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AN EXACTLY SOLUBLE KINETIC EQUATION FOR A CHEMICAL REACTION: EVALUATION OF SEVERAL APPROXIMATION SCHEMES

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A single-velocity-relaxation time Boltzmann equation for an irreversible bimolecular chemical reaction is introduced and solved exactly. The exact results are compared to those of the Chapman–Enskog, Hilbert, multiple-time-scale, and Kapral–Hudson–Ross theories. Non-equilibrium contributions to the chemical rate coefficient, diffusion coefficient, and Rayleigh structure factor are obtained for the exact solution and for each of the above approximations. These non-equilibrium terms are calculated explicitly in the case of a hard-sphere reactive cross section.

1. Introduction

The theoretical study of bimolecular gas-phase reaction kinetics [1 – 10] usually begins with a Boltzmann equation for the distribution function of a reacting species. This equation is then approximately solved by making use of one of several common analytical methods, e.g., the Hilbert perturbation expansion. The resulting (approximate) distribution function then allows the calculation of the average values of the hydrodynamic variables of the reacting species, e.g., the local temperature, velocity, and number density. However, the use of a distribution function which is only an approximate solution of the Boltzmann equation raises questions concerning the validity of the resultant predictions.

The purpose of the research reported in this paper is to investigate the accuracy and range of validity of several approximate solutions of a Boltzmann-like equation for which an exact solution is available. Specifically, we choose to study a single irreversible †, bimolecular, gas-phase chemical reaction with one of the reactants in large excess. Our attention is further restricted to a Boltzmann equation in which the non-reactive collision operator is given in terms of a single velocity relaxation time ††.

In section 3, the exact solution of this model problem is obtained in terms of the parameters of the system and a single quadrature. The long-time behavior of the number density of the dilute reactant is extracted by first asymptotically expanding the dispersion relation in powers of the velocity relaxation time and then keeping only the contribution from the pole whose real part is least negative. This long-time number density immediately determines the chemical rate coefficient, the diffusion coefficient of the dilute reactant, and the Rayleigh light scattering spectrum, all as power series in the velocity relaxation time.

Section 4 contains the approximate solutions of the Boltzmann equation which arise from the Chapman–Enskog (CE) and Hilbert theories. We examine the accuracy of the Hilbert and CE results by making comparisons to the asymptotic expansions of the exact results derived in section 3. A similar analysis of the predictions of the multiple-time-scale ‡ (MTS) and Kapral–Hudson–Ross (KHR) [12] theories is presented in section 5.

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† The reverse reaction was not included because we were not able to solve the Boltzmann equation exactly in this case.

†† Much of the analysis used in this paper was inspired by a series of lectures given at M.I.T. by Visiting Professor E.P. Gross of Brandeis University.

‡ Our treatment of the MTS procedure is based largely on the work of Cukier and Deutch [11].

In section 6, the equilibrium and non-equilibrium contributions to the chemical rate coefficient and to the diffusion coefficient of the dilute reactant are explicitly calculated for an assumed hard-sphere reactive cross section. Section 7 contains our concluding remarks.

Let us now briefly discuss some of the assumptions and conditions involved in the single-relaxation-time Boltzmann equation considered in this research.

2. The model problem

We begin by considering an irreversible, bimolecular gas-phase reaction in which each species possesses a single internal quantum state:

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}. \tag{1}$$

Neglect of the reverse reaction is justified by assuming that the concentration of one reactant (say B) is so large that we need only consider A–B and B–B collisions.

The time dependence of the distribution function of reactant A is now assumed to be governed by the following equation:

$$\partial f_\mathrm{A}(r, \upsilon, t)/\partial t + \upsilon \cdot \nabla f_\mathrm{A}(r, \upsilon, t) = \int \{ f_\mathrm{A}(r, \upsilon', t) f_\mathrm{B}(r, V', t) - f_\mathrm{A}(r, \upsilon, t) f_\mathrm{B}(r, V, t)\} W(\upsilon, V, \upsilon', V')\, \mathrm{d}\upsilon'\, \mathrm{d}V'\, \mathrm{d}V$$

$$- \int f_\mathrm{A}(r, \upsilon, t) f_\mathrm{B}(r, V, t) R(\upsilon, V, \upsilon', V')\, \mathrm{d}\upsilon'\, \mathrm{d}V'\, \mathrm{d}V, \tag{2}$$

where the velocity relaxation kernel (W) and the reaction kernel (R) are taken to be independent of r and t. In subsequent expressions, the r- and t-dependence of $f_\mathrm{A}(r, \upsilon, t)$ and $f_\mathrm{B}(r, \upsilon, t)$ will be suppressed when no confusion can arise. It is consistent to further assume that the initial (the reaction is initiated at $t = 0$) distribution function of species B (taken to be homogeneous in space and maxwellian in velocity) persists * throughout the course of the reaction:

$$f_\mathrm{B}(r, \upsilon, t) = n_\mathrm{B}\, \phi_\mathrm{B}(\upsilon) \tag{3}$$

independent of r for all time, where

$$\phi_\mathrm{B}(\upsilon) \equiv (M_\mathrm{B}/2\pi kT)^{\frac{3}{2}} \exp\left[-M_\mathrm{B}\upsilon^2/2kT\right]. \tag{4}$$

Eqs. (3) and (4), together with the statement of conservation of energy for non-reactive collisions

$$\tfrac{1}{2} m_\mathrm{A} \upsilon^2 + \tfrac{1}{2} m_\mathrm{B} V^2 = \tfrac{1}{2} m_\mathrm{A} \upsilon'^2 + \tfrac{1}{2} m_\mathrm{B} V'^2 \tag{5}$$

allow us to rewrite eq. (2) in the form

$$\partial f_\mathrm{A}/\partial t + \upsilon \cdot \nabla f_\mathrm{A} = \int \{ f_\mathrm{A}(\upsilon')\, \phi_\mathrm{A}(\upsilon) - f_\mathrm{A}(\upsilon)\, \phi_\mathrm{A}(\upsilon')\} S(\upsilon|\upsilon')\, \mathrm{d}\upsilon' - f_\mathrm{A}(\upsilon)\, T(\upsilon), \tag{6}$$

where the kernel $S(\upsilon|\upsilon')$ is defined as

$$S(\upsilon|\upsilon') = n_\mathrm{B} \int [\phi_\mathrm{B}(V)\, \phi_\mathrm{B}(V')/\phi_\mathrm{A}(\upsilon)\, \phi_\mathrm{A}(\upsilon')]^{\frac{1}{2}}\, W(\upsilon, V, \upsilon', V')\, \mathrm{d}V'\, \mathrm{d}V, \tag{7}$$

