\mathrm{d}\mathbf{p}'' \langle \mathbf{p}j|T(E'')|\mathbf{p}''j''\rangle\langle \mathbf{p}''j'''|T^\dagger(E''')|\mathbf{p}j'\rangle \\ & \times \left[\frac{1}{E''' - E' - \mathrm{i}\eta} - \frac{1}{E'' - E + \mathrm{i}(\varepsilon - \eta)}\right] \exp(-\mathbf{p}''^2/2\mu k_B T). \end{aligned} \tag{70}$$

Here the primes on the E are associated with the primes on the internal state label j, while the translational contribution is $p^2/2\mu$ for E and E', and $p''^2/2\mu$ for E'' and E'''. Of particular use for understanding this evolution is the separation between how the matrix element evolves as if it was isolated and how it couples to other matrix elements. The isolated part of the evolution involves the relaxation matrix

$$\begin{aligned} R_{jj';jj'} \equiv {}& \mathrm{i}\Delta\omega_{jj'} + 1/\tau_{jj'} \\ = {}& \frac{(2\pi)^3 \mathrm{i} n\hbar^2}{(2\pi\mu k_B T)^{3/2}} \int \mathrm{d}\mathbf{p}\, [\langle \mathbf{p}j|T(E)|\mathbf{p}j\rangle - \langle \mathbf{p}j'|T^\dagger(E')|\mathbf{p}j'\rangle] \exp(-\mathbf{p}^2/2\mu k_B T) \\ & - \frac{(2\pi)^4 n\hbar^2}{(2\pi\mu k_B T)^{3/2}} \int\!\!\int \mathrm{d}\mathbf{p}\,\mathrm{d}\mathbf{p}'' \langle \mathbf{p}j|T(E)|\mathbf{p}''j\rangle\langle \mathbf{p}''j'|T^\dagger(E')|\mathbf{p}j'\rangle \\ & \times \delta\left(\frac{\mathbf{p}''^2 - \mathbf{p}^2}{2\mu}\right) \exp(-\mathbf{p}^2/2\mu k_B T). \end{aligned} \tag{71}$$

It is possible to identify explicit expressions for the real $1/\tau_{jj'}$ and imaginary $\Delta\omega_{jj'}$ parts of this relaxation matrix element but that detail is not carried out here. It is also noticed that, for this case, the transition matrix elements are on-the-energy-shell, so can be written in terms of the S-matrix. With these notations, the evolution equation (69) for $\rho_{jj'}$ becomes

$$\frac{\partial \rho_{jj'}}{\partial t} = -\left(\frac{1}{\tau_{jj'}} + i\,\bar{\omega}_{jj'}\right)\rho_{jj'} - \sum_{\{j''j'''\} \neq \{jj'\}} R_{jj';\,j''j'''}\,\rho_{j''j'''}, \tag{72}$$

with the frequency of oscillation of $\rho_{jj'}$ given as the sum

$$\bar{\omega}_{jj'} = \frac{\varepsilon_j - \varepsilon_{j'}}{\hbar} + \Delta\omega_{jj'} \tag{73}$$

of the natural independent particle frequency and a collisional shift associated with the interactions with other molecules in the gas. As a last association, if the potential is weak enough, the transition operator T can be approximated as the potential operator V, in which case the collisional shift becomes the difference in first order perturbation contributions to the internal energy levels

$$\Delta\omega_{jj'} = \frac{n}{(2\pi\mu k_B T)^{3/2}} \int \mathrm{d}\mathbf{p}\,[\langle \mathbf{p}j|V|\mathbf{p}j\rangle - \langle \mathbf{p}j'|V|\mathbf{p}j'\rangle] \exp(-\mathbf{p}^2/2\mu k_B T). \tag{74}$$

The collisional decay rate is at least quadratic in the potential and consists of a number of terms which are not detailed here. A general discussion of how these collisional frequency shifts are related to the Boltzmann collision superoperator is given in [32], while Born and distorted wave Born approximations to them are discussed in [46].

Often in experimental situations there is a steady driving force applied to the chemical system, for example by the application of an electrical field or by a temperature difference. If the effective rate at which the matrix element $\rho_{jj'}$ is excited is $\alpha_{jj'}$ (replacing (− times) the sum in equation (72)), then the time dependence is determined both by relaxation and oscillation according to

$$\rho_{jj'}(t) = \exp(-(\mathrm{i}\bar{\omega}_{jj'} + 1/\tau_{jj'})t)\rho_{jj'}(0) + \frac{1 - \exp[-\mathrm{i}(\bar{\omega}_{jj'} + 1/\tau_{jj'})\,t]}{1/\tau_{jj'} + \mathrm{i}\bar{\omega}_{jj'}}\alpha_{jj'}. \tag{75}$$

The exponential terms represent transients while after the transients have died out, the steady state value of $\rho_{jj'}$ is given by

$$\begin{aligned} \rho_{jj'}\big|_{\text{steady state}} &= \frac{1}{1/\tau_{jj'} + i\bar{\omega}_{jj'}}\alpha_{jj'} \\ &= \frac{1/\tau_{jj'} - \mathrm{i}\bar{\omega}_{jj'}}{1/\tau_{jj'}^2 + \bar{\omega}_{jj'}^2}\alpha_{jj'}. \end{aligned} \tag{76}$$

For the particular case in which $\alpha_{jj'}$ is real, this gives the real and imaginary steady state parts of $\rho_{jj'}$. This result can be related to the in-phase and out-of-phase response of a system to a driving force but it is emphasized that the frequency is the natural frequency of the system rather than being an externally applied oscillation. It is seen that the larger the frequency $\bar{\omega}_{jj'}$, the smaller the steady state magnitude of $\rho_{jj'}$. This result is termed [47] the effect of 'partial phase randomization' and was emphasized when discussing the qualitative interpretation of the magnetic field dependence of gas transport coefficients, see section 5. In the general approach to equilibrium, it is this effect that is responsible for causing the density operator to become diagonal in energy representation. While the discussion in this subsection is for the approach to equilibrium for internal states, the same argument can be applied to the position dependence of translational motion, compare equation (67). It was suggested in [18] that it is this effect which gradually eliminates off-diagonal in energy terms in the density operator so that Boltzmann's H-theorem will eventually become valid and complete equilibrium attained.

3.5. *Different entropies*

The exact evolution of a N-molecule system leaves the N-molecule entropy $S^{(N)}$ constant, see equation (9). In contrast, the Boltzmann equation, in particular the H-theorem in terms of the local entropy production σ_s, see equation (60), increases the entropy until equilibrium is reached. This inconsistency is referred to as the reversibility–irreversibility paradox, the discussion of which started with Boltzmann's introduction of his kinetic equation. Some comment is made here about this paradox and how it is to be understood. The following discussion makes use of the association between the concept of entropy and Shannon's [48] neginformation.

It must first be recognized that the N-molecule entropy $S^{(N)}$, equation (8), and the 1-molecule entropy $S^{(1)}$, equation (55), are inherently different in nature, only being equal when the N-molecule density operator factorizes, equation (56). That entropy may have different faces has been nicely presented by Grad [49], with a hierarchy of entropies associated with the reduced distribution functions and the possible relations between them. What is missing in the factorization of the N-molecule density operator is all the (equilibrium) particle correlations that are present in a dense gas, and more relevant for dilute gas kinetic theory, all the correlations that arise as the molecules collide and thus influence each others future evolution. This picture of the development of more and more complicated correlations has been emphasized by Prigogine [50]. Thus Prigogine expresses this as a flow of information from lower to higher ordered correlations. In particular, all the information in an initial state, which could be completely contained in the 1-molecule density operator if the factorization of equation (56) is exact at the initial time, flows into higher correlations. Since $S^{(1)}$ measures only the neginformation in $\rho^{(1)}$, this neginformation increases since information has been removed from the 1-molecule density operator.

A related approach, though not directly related to gas kinetic theory and the Boltzmann equation, is the linear theory of Zwanzig's [51] Generalized Master Equation. In his excellent Boulder lecture [51], he reviews previous related work and presents a simplistic model which shows how decay to equilibrium is valid only for a time-scale large to the individual dynamic (collision) time-scale, but small compared to the periodicity time-scale (Poincaré recurrence time) for the N-molecule system. This illustrates the subjectivity of what any experiment is capable of observing.

4. Spin relaxation

Spin systems have several experimental and theoretical advantages. Since the Zeeman energy is very small compared to normal thermal energies, there is little influence on the rest of a chemical system as a spin is excited and relaxes to equilibrium. Thus modifying a spin state is experimentally a non-invasive method of monitoring a chemical system. From the theoretical point of view, the small energy changes imply that, as a good approximation, the spin system can be treated as if only the spin system is out of equilibrium. As a consequence, the small number of degrees of freedom greatly simplify the mathematics. On the other hand, it is necessary to treat each spin state in detail since the small number of degrees of freedom imply that the usual statistical averaging that occurs in large systems, and often smooths out any novel effect that a particular state may have, is absent. Only a spin–$1/2$ system is considered here, while the treatment of systems with higher spins rapidly becomes more complicated in detail due to the presence of higher multipole moments.

The dynamics of a spin system can be classified according to whether it is due to: (i) external (Zeeman hamiltonian) influences; (ii) intramolecular interactions (typically hyperfine or dipolar interaction); and (iii) intermolecular interactions. In the gas phase, intermolecular interactions occur as collisions. For a typical nuclear spin, the small spin energy has negligible effect on the collision (translational) dynamics, nor is it much affected during a collision. Thus the direct influence of a collision on the dynamics of a spin is of lowest order of importance and can usually be ignored if there are intramolecular spin interactions. The formulation of nuclear magnetic relaxation from a Boltzmann equation perspective has been presented in the case when no intramolecular interactions are present [52], and when spin–rotation and/or dipolar interactions dominate the relaxation [53]. Recent work on muon relaxation [54, 55] has applied the same or more complex dependence on intramolecular interactions. As the intramolecular mechanism with the simplest formulation, the spin–rotation interaction is reviewed with emphasis on exemplifying the aspects of an intramolecular mechanism.

The object of interest is the expectation value $\langle \mathbf{I} \rangle$ of the (nuclear) spin $\mathbf{I}$ *in units of* $\hbar$. This varies with time due to the Zeeman hamiltonian $H_{ZI} = -\gamma_I \hbar \mathbf{B} \cdot \mathbf{I}$ and the spin–rotation hamiltonian $H_{\mathrm{sr}} = c_{\mathrm{sr}} \hbar \mathbf{I} \cdot \mathbf{J}$. The latter hamiltonian couples the spin to the molecular rotational angular momentum $\mathbf{J}$, which is in turn controlled by its own Zeeman hamiltonian $H_{ZJ} = -\gamma_J \hbar \mathbf{B} \cdot \mathbf{J}$, the rotational hamiltonian $H_J = J(J+1)\hbar^2/2\mathcal{I}$ (for a diatomic with moment of inertia $\mathcal{I}$), the spin–rotation hamiltonian and by collision processes. Thus the evolution of the spin system is not directly affected by collisions, but is indirectly affected by collisions through the intermediary of the rotational angular momentum. In terms of the Boltzmann equation (20), the spin Liouville superoperator is the commutator of the spin hamiltonian

$$K = H_{ZI} + H_{ZJ} + H_{\mathrm{sr}} + H_J. \tag{77}$$

Since the Zeeman energies are all small compared to thermal energies, except well below 1 K, it is appropriate to treat the translational degrees of freedom as being at equilibrium, whose only role is to provide a thermal average for any collision cross-section for the rotational angular momentum, thus the translational kinetic energy hamiltonian has been dropped. On recognizing that the rotational energy level separation is very large compared to the Zeeman energy level separation, it follows that the low energies involved in the experiment will be insufficient to cause a significant number of J transitions, so the density operator can be assumed diagonal in J. A further argument for the validity of this is that, on the time-scale for Zeeman frequency effects to be observed, equivalently that Zeeman energy level separations play an important role, rotational energy level differences have all been phase randomized (compare the discussion of equation (76)), so again, the density operator is effectively diagonal in the rotational angular momentum magnitude quantum number J. To make the treatment even simpler, it is assumed that only one value of J needs to be retained. Essentially this is assuming that all J states act in a similar manner and one can lump them together into one effective J value. It is then only the directional aspects of the spin $\mathbf{I}$ and rotational angular momentum $\mathbf{J}$ that need to be considered. The treatment is formally the same if the rotational angular momentum $\mathbf{J}$ is replaced [54] by an electron spin $\mathbf{S}$, whose magnitude is of course fixed. Of course the details of the collision processes must be different, but the formal treatment is the same.

At equilibrium, the spin and rotational angular momentum expectation values are both determined by the spin hamiltonian, but on the basis that all terms are small compared to thermal energies (with a single J value, H_J is a constant that cancels in the normalization of the equilibrium density operator), a linearization of the Boltzmann factor is appropriate so that

$$\langle \mathbf{I} \rangle\big|_{\text{equil.}} \equiv \frac{\operatorname{Tr} \mathbf{I} \exp(-K/k_B T)}{\operatorname{Tr} \exp(-K/k_B T)} = \frac{\operatorname{Tr} \mathbf{I}(1-K/k_B T)}{\operatorname{Tr}(1-K/k_B T)} = \frac{(2J+1)(1/2)\,\gamma_I \hbar/k_B T}{(2J+1)2}\mathbf{B}, \tag{78}$$

which is equivalent to Curie's law for an equilibrium magnetic moment. The trace is over both spin and rotational degrees of freedom, so in the denominator where only the '1' contributes, the factor of $2J+1$ is the degeneracy of the rotational level and the 2 is for the two spin states. Technically the trace over a single spin operator vanishes, most importantly because the trace must be a rotational invariant and a spin (pseudo) vector has no rotationally invariant part. On the other hand the trace over a product of spin operators depends on which components of the operators are involved, specifically if they are different, the trace is zero, while if they are the same, the trace is $1/3$ of the square of the magnitude of the angular momentum times the degeneracy of the level, thus for the spin traces

$$\operatorname{Tr}_I \mathbf{I}_x \mathbf{I}_y = 0; \quad \operatorname{Tr}_I \mathbf{I}_x \mathbf{I}_x = (1/3)\times(3/4)\times 2 = 1/2. \tag{79}$$

That is why the spin expectation value is in the field direction.

If the spin is out of equilibrium, the density operator deviates from its equilibrium Boltzmann form, conveniently written as

$$\rho = \rho\big|_{\text{equil.}}(1+\phi) \approx \frac{1-K/k_B T+\phi}{2(2J+1)}. \tag{80}$$

Since the spin hamiltonian is small, everything is merely additive and the equilibrium term can be subtracted out and ignored in the following. The 'perturbation' operator ϕ is a function of $\mathbf{I}$ and $\mathbf{J}$, so that it may be expanded in powers of these angular momentum operators. To terms at most linear in each angular momentum, this expansion is

$$\phi = 4\mathbf{I}\cdot\langle \mathbf{I}\rangle + \frac{3}{J(J+1)}\mathbf{J}\cdot\langle \mathbf{J}\rangle + \frac{12}{J(J+1)}\mathbf{J}\mathbf{I}:\langle \mathbf{I}\mathbf{J}\rangle + \dots . \tag{81}$$

The coefficients of this expansion are identified as expectation values through the explicit calculation of the expectation values. For the second rank tensor involving the product of the angular momentum operators, the double dot contraction is by convention taken as contracting nearest tensorial indices. That there is no constant (angular momentum operator independent term) is because normalization must be preserved. Higher powers of the angular momenta may be considered. But for a spin–$1/2$ system, the product of any two spin operators is a spin operator, the terms linear in $\mathbf{I}$ cover all possibilities. On the other hand, higher powers of $\mathbf{J}$ can in principle occur, all the way up to the $2J$th, the effect of these higher angular momentum multipoles on the relaxation of the spin depend on powers of the spin–rotation constant c_{sr}, which here is taken as being small. In the hyperfine case, $\mathbf{J}$ is replaced by an electron spin $\mathbf{S}$, and while the hyperfine constant may be large, now all operators of quadratic, or higher powers, can be re-expressed in terms of being at most linear in $\mathbf{S}$.

It has previously been stated that the spin is negligibly affected by collisions, so that only the rotational angular momentum, which is tied to how the molecular frame moves, is modified by collisions. Thus in the Boltzmann equation, as the collision term involves the perturbation ϕ of the spin density operator ρ, only those terms containing $\mathbf{J}$ will be affected by collisions. Retaining only quantities that are at most linear in ϕ, the Boltzmann equation (20) can be linearized

$$\frac{\partial \phi}{\partial t} = -\mathrm{i}\mathscr{H}\phi - \mathscr{R}\phi, \tag{82}$$

to involve a 'linear' relaxation superoperator $\mathscr{R}$, compare the matrix representation, equation (69), of the linearized Boltzmann equation retaining the full internal state density operator ρ. While $\mathbf{I}$ is unaffected by collisions, collisions will cause $\mathbf{J}$ to decay to its equilibrium (Curie law) value, or for the perturbation contribution which is relative to equilibrium, to 0. Moreover, since the collisions are isotropic (it was stated that the Zeeman energies are negligible compared to thermal energies, so can be ignored when calculating the transition operator), then the effect of $\mathscr{R}$ on $\mathbf{J}$ is equivalent to a relaxation time τ,

$$\mathscr{R}\mathbf{J} = \mathbf{J}/\tau. \tag{83}$$

Technically there can be a difference in the effect of $\mathscr{R}$ if it acts on the product $\mathbf{IJ}$, since in that case it must be the same molecule before and after the collision that carries the 'polarization' $\mathbf{IJ}$, while if the polarization only involves $\mathbf{J}$, then there is a possibility of transfer of polarization from one collision partner to the other. These subtleties are ignored here. On calculating the expectation values of the linearized Boltzmann equation (82) within the approximations mentioned above, the closed set of three tensorial kinetic equations [54]

$$\frac{\partial \langle \mathbf{I} \rangle}{\partial t} = -\omega_I \hat{\mathbf{B}} \times \langle \mathbf{I} \rangle - c_{\mathrm{sr}} \langle \mathbf{I} \times \mathbf{J} \rangle, \tag{84}$$

$$\frac{\partial \langle \mathbf{J} \rangle}{\partial t} = -\omega_J \hat{\mathbf{B}} \times \langle \mathbf{J} \rangle + c_{\mathrm{sr}} \langle \mathbf{I} \times \mathbf{J} \rangle - \frac{1}{\tau} \langle \mathbf{J} \rangle, \tag{85}$$

$$\frac{\partial \langle \mathbf{IJ} \rangle}{\partial t} = -\omega_I \hat{\mathbf{B}} \times \langle \mathbf{IJ} \rangle + \omega_J \langle \mathbf{IJ} \rangle \times \hat{\mathbf{B}} + c_{\mathrm{sr}}\, \varepsilon \cdot \left(\frac{1}{3} J(J+1) \langle \mathbf{I} \rangle - \frac{1}{4} \langle \mathbf{J} \rangle \right) - \frac{1}{\tau} \langle \mathbf{IJ} \rangle \tag{86}$$

for the expectation values are obtained. Here $\omega_I = \gamma_I B$ and $\omega_J = \gamma_J B$ are the magnitudes of the Zeeman precession frequencies for the spin and the rotational motion. These have been slightly generalized here to allow J to have any value, whereas in [54], J appeared only as the electron spin $S = 1/2$. The Levi–Civita tensor ε has been used in the above. This is a third rank antisymmetric tensor, having components $\varepsilon_{jkl} = \pm 1$ according to whether j, k, l as a cyclic or anticyclic permutation of the x, y,

z coordinates, and zero if two or more labels are the same. Since each vector has 3 components, these three tensorial equations are equivalent to 15 scalar equations. Their solution determines the time dependence of the coupled motion of the spin and rotational angular momenta.