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* For any desired order of accuracy in the calculation of f_A, the number density of species B can be chosen to be so large that n_B remains essentially unchanged throughout the course of the reaction.

and the reaction function T is given by

$$T(v) = n_B \int \phi_B(V) R(v, V, v', V') \, dv' \, dV' \, dV. \tag{8}$$

The model equation to which we restrict our attention for the remainder of this paper is obtained from eq. (6) by taking $S(v|v')$ to be a constant:

$$S(v|v') = \kappa, \tag{9}$$

which is the reciprocal of the velocity relaxation time * for species A. Our model problem is therefore stated in terms of the following Boltzmann-like equation

$$\partial f_A/\partial t + v \cdot \nabla f_A = -[\kappa + T(v)] f_A + \kappa \phi_A(v) n_A(r, t), \tag{10}$$

where the local number density of species A is

$$n_A(r, t) = \int f_A(r, v, t) \, dv.$$

3. Exact solution of model problem

The exact solution of eq. (10) is most readily accomplished by introducing the Fourier–Laplace transform of $f_A(r, v, t)$:

$$\bar{f}(k, v, z) = \int dr \int_0^\infty dt \, f_A(r, v, t) \exp[-ik \cdot r - zt]. \tag{11}$$

Substituting the transform into eq. (10) yields the following equation for $\bar{f}(k, v, z)$

$$[z + ik \cdot v + \kappa + T] \bar{f}(k, v, z) = \bar{f}(k, v, t = 0) + \kappa \phi_A(v) \bar{n}(k, z), \tag{12}$$

where

$$\bar{f}(k, v, t = 0) = \int dr \, f_A(r, v, t = 0) \exp[-ik \cdot r] \tag{13}$$

and

$$\bar{n}(k, z) = \int dv \, \bar{f}(k, v, z). \tag{14}$$

Eq. (12) gives the distribution function $\bar{f}$ in terms of the unknown number density $\bar{n}$. To obtain a closed algebraic equation for $\bar{n}$, we multiply eq. (12) by

$$\Lambda(k, v, z, \kappa) = [z + \kappa + T + ik \cdot v]^{-1} \tag{15}$$

and integrate over velocity. This gives an equation for $\bar{n}$ whose solution is

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* κ depends on temperature and number density as follows: $\kappa = \bar{\kappa} (kT/\mu)^{1/2} n_B$, where μ is the reduced mass of an A–B pair, and $\bar{\kappa}$ is the velocity relaxation cross section.

$$\bar{n}(\boldsymbol{k}, z) = [1 - \kappa \int \Lambda(\boldsymbol{k}, z, \boldsymbol{v}, \kappa)\, \phi_A(v)\, d\boldsymbol{v}]^{-1} \int \Lambda(\boldsymbol{k}, \boldsymbol{v}, z, \kappa)\, \bar{f}(\boldsymbol{k}, \boldsymbol{v}, t = 0)\, d\boldsymbol{v}. \tag{16}$$

This is an exact formal result for $\bar{n}(k, z)$ in terms of the initial distribution function, the parameters of the problem, and the quadratures involving Λ. Thus, the exact distribution function is given from eq. (12) by

$$\bar{f}(\boldsymbol{k}, \boldsymbol{v}, z) = \Lambda\, [\bar{f}(\boldsymbol{k}, \boldsymbol{v}, t = 0) + \kappa\, \phi_A(v)\, \bar{n}(\boldsymbol{k}, z)]\,. \tag{17}$$

From the theory of Laplace transforms, we know that the time behaviors of $f_A(\boldsymbol{r}, \boldsymbol{v}, t)$ and $n_A(\boldsymbol{r}, t)$ are determined by the functional dependences of $\bar{f}$ and $\bar{n}$, respectively, on the complex variable z. For example, a simple pole at $z = \tilde{z}$ implies a time dependence given by $\exp[\tilde{z}t]$. From eq. (17) it is clear that $\bar{f}$ possesses the same z-behavior as $\bar{n}$ except for an additional simple pole whose location in the z-plane is given by

$$z_s(\kappa, \boldsymbol{k}, \boldsymbol{v}) = -\kappa - T(v) - i\boldsymbol{k} \cdot \boldsymbol{v}. \tag{18}$$

Because we have in mind a situation for which the velocity relaxation rate is larger than the chemical reaction rate

$$\kappa > T(v), \text{ but not necessarily } \kappa \gg T(v), \tag{19}$$

the pole given in eq. (18) contributes to the short-time behavior [*] of $f_A(\boldsymbol{r}, \boldsymbol{v}, t)$.

The long-time dependence of f_A and n_A is what we are probing when we make experimental observations concerning the time behavior of the average values of the hydrodynamical variables of the reacting system. This long-time behavior is governed by the pole of $\bar{n}$ whose real part is least negative. To locate this pole, we first *asymptotically* expand [**] the dispersion relation

$$1 - \int \phi_A(v)\, \{1 + \kappa^{-1}\, [z + T + i\boldsymbol{k} \cdot \boldsymbol{v}]\}^{-1}\, d\boldsymbol{v} = 0 \tag{20}$$

in powers of κ^{-1}. The resulting expansion, when truncated at jth order in κ^{-1}, gives a jth-order polynomial equation in z to be solved for the poles of $\bar{n}$. Taking [†] $j = 2$, we find only one pole which does not violate the original condition

$$|\kappa| > |\,\mathrm{Re}\, z\,| \tag{21}$$

on the asymptotic expansion. This long-time pole is given as follows

$$z_0(k) = -\langle T \rangle + \kappa^{-1} \langle \delta T^2 \rangle - \kappa^{-2} \langle \delta T^3 \rangle - k^2\, [\tfrac{1}{3}\, \kappa^{-1} \langle v^2 \rangle - \kappa^{-2} \langle v^2\, \delta T \rangle], \tag{22}$$

where

$$\delta T(v) = \mathrm{T}(v) - \langle T \rangle \tag{23}$$

and the bracket means an average over $\phi_A(v)$, e.g.,

$$\langle T \rangle = \int d\boldsymbol{v}\, \phi_A(v)\, T(v). \tag{24}$$

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[*] Exponentially decaying time dependence whose time constant is of the same order of magnitude as κ is called short-time behavior. If the exponential decay constant is smaller in magnitude than κ, we refer to this as long-time behavior.