The symmetry of the system, and the kinetic equations, is $C_{\infty v}$ with the magnetic field direction $\hat{\mathbf{B}}$ providing the symmetry axis. Thus solutions can be broken down [54] into sets corresponding to the irreducible representations of $C_{\infty v}$. For spin relaxation one needs only the solutions containing components of $\langle \mathbf{I} \rangle$ which can also be decomposed into irreducible representations of $C_{\infty v}$, namely the invariant part $\langle \mathbf{I} \rangle \cdot \hat{\mathbf{B}}$ and the counterclockwise and clockwise rotating parts $\langle \mathbf{I} \rangle \cdot (\hat{x} \pm i\hat{y})$, with $\hat{x}$, $\hat{y}$ and $\hat{\mathbf{B}}$ a clockwise set of unit vectors. These correspond to the longitudinal and transverse components of the spin. Only the longitudinal relaxation of the spin is treated in greater detail here. The equations for the longitudinal system can be written in a number of ways; in [54] the association was motivated by classifying the operators according to the eigenstates of the spin hamiltonian since c_{sr} is considered to be large compared to the Zeeman energies, while in [53] the emphasis was on the individual spins since c_{sr} was considered to be small. These sets of equations are of course equivalent, differing only in a change of basis. It is the latter description which is most easily seen from the tensorial equations (84), to give the set of four equations

$$\frac{\partial \langle I_B \rangle}{\partial t} = - c_{\mathrm{sr}} \langle \mathbf{I} \times \mathbf{J} \cdot \hat{\mathbf{B}} \rangle, \tag{87}$$

$$\frac{\partial \langle J_B \rangle}{\partial t} = + c_{\mathrm{sr}} \langle \mathbf{I} \times \mathbf{J} \cdot \hat{\mathbf{B}} \rangle - \frac{1}{\tau} \langle J_B \rangle, \tag{88}$$

$$\frac{\partial \langle \mathbf{I} \times \mathbf{J} \cdot \hat{\mathbf{B}} \rangle}{\partial t} = - (\omega_I - \omega_J) \langle I_B J_B - \mathbf{I} \cdot \mathbf{J} \rangle + 2 c_{\mathrm{sr}} \left(\frac{1}{3} J(J+1) \langle I_B \rangle - \frac{1}{4} \langle J_B \rangle \right) - \frac{1}{\tau} \langle \mathbf{I} \times \mathbf{J} \cdot \hat{\mathbf{B}}) \tag{89}$$

$$\frac{\partial \langle I_B J_B - \mathbf{I} \cdot \mathbf{J} \rangle}{\partial t} = (\omega_I - \omega_J) \langle \mathbf{I} \times \mathbf{J} \cdot \hat{\mathbf{B}} \rangle - \frac{1}{\tau} \langle I_B J_B - \mathbf{I} \cdot \mathbf{J} \rangle. \tag{90}$$

If these are written in matrix form whose eigenvectors are to be found, namely in the form

$$\frac{\partial V}{\partial t} = M V = \lambda V, \tag{91}$$

with the four-dimensional vector having components $\langle I_B \rangle$, $\langle J_B \rangle$, $\langle \mathbf{I} \times \mathbf{J} \cdot \hat{\mathbf{B}} \rangle$ and $\langle I_B J_B - \mathbf{I} \cdot \mathbf{J} \rangle$, then the secular determinant for the eigenvalues λ is

$$\begin{aligned} |M - \lambda| &= \begin{vmatrix} -\lambda & 0 & -c_{\mathrm{sr}} & 0 \\ 0 & -\lambda - \frac{1}{\tau} & c_{\mathrm{sr}} & 0 \\ \frac{2}{3} c_{\mathrm{sr}} J(J+1) & -\frac{1}{2} c_{\mathrm{sr}} & -\lambda - \frac{1}{\tau} & -(\omega_I - \omega_J) \\ 0 & 0 & (\omega_I - \omega_J) & -\lambda - \frac{1}{\tau} \end{vmatrix} \\ &= \left(\lambda + \frac{1}{\tau} \right) \left[\lambda^3 + \frac{2}{\tau} \lambda^2 + \lambda \left(\frac{1}{\tau^2} + \frac{1}{2} c_{\mathrm{sr}}^2 + \frac{2}{3} c_{\mathrm{sr}}^2 J(J+1) + (\omega_I - \omega_J)^2 \right) \right. \\ &\quad \left. + \frac{2}{3\tau} c_{\mathrm{sr}}^2 J(J+1) \right] = 0. \end{aligned} \tag{92}$$

Experimentally, it is usually only the slowest decay that is observed. For a weak coupling constant, in the sense that $c_{\mathrm{sr}}^2\,\tau^2 \ll 1$ and $c_{\mathrm{sr}}^2 \ll (\omega_I - \omega_J)^2$, the eigenvalue with smallest negative real part is

$$\lambda = -\frac{\frac{2}{3}c_{\mathrm{sr}}^2\,J(J+1)\,\tau}{1+(\omega_I-\omega_J)^2\tau^2}, \tag{93}$$

the result of [53], and a standard result [56] of NMR for the 'spin–lattice' relaxation time $T_1 = 1/\lambda$ when the decay is due to a spin–rotation mechanism. While the standard method uses a time correlation function method with an introduction of a correlation time τ, the gas kinetic approach presented here has the advantage that τ is a well defined collisional quantity which may be calculated from an appropriate collision cross-section

$$\frac{1}{\tau} = \frac{1}{J(J+1)}\langle \mathbf{J}\cdot\mathscr{R}\mathbf{J}\rangle. \tag{94}$$

The nature of the frequency and density (pressure) dependence can be explained in terms of collision rate and partial phase randomization, see the discussion following equation (76). As $1/\tau$ is proportional to the pressure, it is seen that at high pressures, τ vanishes and the spin lattice relaxation rate $1/T_1 = \lambda$ becomes very small. This is traced to the rapid decay of $\langle \mathbf{J}\rangle$, so there is no rotational angular momentum with which the spin can couple. On the other hand, at low pressures, τ becomes very large and the spin is phase randomized, again leading to a very small spin–lattice relaxation rate.

The other extreme is when the coupling constant is large, such that if $c_{\mathrm{sr}}^2\,\tau^2 \gg 1$ and $c_{\mathrm{sr}}^2 \gg (\omega_I - \omega_J)^2$, then the spin and rotational angular momenta relax together as an effective total angular momentum $\mathbf{F} = \mathbf{I} + \mathbf{J}$. In this case the slowest decay rate, eigenvalue λ of smallest negative value, is given by

$$\lambda = -\frac{\frac{2}{3}J(J+1)/\tau}{\frac{1}{2}+\frac{2}{3}J(J+1)+(\omega_I-\omega_J)^2/c_{\mathrm{sr}}^2}. \tag{95}$$

For H-atom-like radicals, the rotational angular momentum $\mathbf{J}$ in the above formulae can be replaced by the electron spin $\mathbf{S}$, whose magnitude S of $1/2$ and negative gyromagnetic ratio require replacing ω_J by the relatively large $-\omega_S$. At the same time, the coupling constant c_{sr} becomes the hyperfine constant ω_0, so that the slowest decay rate is

$$\lambda = \frac{-1}{2\tau[1+(\omega_I+\omega_S)^2/\omega_0^2]}. \tag{96}$$

This is what is reported in [54] for the muon spin relaxation rate in longitudinal fields. In that reference, connection is also made to other experimental decay rate measurements. These differ in what exactly is measured, so that the slowest decay rate is not always what is observed. Thus an analysis, not only of the precession–relaxation eigenvalues is needed for an elucidation of the observations, but the detailed form of the eigenvectors is also required.

As stated at the beginning of this section, only the intramolecular spin–rotation mechanism of spin relaxation is discussed in detail in this review, and then only the formulae for longitudinal decay have been presented. For most molecules there can be several angular momenta present and then the theoretical treatment requires assessing which spin couplings are of how much importance in order to interpret the experimental data. Recent work in this direction [55] has been addressed to the data on muon spin relaxation in molecular addition radicals. The stable radical C_2H_4Mu, formed by the addition of muonium, μ^+e^-, to ethylene, C_2H_4, has a muon spin $\mathbf{I}$, (unpaired) electron spin $\mathbf{S}$ and rotational angular momentum $\mathbf{J}$, besides a number of proton spins. On the basis that the electron's gyromagnetic moment is about 1000 times that of the other spins, the behaviour of the electron spin should dominate the relaxation of all spins. The muon spin is what is observed, while collisions affect only the rotational angular momentum. Since the proton spins play no inherent role in the muon spin relaxation, they were ignored in that work. Still, to describe all the operators involving the three remaining angular momenta, a reduction based on the irreducible representations of the group $C_{\infty v}$ was made. This was further simplified by allowing at most terms quadratic in $\mathbf{J}$. Even so, for the treatment of the longitudinal relaxation (experimental observation of the spin along the magnetic field direction), a 35-dimensional (real) basis of angular momentum operators was needed. For the transverse (measurement of the spin perpendicular to the magnetic field direction), the basis was 30-dimensional, but now complex. Eigenvector solutions of the corresponding kinetic equations then give respectively 35 and 30 precession–relaxation modes for the motion of the spin system. Comparison between theory and experiment involves finding the values of the coupling constants and collision decay rates that best fit the experimental data. Since these quantities are not known *a priori*, the procedure consists of a search in a multidimensional parameter space for the best fit. It was further discovered that the eigenvector that is responsible for the muon spin relaxation was not the one with the slowest decay rate so an analysis of the nature of the eigenvectors was also required. That the smallest decay rate was not what was being observed was indicated when comparison was made between the experimentally observed precession frequency in the experimental transverse configuration and the oscillation predicted by theory, that is, by the imaginary part of a complex transverse eigenvalue. The radical COMu formed by the addition of muonium to carbon monoxide is unstable. Thus the muon spin relaxation is also affected by the formation rate and lifetime of the radical. The theoretical treatment then requires assessing how the spin variables are affected during the chemical formation and decay. A first attempt in this direction has been made [57].

5. Transport coefficients

The transport of mass, momentum and energy are of obvious importance in engineering processes. There are of course other quantities that may be transported, such as charge or spin angular momentum. But all transport arises in general due to a combination of convective and conductive motion. The former is due to the general movement of the gas as a whole, whereas the conductive transport is relative to the centre of mass of the gas as a whole and can be thought of as associated with Brownian motion and usually governed by a set of transport coefficients. A complete treatment of gas transport theory is very lengthy with many facets. The classic references [58, 59] emphasize the calculation of the transport coefficients for molecules without internal states whereas the work on polyatomics is reviewed by McCourt *et al.* [60]. There are innumerable books that describe gas kinetic theory with a variety of detail and emphasis, a selection being [16, 61–66]. The more mathematical aspects of how the equations of hydrodynamics are related to the Liouville equation is discussed by Chapman and Cowling [58] but greater detail is given in [67–70]. There are also

Green–Kubo formulae for the transport coefficients [71]. Another facet of gas transport is the set of problems at low density, where molecules can travel long distances before they suffer a collision. Aspects of this Knudsen flow are extensively covered by Cercignani [70] while some of the effects of Knudsen corrections to polyatomic transport theory are reviewed in [60]. The discussion in this section is limited to a review of the essential features of how internal states influence gas transport in a simple case, drawn predominantly from [47, 72].

The transport coefficients are the *linear* proportionality constants for the conductive transport of a physical property due to an inhomogeneity in the fluid (gas). Thus in a multicomponent mixture the amount of conductive transport of each species due to the concentration gradients of the different species is determined by a set of diffusion coefficients while conductive momentum transport due to a velocity gradient is governed by a set of viscosities and conductive energy transport due to a temperature gradient is governed by a set of thermal conductivities. The fluid as a whole may move (convect) with a stream velocity $\mathbf{v}_0$, which can carry physical properties such as momentum and energy because the fluid itself is moving. This is the convective transport. While not always the most useful for practical (experimental) purposes, the conceptual separation between convective and conductive motion is based on the fact that it is an unbalanced net force that causes mass to move, so this net mass motion is convection. Thus the stream velocity (convection velocity) is identical to the mass average velocity of the fluid. Conductive transport is in addition to this, having no direct influence on or by the motion of the fluid as a whole.

It was stated in the above that the transport coefficients arise from a linear dependence on inhomogeneities. This requires, both that the discussion is about *local* properties of the fluid and that the variation of the fluid properties from one spatial point to another, and with time, is slow. This is usually referred to as the assumption of local equilibrium or *local thermodynamic equilibrium*, LTE. Thus at any point $\mathbf{r}$ in space and time t, the fluid is parametrized by a density $n(\mathbf{r}, t)$, a temperature $T(\mathbf{r}, t)$ and stream velocity $\mathbf{v}_0(\mathbf{r}, t)$. In a multicomponent mixture, there must be a density for each species together with species velocities and, depending on the system and its mode of treatment, possibly separate temperatures for each species. From the point of the Boltzmann equation, thermodynamic equilibrium in particular arises because of collisions. Thus the LTE and the validity of describing the dynamics of a fluid in terms of local quantities, requires that the molecular motion is collision dominated. This in turn requires, for a gas, that the gas be dense enough that many collisions occur within the range of time and space over which the fluid varies negligibly in its physical properties. The rate at which collisions occur is in essence proportional to the product of the density, the mean molecular (Brownian motion) relative velocity $\bar{v} \equiv (8\pi\mu/k_B T)^{1/2}$ and some effective cross-section σ. If the gas is to be treated ideally, there is also the condition that the second virial coefficient contributes negligibly to the equation of state. Since the second virial coefficient can be considered proportional to the cube of some effective molecular diameter d, this requires $nd^3 \ll 1$. In contrast, the cross-section scales as the square of the molecular diameter, so LTE requires $n\pi d^2 \gg 1/L$, where L is a typical distance over which the fluid has constant physical properties. Grad's [68] mathematical manner for satisfying these conditions is to take the limit that $n \rightarrow \infty$ and $d \rightarrow 0$ in such a way that nd^2 is finite. This was Grad's argument for the validity of the Boltzmann equation, which can be interpreted as saying that the Boltzmann equation is valid in the limit that the molecules become smaller and smaller, while their density becomes larger and larger. In a crude sense, the molecules are very small but there are so many of them that they undergo lots of collisions. The condition on L that it is so large that $L \gg 1/n\sigma$ is the condition for LTE while, if this inequality is not satisfied, then the gas is approaching the Knudsen regime.

The following discussion is limited to a one component gas where local thermodynamic equilibrium is applicable. The density operator for such a system is most easily expressed in terms of a Wigner function for the translational states and a density operator in internal states, see equation (53). This will be dominated by a local equilibrium Wigner function–density operator

$$f^{(0)}(\mathbf{r},\mathbf{p},t) = \frac{n\Lambda^3}{q_{\text{int}}}\exp[-(\mathbf{p}-m\mathbf{v}_0)^2/2mk_B T]\exp(-H_{\text{int}}/k_B T), \tag{97}$$

of the same structure as the equilibrium Wigner function-density operator of equation (62), but whose density, temperature and stream velocity are all position and time dependent. It is for this reason that the Wigner function is convenient, since in phase space, the quotient of the kinetic energy operator $\mathbf{p}^2/2m$ and the position dependent temperature is easily carried out whereas, as operators, since position and momentum do not commute, it is difficult to consider how to represent such a quotient. Deviations from this local equilibrium Boltzmann distribution are standardly treated as a perturbation ϕ,

$$f(\mathbf{r},\mathbf{p},t) = f^{(0)}(\mathbf{r},\mathbf{p},t) + \frac{1}{2}\left[f^{(0)}(\mathbf{r},\mathbf{p},t),\phi\right]_+, \tag{98}$$

which in general does not commute with the internal state hamiltonian H_{int} so one way to maintain ϕ hermitian, is to use an anticommutator, compare the various methods of linearization of a perturbation to the Boltzmann density operator discussed in [73]. Since phase randomization (see the discussion following equation (76)) will cause the density operator to be diagonal for internal state energy differences such that $\Delta\varepsilon/\hbar \gg 1/\tau = n\pi d^2\bar{v}$ for a typical mean free time τ, at ordinary pressures and temperatures where $1/\tau \ll k_B T/\hbar$, the only energy non-diagonalities of the density operator that can survive complete phase randomization will be very small compared to the thermal energy $k_N T$. (The basis for this assessment uses the order of magnitude values of $n \approx 2\times 10^{25}$ m^{-3} and $d \approx 3\times 10^{-10}$ m, $\bar{v} \approx 7\times 10^2$ ms^{-1} at 300 K for N$_2$.) As a consequence, the non-commutation of ϕ and $f^{(0)}$ can in practice be ignored. Under the same conditions, the density operator is diagonal in states of different J magnitude.

The local gas density, stream velocity and mean particle energy $\langle\varepsilon\rangle$ are determined by the Wigner function-density operator according to

$$n = \mathrm{Tr}_{\text{int}}\int f(\mathbf{r},\mathbf{p},t)\,\mathrm{d}\mathbf{p}, \tag{99}$$

$$nm\mathbf{v}_0 = \mathrm{Tr}_{\text{int}}\int \mathbf{p}f(\mathbf{r},\mathbf{p},t)\,\mathrm{d}\mathbf{p}, \tag{100}$$

$$n\langle\varepsilon\rangle = \mathrm{Tr}_{\text{int}}\int\left[\frac{(\mathbf{p}-m\mathbf{v}_0)^2}{2m} + H_{\text{int}}\right]f(\mathbf{r},\mathbf{p},t)\,\mathrm{d}\mathbf{p}. \tag{101}$$

Note that for the energy, only the motion relative to the centre of mass is considered since this is the motion that is associated with Brownian motion. If equilibrium statistical mechanics is used to interpret the mean particle energy in terms of a temperature, it is possible in principle to calculate the temperature from this energy expectation value.

Equations of change for these local expectation values are obtained by taking appropriate averages of the Boltzmann equation (20) which, since there is a need to distinguish local and non-local effects, is most conveniently expressed in terms of the Wigner function-density operator (compare equation (53) for the matrix representation of the internal state dependence)

$$\frac{\partial f_1(\mathbf{r},\mathbf{p})}{\partial t}+\frac{\mathbf{p}}{m}\cdot\nabla f_1(\mathbf{r},\mathbf{p})+\frac{\mathrm{i}}{\hbar}[H_{\mathrm{int},\ 1},f_1(\mathbf{r},\mathbf{p},t)]_- = -\ 8\mathrm{i}(2\pi)^3\hbar^2\mathrm{Tr}_{2,\,\mathrm{int}}\iint \mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{k}$$
$$\times [\langle \mathbf{q}|T|\mathbf{k}\rangle f_1(\mathbf{r},\mathbf{p}+\mathbf{q}-\mathbf{k},t)f_2(\mathbf{r},\mathbf{p}+\mathbf{q}+\mathbf{k},t)\langle \mathbf{k}|\Omega^\dagger|\mathbf{q}\rangle$$
$$-\langle \mathbf{q}|\Omega|\mathbf{k}\rangle f_1(\mathbf{r},\mathbf{p}+\mathbf{q}-\mathbf{k},t)f_2(\mathbf{r},\mathbf{p}+\mathbf{q}+\mathbf{k},t)\langle \mathbf{k}|T^\dagger|\mathbf{q}\rangle]. \tag{102}$$

This is the rate of change for the Wigner function-density operator for molecule 1, and has been written to retain all off-diagonalities in the internal states while limiting all dynamical effects, in particular the collisions, to being local in space. Thus both Wigner functions in the collision term are evaluated at the same spatial point, and moreover at the same point in space as that used on the left hand side of the equation. The momenta $\mathbf{k}$ and $\mathbf{q}$ can be considered as the relative momenta before and after the collision. Finally, it should be emphasized that while $f(\mathbf{r},\mathbf{p},t)$ is clearly indicated to be a function of position, momentum and time, it is also an operator on internal states thus being indicated by the dual notation of being a Wigner function-density operator. The transition and Møller operators also have this dual structure, having their momentum matrix elements explicitly indicated while their internal state properties are inherently of operator form. Equation (102) is the localized form of the Boltzmann equation discussed in [42]. If the Wigner function-density operator is diagonal in internal energy, this reduces to the Wang-Chang–Uhlenbeck equation (54).