[**] The coefficients in this asymptotic expansion, which are obtained by expanding the integral in eq. (20) in powers of κ^{-1}, are given by $(-1)^n \int \phi_A(\boldsymbol{v})\, [z + T + i\boldsymbol{k} \cdot \boldsymbol{v}]^n\, d\boldsymbol{v}$. The remainder term in the expansion will be small if κ obeys $|\kappa|^3 \gg |\langle (z + T)^3 \rangle - k^2 \langle v^2\, (z + T) \rangle|$. Considering κ as given, this inequality restricts the values of z and k for which the long-time pole given in eq. (22) exists.

[†] In the research reported here we obtain all results to second order in κ^{-1}. This choice was made because the interesting features arise already in this order.

The residue of $\bar{n}\,(k, z)$ at the pole z_0 is found to be

$$R_0\,(k) = \bar{n}\,(k, t = 0)\,\{1 - \kappa^{-2}\,[\,\langle \delta T^2\rangle - \tfrac{1}{3}\,k^2\,\langle v^2\rangle]\}\,, \tag{25}$$

where $\bar{n}\,(k, t = 0)$ is the spatial Fourier transform of the initial number density of species A. The short-time poles of $\bar{n}$, whose residues are of order κ^{-2} or smaller, will not be discussed further in this paper. In arriving at the result given in eq. (25), we have taken the initial distribution function to be

$$f_A\,(r, v, t = 0) = n_A\,(r, t = 0)\,\phi_A\,(v), \tag{26}$$

with $n_A\,(r, t = 0)$ arbitrary. This initial condition is assumed for the remainder of the paper.

Knowing the long-time pole z_0 and its associated residue $R_0\,(k)$, we can now write the long-time components of $\bar{n}\,(k, t)$ and $\bar{f}\,(k, v, t)$ as *

$$\bar{n}^{\,\mathrm{LT}}\,(k, t) = R_0\,(k)\,\exp\,[z_0(k)\,t]\;, \tag{27}$$

$$\bar{f}^{\,\mathrm{LT}}\,(k, v, t) = R_0\,(k)\,\phi_A\,(v)\,\exp\,[z_0(k)\,t]\{1 - \kappa^{-1}\,[\delta T + \mathrm{i}k\cdot v] - \kappa^{-2}\,[\langle\delta T^2\rangle - \tfrac{1}{3}\,k^2\,\langle v^2\rangle - (\delta T + \mathrm{i}k\cdot v)^2]\}, \tag{28}$$

with $z_0\,(k)$ and $R_0\,(k)$ given in eqs. (22) and (25), respectively. The effective chemical rate coefficient k_{rate} for the reaction described in eq. (1) can be extracted from the exponential time coefficient of $\bar{n}^{\,\mathrm{LT}}\,(k, z)$ as follows

$$n_B\,k_{\mathrm{rate}} = -\lim_{k\to 0}\,z_0\,(k) = \langle T\rangle - \kappa^{-1}\,\langle\delta T^2\rangle + \kappa^{-2}\,\langle\delta T^3\rangle. \tag{29}$$

Also, the diffusion coefficient of species A is identified as the coefficient of $-k^2$ in the pole $z_0\,(k)$

$$D_A = \tfrac{1}{3}\,\kappa^{-1}\,\langle v^2\rangle - \kappa^{-2}\,\langle v^2\delta T\rangle. \tag{30}$$

The non-equilibrium terms ** in k_{rate} and D_A arise because of the coupling between the velocity relaxation and the chemical reaction. If $T\,(v)$ were independent of velocity, the fluctuation $\delta T\,(v)$ would be zero and the non-equilibrium corrections would vanish identically.

A generalized frequency-dependent rate coefficient $k_{\mathrm{rate}}\,(z)$ may be introduced by Laplace transforming the generalized rate equation

$$\mathrm{d}\bar{n}\,(k \to 0, t)/\mathrm{d}t = -\int_0^t \mathrm{d}t'\,n_B\,k_{\mathrm{rate}}\,(t-t')\,\bar{n}\,(k \to 0, t') \tag{31a}$$

to give

$$n_B\,k_{\mathrm{rate}}\,(z) = \lim_{k\to 0}\,[\bar{n}\,(k, t = 0)/\bar{n}\,(k, z) - z]. \tag{31b}$$

Substituting the general expression † for $\bar{n}\,(k, z)$

$$\bar{n}\,(k, z) = \sum_{i=0}^{\infty}\,R_i(k)\,[z - z_i\,(k)]^{-1} \tag{32}$$

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* Notice that, even to first order in κ^{-1}, the long-time distribution function is not of the local-equilibrium form.

** By non-equilibrium terms we mean those terms involving the fluctuation $\delta T\,(v)$.

† This expression must be modified if $\bar{n}$ has poles which are not simple, but the argument presented below is still valid. In this argument we *do* assume that $\bar{n}$ has no cuts in the z-plane. This assumption is justified by the fact that the expansion of the dispersion relation in powers of κ^{-1}, when truncated at a finite order, gives a finite-order polynomial in z to be solved for the poles of $\bar{n}$.

into eq. (31b) yields an expression for $k_{\text{rate}}(z)$ in terms of the poles and residues of $\bar{n}$:

$$n_{\text{B}}\, k_{\text{rate}}(z) = \lim_{k\to 0} \left\{ \bar{n}\,(k, t=0) \left[\sum_i R_i(k)\,(z-z_i)^{-1} \right]^{-1} - z \right\}. \tag{33}$$

Notice that the zero-frequency limit of $n_{\text{B}}\, k_{\text{rate}}(z)$ does not agree with the effective rate coefficient $n_{\text{B}}\, k_{\text{rate}}$ found in eq. (29). On the other hand, it is clear that the following limit

$$\lim_{z\to -n_{\text{B}}k_{\text{rate}}} n_{\text{B}}\, k_{\text{rate}}(z) = n_{\text{B}}\, k_{\text{rate}} \tag{34}$$

does give the correct long-time chemical rate coefficient. This example indicates the care that must be taken in using zero-frequency transport coefficients in hydrodynamic theories; the zero-frequency limit is plainly not always appropriate.

Knowledge of the exact long-time number density also allows us to calculate the generalized structure factor $S(k, \omega)$ for low frequency Rayleigh light scattering. Assuming that the polarizability of species A is much larger than that of species B, and that only fluctuations in the local number density contribute to fluctuations in the local dielectric coefficient, we find [*]

$$S(k,\omega) \equiv (2/V)\,\text{Re}\,\langle \bar{n}\,(k, z=-\text{i}\omega)\,\bar{n}\,(-k)\rangle = (2/V)\,\langle \bar{n}\,(k)\,\bar{n}\,(-k)\rangle \left\{1-\kappa^{-2}\left[\langle \delta T^2\rangle - \tfrac{1}{3}k^2\langle v^2\rangle\right]\right\} \left[-z_0/(\omega^2+z_0^2)\right]. \tag{35}$$

The half width at half height Γ of this lorentzian line is given as follows

$$\Gamma(k) = n_{\text{B}}\, k_{\text{rate}} + k^2 D_{\text{A}}. \tag{36}$$

The short-time poles of $\bar{n}\,(k, z)$ will contribute to $S(k, \omega)$ in the form of broad high-frequency lines whose amplitudes are of order κ^{-2} or smaller. By extrapolating the experimental low-frequency Rayleigh width to zero scattering angle (corresponding to $k \to 0$), one can measure the chemical rate coefficient $n_{\text{B}}k_{\text{rate}}$. Also, the angular dependence (k-dependence) of $\Gamma(k)$ can be used to extract the diffusion coefficient D_{A}. Finally, the density dependence [**] of the line width can, in principle, yield the non-equilibrium contributions to $n_{\text{B}}\, k_{\text{rate}}$ and D_{A}.

Having obtained asymptotic expansions of the *exact* $n_{\text{B}}\, k_{\text{rate}}$, D_{A}, $S(k, \omega)$, $\bar{n}^{\text{LT}}(k, t)$ and $\bar{f}^{\text{LT}}(k, v, t)$, let us now turn to investigate the results of several theories which yield only approximate solutions of the model Boltzmann equation. Mathematically, emphasis is placed on the difference between using an ansatz expansion of $\bar{f}\,(k, v, z)$ in solving the Boltzmann equation and asymptotically expanding the exact $\bar{f}\,(k, v, z)$, once it has been found. Physically, we are interested in determining under what conditions (on the reactive and non-reactive collision cross sections) the approximate distribution functions can deviate significantly from the exact $\bar{f}\,(k, v, t)$, especially for long times.

4. The Hilbert and Chapman–Enskog theories

In the Hilbert approximation method [†], we assume that the distribution function $\bar{f}\,(k, v, z)$ can be expanded in powers of κ^{-1}

$$\bar{f}\,(k, v, z) = \sum_{m=0}^{\infty} \bar{f}_m\,(k, v, z)\,\kappa^{-m}. \tag{37}$$

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[*] The brackets here indicate an average over the equilibrium ensembles of the system.

[**] See footnote * on page 29.

[†] Much of our treatment of the Hilbert and Chapman–Enskog methods follows the excellent paper by Hauge [13]. We refer the interested reader to this paper for mathematical details.

The coefficients $\bar{f}_m$ in this expansion are determined by substituting the above ansatz into eq. (12) and equating each power of κ^{-1}. The resulting set of equations is compactly written with the aid of the projection operator P defined by

$$P\,g(v) \equiv \phi_{\mathrm{A}}(v) \int g(\mathbf{v}')\,\mathrm{d}\mathbf{v}' \tag{38}$$

as follows

$$(1-P)\,\bar{f}_0(k,\mathbf{v},z) = 0, \tag{39a}$$

$$(1-P)\,\bar{f}_{m+1}(k,\mathbf{v},z) = \bar{f}_m(k,\mathbf{v},t=0) - (z + \mathrm{i}k\cdot\mathbf{v} + T)\,\bar{f}_m(k.\mathbf{v},z), \tag{39b}$$

$$P\bar{f}_m = [z + \langle T\rangle]^{-1}\,\{P\bar{f}_m(k,\mathbf{v},t=0) - P\,[\,(z + T + \mathrm{i}k\cdot\mathbf{v})\,(1-P)\,\bar{f}_m]\}\,, \quad m \geqslant 0. \tag{39c}$$

The complete $\bar{f}$ is, of course, the sum of $P\bar{f}$ and $(1-P)\bar{f}$. The initial distribution function has also been expanded in powers of κ^{-1}

$$\bar{f}\,(k,\mathbf{v},t=0) = \sum_{m=0}^{\infty} \bar{f}_m(k,\mathbf{v},t=0)\,\kappa^{-m}. \tag{40}$$

To solve the above system of equations recursively, we need only know the projected components $P\bar{f}_m(k,\mathbf{v},t=0)$ of the initial distribution function; the orthogonal components $(1-P)\,\bar{f}_m(k,\mathbf{v},t=0)$ are *determined* by eqs. (39a) and (39b). Moreover, we see from eq. (39c) that the complete $\bar{f}\,(k,\mathbf{v},z)$ and $\bar{n}\,(k,z)$ will involve the sum $\Sigma_{m=0}^{\infty}\,\kappa^{-m}\,P\bar{f}_m(k,\mathbf{v},t=0)$ $[\,= P\bar{f}\,(k,\mathbf{v},t=0)]$. Therefore, the *only initial information* required in the Hilbert scheme is the projection $P\bar{f}\,(k,\mathbf{v},t=0)$; the *individual* $P\bar{f}_m(k,\mathbf{v},t=0)$ are not required. It is a general feature of the Hilbert theory that only the hydrodynamic moments $[P\bar{f}\,(k,\mathbf{v},t=0)$ in our case$]$ of the initial distribution are necessary as input data.

Before presenting and analyzing the results of the Hilbert formalism, we will briefly sketch the philosophy and mathematics of the CE theory. The *identical results* of the Hilbert and CE approximations will then be treated simultaneously.