Averages of equation (102) are now taken. For the density, this gives the equation of continuity

$$\frac{\partial n}{\partial t} = -\ \nabla\cdot(n\mathbf{v}_0), \tag{103}$$

having no contribution from the collision term since integrating the collision term over $\mathbf{p}$ and the relation $T = V\Omega$ between the transition and Møller operators, imply that the collision term reduces to the trace of a commutator, which naturally vanishes. For the stream velocity, symmetry of the collision term between the two particles allows $\mathbf{p}$ to be replaced by $\mathbf{p}+\mathbf{q}$, which is the centre of mass momentum that commutes with the potential and all collision operators. Thus there is no contribution from the collision term to the rate of change of momentum density and

$$\frac{\partial nm\mathbf{v}_0}{\partial t} = -\ \nabla\cdot(nm\mathbf{v}_0\,\mathbf{v}_0+\mathbf{P}), \tag{104}$$

where

$$\mathbf{P} \equiv \mathrm{Tr}_{\mathrm{int}}\int\frac{(\mathbf{p}-m\mathbf{v}_0)(\mathbf{p}-m\mathbf{v}_0)}{m}f(\mathbf{r},\mathbf{p},t)\,\mathrm{d}\mathbf{p} \tag{105}$$

is the pressure tensor. This second rank tensor has two indices, and while symmetric in this work, the first index refers to the direction of transport while the second index describes the direction of the momentum which is being transported, thus $\mathbf{P}_{xy}$ is the rate of transport (kg m s^{-1}) (m^2 s)$^{-1}$ in the $\hat{x}$ direction, of momentum in the $\hat{y}$ direction. At local equilibrium, the pressure tensor is given by $\mathbf{P} = nk_\mathrm{B}T\mathbf{U}$, in terms of the local pressure $P = nk_\mathrm{B}T$ of the (low density) gas. Here $\mathbf{U}$ is the identity tensor, having components $\mathsf{U}_{jl} = \delta_{jl}$. Finally, using an argument similar to that for the momentum, the rate of change of the energy density is unaffected by collisions so that

$$\frac{\partial}{\partial t}\left[n\left(\frac{m\mathsf{v}_0^2}{2}+\langle\varepsilon\rangle\right)\right] = -\nabla\cdot\left[n\mathsf{v}_0\left(\frac{m\mathsf{v}_0^2}{2}+\langle\varepsilon\rangle\right)+\mathbf{P}\cdot\mathsf{v}_0+\mathsf{q}^K\right]. \tag{106}$$

This has to take into account the time and spatial dependence of the convective energy density $nm\mathsf{v}_0^2/2$ and involves the (kinetic) heat flux vector

$$\mathsf{q}^K \equiv \mathrm{Tr}_{\mathrm{int}}\int\frac{(\mathsf{p}-m\mathsf{v}_0)}{m}\left[\frac{(\mathsf{p}-m\mathsf{v}_0)^2}{2m}+H_{\mathrm{int}}\right]f(\mathsf{r},\mathsf{p},t)\,\mathrm{d}\mathsf{p}, \tag{107}$$

which vanishes at equilibrium. These formal equations of change need to be supplemented by expressions for $\mathbf{P}$ and q^K in terms of n, v_0, T and their spatial derivatives, in order to get a set of closed equations, namely the hydrodynamic equations, that can be solved for the fluid's motion. Towards that end, fluid dynamics standardly assumes that the energy density is a property of local equilibrium, so is determined completely by equilibrium, as is the density and stream velocity. The Boltzmann equation can be solved, and standardly is solved, with these constraints imposed on the solution. This implies, in particular, that the equation of change for the energy can be expressed as an equation for the change in temperature, using the heat capacity

$$C_v \equiv \frac{\partial\langle\varepsilon\rangle}{\partial T} = \frac{3}{2}k_{\mathrm{B}} + C_{\mathrm{int}}. \tag{108}$$

On removing the convective energy contribution with the help of the equations of change for number density and momentum density, the equation of change for the temperature is

$$\frac{\partial T}{\partial t} = -\mathsf{v}_0\cdot\nabla T - \frac{1}{nC_v}(\mathbf{P}^t:\nabla\mathsf{v}_0 + \mathsf{q}^K). \tag{109}$$

While the pressure tensor is symmetric in the dilute gas case, formally the transpose ^{t} occurs. This is important when angular momentum relaxation is important for the fluid flow.

For a gas close to local equilibrium, the gradients of stream velocity and temperature are small so these are a good measure of how the gas deviates from equilibrium. From the point of view of the equations of change, this suggests that the non-equilibrium part of the pressure tensor $\boldsymbol{\Pi} \equiv \mathsf{P} - nk_{\mathrm{B}}T\mathbf{U}$ and of the heat flux be proportional to these gradients. The governing principle for the nature of the proportionality constants is the Curie principle (see in particular [45]) namely that they have the symmetry of the local equilibrium state. This is reasonable, since the deviation from equilibrium is being treated linearly so that the proportionality constants are local equilibrium properties. In this presentation it is assumed that a magnetic field can be present so the local symmetry is $C_{\infty v}$. Another way of expressing this is to recognize that, except for the magnetic field B, the local equilibrium state is isotropic, so that the only thing with a direction on which the proportionality constants can depend is B. For the heat flux, which is a polar vector (that is, q^K is a vector that is odd to parity (space inversion) while B is a pseudovector, being even to parity), this implies that q^K cannot be dependent only on B, but must be linearly dependent on the temperature gradient, namely

$$\mathsf{q}^K = -\lambda(\mathsf{B})\cdot\nabla T. \tag{110}$$

$\lambda(\mathbf{B})$ is the second rank thermal conductivity tensor that depends on $\mathbf{B}$, whose first index indicates the direction of heat flow while the second index is the direction of the applied temperature gradient. If $\mathbf{B} = 0$, then the thermal conductivity is a scalar, $\lambda(0) = \lambda^0\mathbf{U}$, the usually discussed thermal conductivity. The pressure tensor is second rank so it has 9 individual components, as does the stream velocity gradient. That means there are in general 81 proportionality constants (viscosity coefficients) connecting $\mathbf{\Pi}$ and $\nabla\mathbf{v}_0$. Any symmetry that organizes the result can be a great simplifying feature. In the absence of a magnetic field, the local equilibrium symmetry is that of the improper three-dimensional rotation group O(3). It is useful, and standard to first classify the components of $\mathbf{\Pi}$ and $\nabla\mathbf{v}_0$ according to the irreducible representations of O(3). Thus $\mathbf{\Pi}$ can be written as the linear combination

$$\mathbf{\Pi} = \Pi\mathbf{U} + \varepsilon\cdot\mathbf{P}^a + \mathbf{\Pi}^{(2)}, \tag{111}$$

where the irreducible parts of $\mathbf{\Pi}$, and the corresponding parts of $\nabla\mathbf{v}_0$, have the O(3) group theory associations

Irreducible representation	$\mathbf{\Pi}$	$\nabla\mathbf{v}_0$
1-dimensional	Π	$\nabla\cdot\mathbf{v}_0$
3-dimensional	$\mathbf{P}^a$	$\nabla\times\mathbf{v}_0$
5-dimensional	$\mathbf{\Pi}^{(2)}$	$[\nabla\mathbf{v}_0]^{(2)}$

(112)

and are identified, for the pressure tensor $\mathbf{\Pi}$, as the scalar, antisymmetric (which is equivalent to a vector) and symmetric traceless parts of the second rank tensor, specifically

$$\Pi \equiv \frac{1}{3}\mathbf{U}:\mathbf{\Pi}$$

$$\mathbf{P}^a \equiv -\frac{1}{2}\varepsilon:\mathbf{\Pi}$$

$$\mathbf{\Pi}^{(2)} \equiv \frac{1}{2}[\mathbf{\Pi} + \mathbf{\Pi}^t] - \frac{1}{3}\mathbf{U}[\mathbf{U}:\mathbf{\Pi}]. \tag{113}$$

Similar definitions are appropriate for the stream velocity gradient. ε is the Levi–Civita tensor, see the discussion following equation (86).

In the field independent case, the *phenomenological equations* relating the components of $\mathbf{\Pi}$ and $\nabla\mathbf{v}_0$ are

$$\Pi = -\eta_V^0\nabla\cdot\mathbf{v}_0, \tag{114}$$

$$\mathbf{P}^a = -\eta_r^0\nabla\times\mathbf{v}_0 \tag{115}$$

$$\mathbf{\Pi}^{(2)} = -2\eta^0[\nabla\mathbf{v}_0]^{(2)}, \tag{116}$$

defining the bulk viscosity η_V^0, the rotational relaxation constant η_r^0 and the shear viscosity η^0. The antisymmetric parts only arise when angular momentum effects such as spin relaxation are of importance. This connection is not discussed here, but see [42, 45, 74]. Sine $\mathbf{P}$ is symmetric in this review, essentially because the collision term is treated as local, the neglect of P^{a} is consistent with this limited treatment. On substituting these phenomenological equations into the equations of change, the three hydrodynamical equations: (i) the equation of continuity (103); (ii) the Navier–Stokes equation

$$\frac{\partial \mathbf{v}_0}{\partial t} = - \mathbf{v}_0 \cdot \nabla \mathbf{v}_0 - \frac{1}{nm} \nabla P + \frac{\eta^0}{nm} \nabla^2 \mathbf{v}_0 + \frac{\eta_V^0 + \frac{1}{3}\eta^0}{nm} \nabla\nabla \cdot \mathbf{v}_0 ; \tag{117}$$

and (iii) the ‘heat’ equation

$$\frac{\partial T}{\partial t} = - \mathbf{v}_0 \cdot \nabla T - \frac{1}{nC_v} (P \nabla \cdot \mathbf{v}_0 - \lambda^0 \nabla^2 T) \tag{118}$$

are obtained. This closed set of equations is the usual starting point for most analyses of fluid flow.