In the CE theory we assume that the z-dependence of the distribution function $\bar{f}\,(k,\mathbf{v},z)$ can be attributed completely to a functional dependence on $\bar{n}\,(k,z)$:

$$\bar{f}\,(k,\mathbf{v},z) = \bar{f}\,(k,\mathbf{v},\bar{n}\,(k,z)). \tag{41}$$

Because our model Boltzmann equation is linear in $\bar{f}$, the distribution function must be a *linear functional* of $\bar{n}\,(k,z)$. This relationship can be expressed as follows

$$\bar{f}\,(k,\mathbf{v},z) = \phi_{\mathrm{A}}(v)\,\bar{n}\,(k,z)\,[1 + F(k,\mathbf{v})]\,. \tag{42a}$$

The form of $\bar{f}$ in eq. (42a) has been chosen so that $F(k,\mathbf{v})$ represents the deviation of $\bar{f}$ from local equilibrium. From eq. (42a) it follows that $F(k,\mathbf{v})$ must obey

$$0 = \int \phi_{\mathrm{A}}(v)\,F(k,\mathbf{v})\,\mathrm{d}\mathbf{v}, \tag{42b}$$

which in turn implies that

$$(1-P)\,\bar{f}\,(k,\mathbf{v},z) = F(k,\mathbf{v})\,P\bar{f}\,(k,\mathbf{v},z). \tag{42c}$$

Thus, in the CE approximation, the $(1-P)\,\bar{f}$ component of the distribution function is related to the $P\bar{f}$ component by the proportionality factor $F(k,\mathbf{v})$ which is *independent of z*.

Premultiplying the model Boltzmann equation by P and then by $(1-P)$ gives a pair of equations * for the two components $P\bar{f}$ and $(1-P)\bar{f}$ of the distribution function. The resultant solution for $(1-P)\bar{f}$ (in terms of $F(k, \mathbf{v})$ and the parameters of the problem) is then set equal to $F(k, \mathbf{v})$ times the solution for $P\bar{f}$ (according to eq. (42c)). This step results in a closed integral equation for $F(k, \mathbf{v})$

$$1 + F(k, \mathbf{v}) = \{1 + \kappa^{-1} [\mathrm{i}k \cdot \mathbf{v} + T - \langle T \rangle - g(k)]\}^{-1} \tag{43a}$$

where

$$g(k) = \int \phi_{\mathrm{A}}(v)\, (\mathrm{i}k \cdot \mathbf{v} + T(\mathbf{v}))\, F(k, \mathbf{v})\, \mathrm{d}\mathbf{v}\,. \tag{43b}$$

Using eq. (42b) and eq. (43a) we find an equation which determines the value of $g(k)$ to any order in κ^{-1}

$$1 = \int \phi_{\mathrm{A}}(v)\, \{1 + \kappa^{-1} [\mathrm{i}k \cdot \mathbf{v} + \delta T - g(k)]\}^{-1}\, \mathrm{d}\mathbf{v}\,. \tag{43c}$$

Expanding the above integral asymptotically to order κ^{-2} yields an equation for $g(k)$ whose solution is

$$g(k) = -z_0(k) + \langle T \rangle, \tag{43d}$$

which, when substituted into eq. (43a), gives the function $F(k, \mathbf{v})$ to order κ^{-2}.

The distribution functions and number densities resulting from the Hilbert and CE theories are identical as power series in κ^{-1}, and are given as follows

$$\bar{n}(k, z) = \bar{n}(k, t=0)\, [z + \langle T \rangle]^{-1} \left\{ 1 + \kappa^{-1} \frac{\langle \delta T^2 \rangle - \frac{1}{3} k^2 \langle v^2 \rangle}{z + \langle T \rangle} - \kappa^{-2} \frac{\langle \delta T^3 \rangle - k^2 \langle v^2 \delta T \rangle}{z + \langle T \rangle} + \kappa^{-2} \frac{[\langle \delta T^2 \rangle - \frac{1}{3} k^2 \langle v^2 \rangle]^2}{[z + \langle T \rangle]^2} \right\} \tag{44a}$$

and

$$\bar{f}(k, \mathbf{v}, z) = \bar{n}(k, z)\, \phi_{\mathrm{A}}(v)\, \{1 - \kappa^{-1} [\delta T + \mathrm{i}k \cdot \mathbf{v}] - \kappa^{-2} [\langle \delta T^2 \rangle - \tfrac{1}{3} k^2 \langle v^2 \rangle] + \kappa^{-2} [\delta T + \mathrm{i}k \cdot \mathbf{v}]^2\}\,. \tag{44b}$$

By expanding the exact *long-time* results of eqs. (27) and (28) in powers of κ^{-1}, we find agreement with the above Hilbert–CE results *except* for the replacement of the exact residue $R_0(k)$ by the initial number density * $\bar{n}(k, t=0)$. This replacement can be seen from eq. (25) to give rise to errors of order κ^{-2}. We notice that the expansion of $\bar{n}(k, z)$ in powers of κ^{-1} given in eq. (44a) is equivalent to order κ^{-2} to the following

$$\bar{n}(k, z) = \bar{n}(k, t=0)\, \{z + \langle T \rangle - \kappa^{-1} [\langle \delta T^2 \rangle - \tfrac{1}{3} k^2 \langle v^2 \rangle] + \kappa^{-2} [\langle \delta T^3 \rangle - k^2 \langle v^2 \delta T \rangle]\}^{-1}, \tag{44c}$$

which possesses the exact *long-time* pole defined in eq. (22). Thus the chemical rate coefficient and diffusion coefficient contained in the Hilbert–CE number density are exact; only the amplitude (residue) of the number density is in error.

From eqs. (31b), (35), and (44a) we easily calculate the frequency-dependent rate coefficient and Rayleigh structure factor for the Hilbert–CE number density

$$n_{\mathrm{B}}\, k_{\mathrm{rate}}(z) = -\lim_{k \to 0} z_0(k) = n_{\mathrm{B}}\, k_{\mathrm{rate}} \tag{45}$$

and

$$S(k, \omega) = (2/V)\, \langle \bar{n}(k)\, \bar{n}(-k) \rangle\, [-z_0/(\omega^2 + z_0^2)]\,. \tag{46}$$

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* See footnote † on page 32.

** This point is discussed in more detail by Hauge [13] for the non-reactive case.

The Hilbert–CE frequency dependent rate coefficient is equal to the exact effective rate coefficient, independent of z; whereas the above structure factor is in error as a consequence of the replacement of the exact residue $R_0(k)$ by $\bar{n}(k, t=0)$. The angle-dependent error in $S(k, \omega)$ is, according to eq. (25), of second order in κ^{-1}.

From the discussion of this section, we see that neither the Hilbert nor the CE theory is capable of producing the correct long-time behavior of $\bar{f}(k, \mathbf{v}, t)$ and $\bar{n}(k, t)$. Assuming that the prescriptions of the Hilbert and CE methods have been correctly applied to the model problem, we must therefore conclude that the basic assumptions expressed in eqs. (37) and (42a) are not entirely valid. The z-dependence of the exact $\bar{f}$ cannot be attributed to a functional dependence on $\bar{n}(k, z)$, and the exact $\bar{f}$ cannot be *analytically* expanded in powers of κ^{-1}. This last statement does not mean that the exact distribution function, once calculated, cannot be *asymptotically* expanded in powers of κ^{-1}, as was done in section 3.

Although our stated conclusions are based on results of a specific model calculation, they are certainly valid because they are of a negative nature. Also, our statements regarding the zero-frequency limit of $n_B k_{\text{rate}}(z)$ are easily seen to be valid, independent of the model considered in this paper.

Let us now turn to investigate two alternative approaches to approximately solving our Boltzmann equation. These theories begin by assuming a different type of expansion of $f_A(r, \mathbf{v}, t)$ than that assumed in the Hilbert method.

5. The multiple-time-scale and Kapral–Hudson–Ross theories

To begin the MTS analysis [11] we introduce an ordering parameter λ into the Boltzmann equation

$$\partial f_A / \partial t + \mathbf{v} \cdot \nabla f_A = \kappa \phi_A(v)\, n_A(r, t) - \kappa f_A - \lambda T(\mathbf{v}) f_A(r, \mathbf{v}, t). \tag{47}$$

The value of λ will eventually be allowed to approach unity through positive numbers. The next step is to replace the single time variable t by a *set* of variables $\{t_0, t_1, t_2, \ldots\}$, each of which is considered to be independent. The distribution function and number density, treated as functions of this set of variables, are then expanded in powers of λ

$$f_A(r, \mathbf{v}, t_0, t_1, \ldots) = \sum_{m=0}^{\infty} \lambda^m f_A^{(m)}(r, \mathbf{v}, t_0, t_1, \ldots), \tag{48}$$

$$n_A(r, t_0, t_1, \ldots) = \sum_{m=0}^{\infty} \lambda^m n_A^{(m)}(r, t_0, t_1, \ldots). \tag{49}$$

The time derivative is also formally expanded in powers of λ

$$\partial/\partial t = \sum_{m=0}^{\infty} \lambda^m \partial/\partial t_m. \tag{50}$$

Substituting eqs. (48–50) into eq. (47) and equating coefficients of each power of λ generates a set of equations to be solved for the unknowns $f_A{}^{(m)}(r, \mathbf{v}, t)$ and $n_A{}^{(m)}(r, t)$. For example, the first two equations are written as

$$\partial f_A^{(0)} / \partial t_0 + \mathbf{v} \cdot \nabla f_A^{(0)} = -\kappa f_A^{(0)} + \kappa \phi_A n_A^{(0)}, \tag{51}$$

$$\partial f_A^{(1)} / \partial t_0 + \partial f_A^{(0)} / \partial t_1 + \mathbf{v} \cdot \nabla f_A^{(1)} = -\kappa f_A^{(1)} + \kappa \phi_A n_A^{(1)} - T f_A^{(0)}. \tag{52}$$

The set of MTS equations are to be solved subject to the initial conditions

$$f_{\mathrm{A}}^{(0)}(r, \mathbf{v}, 0, 0, \ldots) = \phi_{\mathrm{A}}(v)\, n_{\mathrm{A}}(r, t = 0), \tag{53a}$$

$$f_{\mathrm{A}}^{(m)}(r, \mathbf{v}, 0, 0, \ldots) = 0 \qquad \text{for } m \geqslant 1, \tag{53b}$$

where the initial number density $n_{\mathrm{A}}(r, t = 0)$ is *given* as input to the calculation. The additional freedom gained by introducing multiple time variables is used to eliminate secular behavior whenever it arises in solving the MTS equations. The resulting MTS distribution function and number density are functions of the time variables $(t_0, t_1, \ldots)$. To return to the single-time-variable language, we replace t_m by $\lambda^m t$ and allow the parameter λ to approach unity through positive numbers.

Before discussing the results of the MTS theory, we will develop an extension (to higher orders in λ) of the procedure proposed by Kapral et al. [12]. We can then simultaneously analyze the *identical results* of the MTS and KHR formalisms.

The original KHR theory was restricted to a spatially homogeneous reacting system. For ease of presentation, we maintain this restriction in our development, while giving final results for the spatially inhomogeneous case.

The starting point of the KHR procedure is the assumption that $f_{\mathrm{A}}(r, \mathbf{v}, t)$ can be written as follows

$$f_{\mathrm{A}} = f_{\mathrm{A}}^{\mathrm{LE}}(r, \mathbf{v}, t)\, [1 + \lambda\, \chi^{(1)}(r, \mathbf{v}, t) + \lambda^2 \chi^{(2)}(r, \mathbf{v}, t) + \ldots], \tag{54}$$

where $f_{\mathrm{A}}^{\mathrm{LE}}$ is a local-equilibrium distribution function

$$f_{\mathrm{A}}^{\mathrm{LE}}(r, \mathbf{v}, t) = n_{\mathrm{A}}(r, t)\, [m_{\mathrm{A}}/2\pi k\, T(r, t)]^{3/2} \exp\left[-m_{\mathrm{A}} v^2/2k\, T(r, t)\right]. \tag{55}$$

and the $\chi^{(m)}(r, \mathbf{v}, t)$ are to be calculated by following the procedure outlined below. Because of the assumed large excess of species B, the local temperature $T(r, t)$ will not deviate appreciably from the temperature T appearing in $\phi_{\mathrm{A}}(v)$. Hence, for our special conditions, the local-equilibrium distribution function is equal to the local number density n_{A} multiplied by $\phi_{\mathrm{A}}(v)$.