For a finite magnetic field, the symmetry group is $C_{\infty v}$ and the irreducible representations of O(3) are reduced into those of $C_{\infty v}$. In particular the 5-dimensional irreducible representation of O(3) reduces completely into five 1-dimensional irreducible representations of $C_{\infty v}$, which are classified according to the weight (eigenvalue) α; $\alpha = - 5, - 4, \ldots, 5$ of the infinitesimal rotation operator about the field direction. These correspond exactly with the spherical harmonics $Y_{2\alpha}(\mathbf{p})$ if the quantity being classified by the group was the second rank tensor $[\mathbf{p}]^{(2)}$. Thus $\Pi^{(2)}$ reduces to the five quantities $\mathbf{\Pi}^{(2,\alpha)}$. Except for $\alpha = 0$, there is only one stream velocity gradient classified by α, thus the phenomenological equations become, for $\alpha \neq 0$,

$$\Pi^{(2,\alpha)} = - 2\eta_\alpha [\nabla \mathbf{v}_0]^{(2,\alpha)}. \tag{119}$$

For $\alpha = 0$ there are two components of the stream velocity gradient that are invariant to a rotation about the symmetry axis, and since these can be coupled, the phenomenological equations for these components become

$$\left.\begin{aligned} \mathbf{\Pi}^{(2,0)} &= - 2\eta_0 [\nabla \mathbf{v}_0]^{(2,0)} + (2/3)^{1/2} \zeta \nabla \cdot \mathbf{v}_0 \\ \mathbf{\Pi} &= (2/3)^{1/2} \zeta [\nabla \mathbf{v}_0]^{(2,0)} - \eta_v \nabla \cdot \mathbf{v}_0 . \end{aligned}\right\} \tag{120}$$

All η_m as well as ζ and η_v are dependent on the magnetic field magnitude B. That the two cross terms between the shear and bulk viscosities are equal is an example of Onsager’s reciprocal relations [45, 75].

> **Technical note:** In this review of the field dependent transport coefficients the spherical components of tensors are used on the basis that such quantities are more familiar to most readers, than are the irreducible Cartesian tensors [76] which are convenient for connecting to the directions of an experimental set-up and used in the literature of this subject. In particular, the coupling of irreducible Cartesian tensors takes some time to properly present, and is not done here. The consequence for this presentation is that there are a number of factors such as the $(2/3)^{1/2}$ that appear arbitrarily introduced. These are in fact conversion factors between the spherical and Cartesian forms for the tensors so that the quantities entering here are consistent with those in the literature as used in the detailed survey of [60].

The method of solving the Boltzmann equation to obtain the hydrodynamic equations is known as the Chapman–Enskog method (see in particular the discussion in [58] or [68] for the reasoning behind this procedure). A simple view is that this method can be considered as a steady state expansion of the Boltzmann equation up to terms linear in the gradients, attributing the time dependence of the density operator to be solely due to the time and spatial dependence of the density, stream velocity and temperature. Such an expansion requires that the Wigner function-density operator be expanded $f = f^{(0)}(1+\phi)$ with a local equilibrium leading term and a perturbation function-operator ϕ that is linear in the gradients. In analogy to the discussion in section 4, the density operator will be diagonal in those energies that are of size comparable to $k_B T$, so in practice, $f^{(0)}$ and ϕ can be assumed to commute.

The expansion of the Boltzmann equation requires the calculation of the time and spatial rates of change of the local equilibrium Wigner function. Equation (64) does this for the Wang-Chang–Uhlenbeck equation, and the only generalization needed of that result, is removing the state label j wherever it occurs and replacing the eigenvalue ε by the internal state hamiltonian H_{int}. The remaining time dependences of n, T and $\mathbf{v}_0$ are removed by using the equations of change (103), (104) and (109), truncated to being first order in gradients. As a result, the linear in gradients part of the Boltzmann equation can be written in what will be referred to as the Chapman–Enskog equation

$$\begin{aligned}\frac{\partial f^{(0)}(\mathbf{r},\mathbf{p})}{\partial t} + \frac{\mathbf{p}}{m}\cdot\nabla f^{(0)}(\mathbf{r},\mathbf{p}) = f^{(0)}(\mathbf{r},\mathbf{p})\Bigg\{&\left(\frac{(\mathbf{p}-m\mathbf{v}_0)^2}{2mk_B T} - \frac{5}{2} + \frac{H_{\mathrm{int}} - \langle H_{\mathrm{int}}\rangle}{k_B T}\right)\frac{\mathbf{p}-m\mathbf{v}_0}{mk_B T}\cdot\nabla\ln T \\ &+ \frac{1}{mk_B T}[\mathbf{p}-m\mathbf{v}_0]^{(2)}:[\nabla\mathbf{v}_0]^{(2)} + \left[\frac{2C_{\mathrm{int}}}{3C_v}\left(\frac{(\mathbf{p}-m\mathbf{v}_0)^2}{2mk_B T} - \frac{3}{2}\right) - \frac{H_{\mathrm{int}} - \langle H_{\mathrm{int}}\rangle}{C_v T}\right]\nabla\cdot\mathbf{v}_0\Bigg\} \\ = -\, f^{(0)}(\mathbf{r},\mathbf{p})(\mathscr{R} + \mathrm{i}\mathscr{L}_{\mathrm{int}})\,\phi. \qquad (121)\end{aligned}$$

The perturbation enters both through the linearization of the collision superoperator appearing in equation (102), which is expressed as the linear collision superoperator $\mathscr{R}$, and the commutator superoperator $\mathscr{L}_{\mathrm{int}}$ of the internal state hamiltonian. At low densities, it is only the Zeeman energy differences that are small enough that they are not fully phase randomized, so the internal state commutator can be simplified to the Zeeman commutator $\mathscr{L}_Z$, and of course the Zeeman energies are negligible as far as contributing to the internal energy, so the internal state hamiltonian H_{int} can be replaced everywhere it appears by the rotational hamiltonian H_{rot}. At low temperatures most simple molecules are effectively in their ground vibrational state, so vibrational excitation can usually be ignored.

To simplify the present review, it is assumed in the following that the gas is isothermal, so that all terms dealing with temperature and energy fluxes are dropped from further discussion. It is also noticed that the coefficient of $\nabla\cdot\mathbf{v}_0$ is the difference between translational and internal energies weighted with different factors such that it is orthogonal to the total energy, see the operator in equation (101). Since it is the divergence of the stream velocity that is associated with the bulk viscosity, it follows that the bulk viscosity is associated with the conversion of translational energy to and from the internal energy.

Since the collision superoperator is rotationally invariant, it follows that the Chapman–Enskog equations can be reduced according to the local symmetry group of the gas, in particular according O(3) if there is no magnetic field and according to $C_{\infty v}$ in the presence of a magnetic field. It is the latter which is assumed in the following, while the field-free case follows as a special case. The perturbation can thus be expanded in the $C_{\infty v}$ irreducible components of $\nabla \mathbf{v}_0$, thus

$$\phi = - \sum_{\alpha} (-1)^{\alpha} \mathbf{B}^{(2,-\alpha)} [\nabla \mathbf{v}_0]^{(2,\alpha)} - B^{(0)} \nabla \cdot \mathbf{v}_0, \tag{122}$$

with tensorial expansion coefficients $\mathbf{B}^{(2,-\alpha)}$ and $B^{(0)}$ dependent on the local thermodynamic equilibrium parameters n and T as well as the vector variables $\mathbf{p} - m\mathbf{v}_0$, $\mathbf{J}$ and $\mathbf{B}$. On the basis that the different components of the stream velocity gradient are independent, the viscosity part of the Chapman–Enskog equation separates into the six equations

$$2[\mathbf{W}]^{(2,-\alpha)} = (\mathscr{R} + \mathrm{i}\mathscr{L}_Z) \mathbf{B}^{(2,-\alpha)} \tag{123}$$

$$\left[\frac{2C_{\mathrm{rot}}}{3C_v} \left(W^2 - \frac{3}{2} \right) - \frac{H_{\mathrm{rot}} - \langle H_{\mathrm{rot}} \rangle}{C_v T} \right] = (\mathscr{R} + \mathrm{i}\mathscr{L}_Z) B^{(0)}. \tag{124}$$

Here the dimensionless momentum $\mathbf{W} \equiv (\mathbf{p} - m\mathbf{v}_0)/(2mk_{\mathrm{B}}T)^{1/2}$, whose magnitude is W has been introduced for notational convenience. A first order approximate solution of these equations is to be obtained by choosing an approximate representation of $\mathbf{B}^{(2,-\alpha)}$ and $B^{(0)}$.

The general expansion of $\mathbf{B}^{(2,-\alpha)}$ and $B^{(0)}$ can be considered. However, for a gas such as N_2, comparison of the theoretical predictions with the experimental field and pressure dependence of the viscosity, shows that a good approximation is obtained by limiting the expansion to

$$\begin{aligned} \mathbf{B}^{(2,-\alpha)} = {} & b_{20}^{(2,-\alpha)} [\mathbf{W}]^{(2,-\alpha)} + b_{D}^{(2,-\alpha)} \left[\frac{2}{3} \left(W^2 - \frac{3}{2} \right) - \frac{H_{\mathrm{rot}} - \langle H_{\mathrm{rot}} \rangle}{C_{\mathrm{rot}}\, T} \right] \\ & + b_{02}^{2,-\alpha} [\mathbf{J}]^{(2,-\alpha)} + \sum_{\beta,\gamma} (-1)^{\beta+\gamma} b_{22,\beta\gamma}^{(2,-\alpha)} [\mathbf{W}]^{(2,\beta)} [\mathbf{J}]^{(2,\gamma)} \end{aligned} \tag{125}$$

$$\begin{aligned} B^{(0)} = {} & b_{D}^{(0)} \left[\frac{2}{3} \left(W^2 - \frac{3}{2} \right) - \frac{H_{\mathrm{rot}} - \langle H_{\mathrm{rot}} \rangle}{C_{\mathrm{rot}}\, T} \right] + \sum_{\beta} (-1)^{\beta} b_{20,\beta}^{(0)} [\mathbf{W}]^{(2,-\beta)} \\ & + \sum_{\beta,\gamma} (-1)^{\beta+\gamma} b_{22,\beta\gamma}^{(0)} [\mathbf{W}]^{(2,\beta)} [\mathbf{J}]^{(2,\gamma)}, \end{aligned} \tag{126}$$

with the $b_{pq,\ldots}^{(\bullet)}$ as constant coefficients (for a fixed n and T) for the four function-operators Φ_{pq}. Several aspects of the notation and choice of expansion terms deserve comments. The notation for the expansion coefficients $b_{pq,\ldots}^{(\bullet)}$ is not standard, but sufficient and descriptive for the present purpose, with p and q denoting the tensorial orders in $\mathbf{W}$ and $\mathbf{J}$, respectively. The two leading terms in each expansion are independent of the directions of $\mathbf{J}$ and have the same form as the ϕ independent parts of the Chapman–Enskog equations. They determine the major contribution to the field-free viscosity coefficients. It is to be noticed that no terms in the expansion contribute to the local average density, stream velocity or energy density, equations (99)–(101), a requirement of the Chapman–Enskog method of solution. The added terms are $\mathbf{J}$ direction dependent and are affected by the magnetic field to determine the field dependence of the viscosity coefficients, namely the Senftleben–Beenakker effects [72]. There is a question as to whether only the angles of **J** should appear in the tensorial terms, rather than the whole vector **J**, since the form listed above gives a very large weighting to large J magnitudes, but since this does not affect the qualitative picture which is emphasized here, this detail will be ignored. Experimentally it has been found that the field dependence of the viscosity is small, being typically of the order of less than 1 %, thus the **J** dependent terms are expected to be of small magnitude so they can be treated in a perturbative manner.