The second step of the KHR method is to use eqs. (54) and (55) to write

$$\mathrm{d}f_{\mathrm{A}}/\mathrm{d}t = \phi_{\mathrm{A}}\, [1 + \lambda\, \chi^{(1)} + \ldots]\, \mathrm{d}n_{\mathrm{A}}/\mathrm{d}t + n_{\mathrm{A}}\, \phi_{\mathrm{A}}\, [\lambda\, \mathrm{d}\chi^{(1)}/\mathrm{d}t + \lambda^2\, \mathrm{d}\chi^{(2)}/\mathrm{d}t + \ldots]. \tag{56}$$

Integrating eq. (47) over velocity gives, in the spatially homogeneous case,

$$\mathrm{d}n_{\mathrm{A}}/\mathrm{d}t = -\lambda\, n_{\mathrm{A}} \langle T\rangle - \lambda^2 n_{\mathrm{A}} \int \phi_{\mathrm{A}}(v)\, \chi^{(1)}(r, \mathbf{v}, t)\, T(\mathbf{v})\, \mathrm{d}\mathbf{v}, \tag{57}$$

which, when substituted into eq. (56), yields the first of two expressions for $\mathrm{d}f_{\mathrm{A}}/\mathrm{d}t$. The second expression is obtained directly from eq. (47):

$$\mathrm{d}f_{\mathrm{A}}/\mathrm{d}t = -\kappa\, \phi_{\mathrm{A}}\, n_{\mathrm{A}}\, [\lambda\, \chi^{(1)} + \lambda^2 \chi^{(2)} + \ldots] - \lambda\, T \phi_{\mathrm{A}}\, n_{\mathrm{A}}\, [1 + \lambda\, \chi^{(1)} + \ldots]. \tag{47$'$}$$

We can now obtain a set of equations for the $\chi^{(m)}(r, \mathbf{v}, t)$ by first setting $\mathrm{d}f_{\mathrm{A}}/\mathrm{d}t$ as given in eq. (47′) equal to the result of substituting eq. (57) into eq. (56), and then equating the coefficients of each power of λ. For example, the first two equations in this set are

$$\mathrm{d}\chi^{(1)}(r, \mathbf{v}, t)/\mathrm{d}t = -\kappa\, \chi^{(1)} - \delta\, T(\mathbf{v}) \tag{58a}$$

and

$$\mathrm{d}\chi^{(2)}/\mathrm{d}t + \kappa\, \chi^{(2)} = -\delta\, T(\mathbf{v})\, \chi^{(1)} + \int \phi_{\mathrm{A}}(\mathbf{v})\, \chi^{(1)}(\mathbf{v})\, T(\mathbf{v})\, \mathrm{d}\mathbf{v}, \tag{58b}$$

whose solutions, subject to the initial condition

$$f_{\mathrm{A}}(r, \mathbf{v}, t=0) = n_{\mathrm{A}}(r, t=0)\, \phi_{\mathrm{A}}(v) \tag{59a}$$

are given (still for the spatially homogeneous case) by

$$\chi^{(1)}(\mathbf{v}, t) = -\kappa^{-1}\, \delta T(\mathbf{v})\, [1 - \exp(-\kappa t)] \tag{59b}$$

and

$$\chi^{(2)}(\mathbf{v}, t) = \kappa^{-2}\, [\delta T^2(\mathbf{v}) - \langle \delta T^2 \rangle]\; [\kappa t \exp(-\kappa t) + 1 - \exp(-\kappa t)]\,. \tag{59c}$$

The distribution functions and number densities resulting from the MTS and KHR theories are identical as power series in κ^{-1} and are given, for the spatially *inhomogeneous* case, as follows

$$\begin{aligned} f(k, \mathbf{v}, t) = \bar{n}(k, t=0)\, \phi_{\mathrm{A}} \exp(z_0 t)\, \{ & 1 - \kappa^{-1} [\delta T + ik \cdot \mathbf{v}]\, (1 - \exp(-\kappa t)) \\ & + \kappa^{-2} [\, (\delta T^2 - 2 \langle \delta T^2 \rangle + \tfrac{2}{3} k^2 \langle v^2 \rangle + (ik \cdot \mathbf{v})^2 + 2\, \delta T\, ik \cdot \mathbf{v})\, (1 - \exp(-\kappa t)) \\ & + (\delta T^2 - \langle \delta T^2 \rangle + \tfrac{1}{3} k^2 \langle v^2 \rangle + (ik \cdot \mathbf{v})^2)\, \kappa t \exp(-\kappa t)] \} \end{aligned} \tag{60}$$

and

$$\bar{n}(k, t) = \bar{n}\, (k, t=0) \exp(z_0 t)\, \{1 - \kappa^{-2}\, [\langle \delta T^2 \rangle - \tfrac{1}{3} k^2 \langle v^2 \rangle]\, (1 - \exp(-\kappa t))\}\,, \tag{61}$$

where $z_0\,(k)$ is the exact long-time pole of eq. (22).

By expanding the exact long-time results of eqs. (27) and (28) in powers of κ^{-1}, we find complete agreement with the *long-time limits* of eqs. (60) and (61). Although the long-time components of the MTS–KHR distribution function and number density are correct, the short-time contributions are characterized by a time constant κ which is not a solution of the dispersion relation [eq. (20)]. Thus, the MTS–KHR results are valid for long times only.

The effective chemical rate coefficient and diffusion coefficient contained in the long-time limit of the MTS–KHR number density are exact, as are the frequency-dependent rate coefficient and Rayleigh structure factor calculated using eqs. (31b), (35) and (61).

From the discussion of this section, we see that the MTS and KHR theories yield identical distribution functions which agree with the exact result for long time. However, the short-time component of the MTS–KHR distribution function is not exact. Assuming that the prescriptions of the MTS and KHR procedures have been carried out correctly, we therefore conclude that the expansions of $f_{\mathrm{A}}\,(r, \mathbf{v}, t)$ assumed in eqs. (48) and (54) are not valid. The exact distribution function cannot be *analytically* expanded in powers of $\boldsymbol{\lambda}$, as can be seen from eqs. (22) and (27).