The, in general field dependent, transport coefficients are determined by the scalar expansion coefficients $b_{\cdots}^{(\bullet)}$ according to

$$\eta_\alpha = \frac{1}{2} n k_{\mathrm{B}} T b_{20}^{(2,-\alpha)} \tag{127}$$

$$\eta_V = \frac{2}{3} n k_{\mathrm{B}} T b_D^{(0)} \tag{128}$$

$$\zeta = -\left(\frac{3}{2}\right)^{1/2} n k_{\mathrm{B}} T b_{20,0}^{(0)} = -\left(\frac{2}{3}\right)^{1/2} n k_{\mathrm{B}} T b_D^{(2,0)}. \tag{129}$$

Matrix elements of the six Chapman–Enskog equations with respect to the operators in equations (125) using the above form for the perturbation ϕ gives four equations for each $\mathbf{B}^{(2,-\alpha)}$ component, namely

$$\begin{aligned}
n &= \frac{1}{2} n^2 \langle v \rangle \mathfrak{S}(20) b_{20}^{(2,-\alpha)} + \frac{n^2 \langle v \rangle}{(2N_J)^{1/2}} \mathfrak{S}\begin{pmatrix}20\\02\end{pmatrix} b_{02}^{(2,-\alpha)} \\
&\quad + \frac{n^2 \langle v \rangle}{2(N_J)^{1/2}} \left(\frac{35}{12}\right)^{1/2} \mathfrak{S}\begin{pmatrix}20\\22\end{pmatrix} \sum_{\beta\gamma} \begin{pmatrix}2 & 2 & 2\\ \alpha & \beta & \gamma\end{pmatrix} b_{22,\beta\gamma}^{(2,-\alpha)} \\
0 &= \frac{n^2 \langle v \rangle}{(2N_J)^{1/2}} \mathfrak{S}\begin{pmatrix}02\\20\end{pmatrix} b_{20}^{(2,-\alpha)} + \frac{1}{N_J} (n^2 \langle v \rangle \mathfrak{S}(02) + \mathrm{i} n \alpha \omega_J) b_{02}^{(2,-\alpha)} \\
&\quad + \frac{n^2 \langle v \rangle}{N_J (2)^{1/2}} \left(\frac{35}{12}\right)^{1/2} \mathfrak{S}\begin{pmatrix}02\\22\end{pmatrix} \sum_{\beta\gamma} \begin{pmatrix}2 & 2 & 2\\ \alpha & \beta & \gamma\end{pmatrix} b_{22,\beta\gamma}^{(2,-\alpha)} \\
0 &= \frac{n^2 \langle v \rangle}{2(N_J)^{1/2}} \left(\frac{35}{12}\right)^{1/2} \mathfrak{S}\begin{pmatrix}22\\20\end{pmatrix} \begin{pmatrix}2 & 2 & 2\\ \alpha & \beta & \gamma\end{pmatrix} b_{20}^{(2,-\alpha)} \\
&\quad + \frac{n^2 \langle v \rangle}{(2N_J)^{1/2}} \left(\frac{2C_{\mathrm{v}}}{3C_{\mathrm{rot}}}\right)^{1/2} \mathfrak{S}\begin{pmatrix}22\\D\end{pmatrix} (-1)^\beta \delta_{\beta,-\gamma} b_D^{(2,-\alpha)} \\
&\quad + \frac{n^2 \langle v \rangle}{N_J (2)^{1/2}} \left(\frac{35}{12}\right)^{1/2} \mathfrak{S}\begin{pmatrix}22\\02\end{pmatrix} \begin{pmatrix}2 & 2 & 2\\ \alpha & \beta & \gamma\end{pmatrix} b_{02}^{(2,-\alpha)} \\
&\quad + \frac{1}{2N_J} (n^2 \langle v \rangle \mathfrak{S}(22) - \mathrm{i} n \gamma \omega_J) b_{22,\beta\gamma}^{(2,-\alpha)} \\
0 &= n^2 \langle v \rangle \left(\frac{C_{\mathrm{v}}}{3C_{\mathrm{rot}} N_J}\right)^{1/2} \mathfrak{S}\begin{pmatrix}D\\22\end{pmatrix} \sum_\beta (-1)^\beta b_{22,\beta,-\beta}^{(2,-\alpha)} + \frac{2C_{\mathrm{v}}}{3C_{\mathrm{rot}}} n^2 \langle v \rangle \mathfrak{S}(D) b_D^{(2,-\alpha)}.
\end{aligned} \tag{130}$$

Here the $[\mathbf{J}]^{(2)}$ normalization factor is (for a diamagnetic diatomic)

$$\begin{aligned}\frac{1}{N_J} &= \mathrm{Tr}_{\mathrm{rot}}[\mathbf{J}]^{(2)}\!:\![\mathbf{J}]^{(2)}\exp(-H_{\mathrm{rot}}/k_{\mathrm{B}}T)/5\mathrm{Tr}_{\mathrm{rot}}\exp(-H_{\mathrm{rot}}/k_{\mathrm{B}}T)\\ &= \sum_j (2j+1)j(j+1)[4j(j+1)-3]\exp(-j(j+1)/2Ik_{\mathrm{B}}T)\\ &\quad /30\sum_j (2j+1)\exp(-j(j+1)/2Ik_{\mathrm{B}}T) \end{aligned} \tag{131}$$

while the Zeeman superoperator $\mathscr{L}_Z$ gives rise to the ω_J terms and the kinetic, that is, thermally averaged, cross-sections

$$\mathfrak{S}\begin{pmatrix} jk \\ j'k' \end{pmatrix} = \frac{1}{n^2\langle v\rangle}\mathrm{Tr} f^{(0)}\Phi_{jk}\mathscr{R}\Phi_{j'k'} \tag{132}$$

determine the amount of collisional coupling that occurs between the normalized versions Φ_{jk}, $\Phi_{j'k'}$ of the operators labelled by jk and $j'k'$. $\mathfrak{S}(jk)$ is the diagonal version of this, corresponding to the collisional relaxation of the jk operator. Except for the 'D' operator, all operators are components of tensors so that the rotational invariance of $\mathscr{R}$ restricts what coupling cross-sections can occur. This has been taken into account in the above and is responsible for the presence of the $3j$-coefficients

$$\begin{pmatrix} 2 & 2 & 2 \\ \alpha & \beta & \gamma \end{pmatrix}.$$

On the basis that all cross-sections' coupling velocity and angular momenta are small, the only relaxation cross-section associated with '22' that has been retained is the one which treats the tensorial nature of the collision as if there is no coupling between the velocity and angular momenta. This has been labelled as $\mathfrak{S}(22)$. Again, on the basis that the coupling cross-sections are small, these equations can be solved for $b_{20}^{(2,-\alpha)}$ and $b_D^{(2,-\alpha)}$ to at most second order in the coupling cross-sections. The results of these solutions determine η_α and ζ according to equations (127), to give

$$\begin{aligned}\eta_\alpha = \frac{k_{\mathrm{B}}T}{\langle v\rangle\mathfrak{S}(20)}\Bigg[1 &+ \frac{\mathfrak{S}\binom{20}{02}^2}{\mathfrak{S}(20)\mathfrak{S}(02)}\frac{1}{1+\mathrm{i}\alpha\omega_J\tau_{02}}\\ &+ \frac{35\mathfrak{S}\binom{20}{02}^2}{12\mathfrak{S}(20)\mathfrak{S}(22)}\sum_{\beta\gamma}\begin{pmatrix} 2 & 2 & 2 \\ \alpha & \beta & \gamma \end{pmatrix}^2\frac{1}{1-\mathrm{i}\gamma\omega_J\tau_{22}}\Bigg] \end{aligned} \tag{133}$$

and

$$\begin{aligned}\zeta &= -\left(\frac{35C_{\mathrm{rot}}}{6C_{\mathrm{v}}}\right)^{1/2}\frac{k_{\mathrm{B}}T\mathfrak{S}\binom{D}{22}\mathfrak{S}\binom{22}{20}}{\langle v\rangle\mathfrak{S}(20)\mathfrak{S}(D)\mathfrak{S}(22)}\sum_\beta(-1)^\beta\begin{pmatrix} 2 & 2 & 2 \\ 0 & \beta & -\beta \end{pmatrix}\frac{1}{1+\mathrm{i}\beta\omega_J t_{22}}\\ &= \eta_V^0\left(\frac{3C_{\mathrm{v}}}{4C_{\mathrm{rot}}}\right)^{1/2}\frac{\mathfrak{S}\binom{D}{22}\mathfrak{S}\binom{22}{20}}{\mathfrak{S}(20)\mathfrak{S}(22)}\left[\frac{8\omega_J^2\tau_{22}^2}{1+4\omega_J^2\tau_{22}^2}-\frac{\omega_J^2\tau_{22}^2}{1+\omega_J^2\tau_{22}^2}\right]. \end{aligned} \tag{134}$$

Here $1/\tau_{jk} = n\langle v\rangle\mathfrak{S}(jk)$ is the relaxation rate for the operator associated with jk. It is clear that the cross effect ζ vanishes at zero field. The magnitude of ζ is in agreement with the original publication [72] while there seems to be a typo in the general review [60].

The three equations for the components of $B^{(0)}$ are

$$
\begin{aligned}
n &= \frac{C_V}{C_{\text{rot}}} n^2 \langle v \rangle \mathfrak{S}(D)\, b_D^{(0)} + n^2 \langle v \rangle \left(\frac{3C_V}{4C_{\text{rot}} N_J} \right)^{1/2} \mathfrak{S}\begin{pmatrix} D \\ 22 \end{pmatrix} \sum_\gamma (-1)^\gamma b_{22,-\gamma\gamma}^{(0)} \\
0 &= n^2 \langle v \rangle \left(\frac{C_V}{3C_{\text{rot}} N_J} \right)^{1/2} \mathfrak{S}\begin{pmatrix} 22 \\ D \end{pmatrix} (-1)^\beta \delta_{\beta,-\gamma} b_D^{(0)} + \frac{1}{2N_J} (n^2 \langle v \rangle \mathfrak{S}(22) - \mathrm{i} n \gamma \omega_J)\, b_{22,\beta\gamma}^{(0)} \\
&\quad + \frac{n^2 \langle v \rangle}{2(N_J)^{1/2}} \mathfrak{S}\begin{pmatrix} 22 \\ 20 \end{pmatrix} \left(\frac{35}{12} \right)^{1/2} \sum_\alpha (-1)^\alpha \begin{pmatrix} 2 & 2 & 2 \\ -\alpha & \beta & \gamma \end{pmatrix} b_{20,\alpha}^{(0)} \\
0 &= \frac{n^2}{2} \langle v \rangle \mathfrak{S}(20)\, b_{20,\alpha}^{(0)} + \frac{n^2 \langle v \rangle}{2(N_J)^{1/2}} \mathfrak{S}\begin{pmatrix} 20 \\ 22 \end{pmatrix} \left(\frac{35}{12} \right)^{1/2} \sum_{\beta\gamma} (-1)^{\beta+\gamma} \begin{pmatrix} 2 & 2 & 2 \\ -\alpha & \beta & \gamma \end{pmatrix} b_{22,\beta\gamma}^{(0)} \qquad (135)
\end{aligned}
$$

With the same type of approximations, these determine ζ as given above, as well as the bulk viscosity

$$
\eta_V = \frac{2C_{\text{rot}} k_B T}{3C_V \langle v \rangle \mathfrak{S}(D)} \left[1 + \left(1 + \frac{2}{1 + \omega_J^2 \tau_{22}^2} + \frac{2}{1 + 4\omega_J^2 \tau_{22}^2} \right) \frac{\mathfrak{S}\binom{22}{D}^2}{\mathfrak{S}(22)\mathfrak{S}(D)} \right]. \qquad (136)
$$

The field dependence of all these viscosity coefficients arise through combinations of the form $\omega_J \tau_{jk} \propto B/P$. Thus experimentally the various viscosity coefficients are appropriately expressed as a function of B/P, the ratio of field to pressure. The ratio $\omega_J \tau$ is exactly the ratio of the precession frequency to the collision frequency. Thus if this ratio is large, there are many precessions between each time a molecule collides. As a consequence, when the molecule does again collide, the angular momentum has been randomized in direction and this eliminates such terms from contributing to the momentum transfer, compare the discussion relative to equation (76). At zero field all shear viscosity coefficients η_α are equal, having a dominant contribution from the $[\mathbf{W}]^{(2)}$ component of the perturbation function ϕ plus, within the approximations presented here, small contributions from the $[\mathbf{J}]^{(2)}$ and $[\mathbf{W}]^{(2)}$ $[\mathbf{J}]^{(2)}$components. As the field increases, the latter are phase randomized, so their contributions decrease. That is, at large fields the viscosity coefficients are smaller than at zero field. The bulk viscosity has the same type of behaviour. It needs to be stated that this is the behaviour for many molecular systems, but if operators dependent on odd powers of $\mathbf{J}$ are important, as is usual for molecules with permanent dipoles, then the behaviour can be different. Paramagnetic molecules such as O_2 have a more complicated behaviour because the large gyromagnetic ratio of an electron spin means that the precession of the spin can couple with the rotational angular momentum and significantly influence the detailed nature of the field dependence [77, 78].

Inherently the viscosity is the resistance to flow and depending on the geometry of the apparatus, different viscosity coefficients can, and have, been measured, see [60] for a comprehensive review. Again, flow involves the stream velocity, and viscosity has to do with how the molecular velocity distribution differs from a local equilibrium Maxwellian due to a non-uniform stream velocity. Thus the main contribution to the (shear) viscosity is due to the decay of the directional, in particular the $[\mathbf{W}]^{(2)}$, dependence of the velocity distribution function. For neutral molecules, a magnetic field does not affect the velocity of a molecule so for the field to influence the viscosity, there must be a coupling to the rotational motion of the molecule. Since this can not occur intramolecularly, it must arise via collisional coupling. It is the presence of the resulting non-equilibrium angular momentum part of the density operator that is responsible for the field effects. This necessarily involves collisional coupling from the velocity directions to the angular momentum directions and back again, thus the requirement that the Senftleben–Beenakker effects be quadratic in 'production' cross-sections. As well, the 'relaxation' cross-sections that cause the decay of the angular momentum and velocity non-equilibrium contributions also appear. It is noted in the above that the coupling between shear and bulk viscosities requires the density operator to have aspects of non-equilibrium that simultaneously involve the directions of both velocity and angular momentum, specifically in the above presentation, the operator $[\mathsf{W}]^{(2)}[\mathsf{J}]^{(2)}$. It is only because this operator can have a scalar (rotationally invariant) component that it allows a coupling to the scalar energy difference operator that determines the bulk velocity.

6. Discussion

This review has attempted to describe the basic theoretical concepts governing relaxation and transport of molecular systems in the gas phase with an emphasis on the role of internal states. Necessarily, the author's bias has influenced what is emphasized and discussed, as well as space and time constraints. Anything to do with the decay to equilibrium is naturally associated with an increase in entropy whereas a mechanical system conserves entropy. This review's coverage of this reversibility–irreversibility paradox thus started with a review of the constancy of the N-molecule entropy for a N-molecule mechanical system. The approximate evolution for a dilute gaseous system that leads to irreversibility is governed by the Boltzmann equation. Section 3.1 presented two methods for the 'derivation' of this equation for molecular (quantum) systems while section 3.4 showed how the combination of intramolecular and collisional motion described by the Boltzmann equation implies that the 1-molecule entropy increases until equilibrium is reached. Section 3.5 commented on the contrasting natures of the meanings and properties of these two different entropies.

The Boltzmann equation is simple in concept, namely the description of the time dependence of the distribution of molecular states caused by collisions and the free motion of molecules between collisions. But the quantum version has a number of complex technical aspects that are important for some applications, yet appear to be irrelevant for other applications. These complexities are associated with the inherent quantum property of superposition, which is reflected in the fact that the molecular density operator, expressed as a matrix using an energy parametrized basis, is in general non-diagonal. These can lead to oscillatory time dependent contributions associated with the motion of the molecules between collisions. The collisional treatment of such energy non-diagonal terms requires a careful treatment of all the differing energies that enter into the collision superoperator. This has been reviewed in section 3.2, both in general and for the special case when the collisions are 'on-the-frequency-shell', a case that is often found in practice. In that case the collision superoperator reduces to a simple form. Section 3.3 discussed the further simplifications when the density operator is diagonal in both internal states and momentum, and its extension to allow position dependence with the assumption that collisions are spatially local. It was stressed in section 3.4 that the approach to equilibrium is governed in all cases by a combination of collisional motion which drives diagonal-in-energy elements of the density operator to a Boltzmann distribution, while the non-diagonal-in-energy terms are eliminated by a process of phase randomization, caused by the (free) motion of the molecules between collisions.

Two applications of the general decay have been presented. Section 4 presented the theory of spin decay in the presence of a magnetic field when the decay is dominated by an intramolecular mechanism. Section 5 described the calculation of the set of shear and bulk viscosities and their cross effect in the presence of a magnetic field. These applications illustrate the two limiting cases discussed in section 3.4, and involve a combination of the effects of precession and collisional motions. While the particular mechanism for spin relaxation discussed depends on an intramolecular coupling between the spin and the rotational angular momentum for there to be any relaxation, the field dependence (Senftleben–Beenakker effects) of the viscosities requires an intermolecular (collisional) coupling between velocity and angular momentum components of the density operator.

There are many aspects of kinetic theory which have not been touched upon in this review. The whole area of gas flow according to particular geometries and conditions have not been covered. Usually these can be described using the hydrodynamic equations (103), (117) and (118), supplemented by a set of diffusion equations when the gas is a chemical mixture. But when the gas has large spatial inhomogeneities such as in a shock wave, or the gas is so dilute that the gas is not dominated by collisions and local equilibrium is not a valid first approximation for the density operator, then it is necessary to go back to the Boltzmann equation and solve it by alternate methods. A recent introductory coverage of these topics for a reader interested in applications is the book by Gombosi [65], while a more rigorous coverage is found in the books by Cercignani [69, 70]. The molecular treatment of the physical properties of interstellar gases and the upper atmosphere also require special treatment [79]. Measurements of the field effects at very low density where surface effects are important are reviewed in [60]. If a chemical reaction is very fast, then the velocity distribution of the reactant may be driven out of equilibrium. This has been a problem with a long history of interest. Hot atom reactions are a particular case [80].

Another topic that is very closely related to the general properties of the Boltzmann equation with inclusion of internal states is the absorbtion and emission of radiation and the pressure broadening of spectral lines. Initial formal connections for simple cases [81] and model collision kernels [82] have been made. Recently Monchick [83] has made a detailed comparison of Fano's line shape theory [38] with the properties of the Boltzmann equation. While they share the same frequency parametrized transition superoperator, equation (33), the frequency parameter is the observed frequency in line shape theory, whereas it was stressed in section 3.2 that the Boltzmann equation requires this parameter to be the free particle frequency on which $\mathscr{T}$ acts. A common approximation ignores this difference for the calculation of line width cross-sections, which often leads to reasonable agreement with experiment [39, 84]. But an understanding of the detailed shape of the wings of a spectral line appears to need the more precise treatment.

Much of the modern discussion of the theory of transport coefficients is phrased in terms of time correlation functions [71]. But for gas phase applications, it is well known that the numerical evaluation of the time correlation function reduces to solving an integral equation which is equivalent to the corresponding Chapman–Enskog equation. Such connections have not been discussed here. An advantage of the Boltzmann equation approach, is that it makes a direct connection to the time dependence of the gas a whole by which an assessment can be made whether or not the flow is collisionally dominated and the hydrodynamic equations are valid, or whether a more general description of the flow is needed.

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