6. Calculations for an assumed reactive cross section

For the hard-sphere reactive cross section $\sigma\,(u)$ defined by

$$\begin{aligned} \sigma(u) &= 0 \qquad\qquad , \quad \text{if } u \leqslant \bar{u}\,, \\ &= \bar{\sigma}\,(1 - \bar{u}^2/u^2), \quad \text{if } u \geqslant \bar{u}\,, \end{aligned} \tag{62}$$

we can calculate the equilibrium and non-equilibrium contributions to the chemical rate coefficient $n_{\mathrm{B}} k_{\mathrm{rate}}$ and to the diffusion coefficient of species A (D_{A}). This calculation is carried out so that we can gain some insight regarding the conditions under which the non-equilibrium corrections become significant.

The reaction function $T(\mathbf{v})$ which appears in our expressions for $n_{\mathrm{B}} k_{\mathrm{rate}}$ and D_{A} is related to the cross section $\sigma\,(u)$ in the following manner

$$T(\mathbf{v}) = n_B \int \phi_B(\mathbf{V})\, R(\mathbf{v}, \mathbf{V}, \mathbf{v}', \mathbf{V}')\, d\mathbf{v}'\, d\mathbf{V}'\, d\mathbf{V}, \tag{63}$$

where the reaction kernel $R(\mathbf{v}, \mathbf{V}, \mathbf{v}', \mathbf{V}')$ is given by

$$R(\mathbf{v}, \mathbf{V}, \mathbf{v}', \mathbf{V}') = \delta(\boldsymbol{w} - \boldsymbol{w}')\, \delta(\tfrac{1}{2}\mu u^2 - \tfrac{1}{2}\mu u'^2 - \Delta E)\ [u\,\sigma(u)/u'^2]. \tag{64}$$

The notation in the above equations is as follows

Before reactive collision		After reactive collision	
velocity of A molecule	$\mathbf{v}$	velocity of C molecule	$\mathbf{v}'$
velocity of B molecule	$\mathbf{V}$	velocity of D molecule	$\mathbf{V}'$
reduced mass	μ	reduced mass	μ'
center-of-mass velocity	$\boldsymbol{w}$	center-of-mass velocity	$\boldsymbol{w}'$
relative velocity	$\boldsymbol{u}$	relative velocity	$\boldsymbol{u}'$

and ΔE is the change in internal energy for the reaction: $\Delta E = E_C + E_D - E_A - E_B$.

The equilibrium contribution to D_A is independent of any assumption about the reactive cross section, and is given by

$$\tfrac{1}{3}\kappa^{-1}\langle v^2\rangle = (kT/\mu)^{1/2}(\mu/m_A)(n_B\bar{\kappa})^{-1}, \tag{65}$$

where the velocity relaxation time has been expressed in terms of a velocity relaxation cross section $\bar{\kappa}$ as

$$\kappa = (kT/\mu)^{1/2} n_B \bar{\kappa}. \tag{66}$$

The equilibrium contribution to $n_B k_{\text{rate}}$ is easily calculated using eqs. (62) – (64)

$$\langle T\rangle = \int \phi_A(v)\, T(\mathbf{v})\, d\mathbf{v} = 8\,\bar{\sigma}\, n_B\, (2\pi k T/\mu)^{1/2} \exp[-\mu \bar{u}^2/2kT]. \tag{67}$$

This is of the familiar Arrhenius form with frequency factor A given in terms of the reaction amplitude $\bar{\sigma}$

$$A = 8\, n_B\, \bar{\sigma}\, (2\pi kT/\mu)^{1/2} \tag{68a}$$

and the activation energy expressed in terms of the threshold speed $\bar{u}$

$$E_{\text{act}} = \tfrac{1}{2}\mu\bar{u}^2. \tag{68b}$$

The non-equilibrium corrections to D_A and $n_B k_{\text{rate}}$ are given for the hard-sphere cross section, respectively, as follows

$$-\kappa^{-2}\langle v^2 \delta T\rangle = -\frac{8\bar{\sigma}}{n_B \bar{\kappa}^2}\left(\frac{2\pi kT}{\mu}\right)^{1/2}\left(\frac{m_B - \mu}{m_A + m_B}\right)\left(1 + \frac{\mu\bar{u}^2}{2kT}\right)\exp\left[1 - \frac{\mu\bar{\mu}^2}{2kT}\right], \tag{69}$$

and

$$\kappa^{-1}\langle \delta T^2\rangle = \frac{128\,\pi\,\bar{\sigma}^2 n_B}{\bar{\kappa}}\left(\frac{kT}{\mu}\right)^{1/2}\frac{m_A^2}{m_B \mu^{3/2}}\, F(\mu, m_A, m_B, T)\exp\left[-\frac{\mu\bar{u}^2}{kT}\right], \tag{70}$$

where $F(\mu, m_A, m_B, T)$ is a very complicated function which is bounded by zero and unity. Because we are interested here only in determining under what conditions the above non-equilibrium corrections become significant, the precise value of F is unimportant and will not be discussed further.

By forming the ratios of eq. (69) to eq. (65) and of eq. (70) to eq. (67), we see that the non-equilibrium terms can amount to a significant fraction of the equilibrium contributions, if two conditions are fulfilled. First, the ratio of the reaction amplitude $\overline{\sigma}$ to the velocity relaxation cross section $\overline{\kappa}$ must be non-negligible. Secondly, the ratio of the threshold energy $\frac{1}{2}\,\mu\overline{u}^2$ to the thermal energy kT must be of the order of unity or smaller, i.e., $\exp\,[-\mu\overline{u}^2/2kT]$ must be non-negligible. Many ion–molecule reactions are prime candidates for satisfying these two conditions.

These conclusions regarding the *relative* magnitudes of the equilibrium and non-equilibrium terms in no way involve the dominant number density n_{B}. Only the threshold energy and cross section for reaction and velocity relaxation are involved.

7. Concluding remarks

For the single-velocity-relaxation-time Boltzmann equation introduced in section 2, we have obtained expressions for the exact number density and distribution function in terms of the parameters of the problem and a single quadrature. By expanding the quadrature in powers of κ^{-1}, and truncating at second order, asymptotic expansions of $\overline{n}\ (k, z)$ and $\overline{f}\ (k, v, z)$ were derived. The long-time limits of $\overline{n}$ and $\overline{f}$ were extracted from these asymptotic expansions by calculating the pole z_0 and the residue $R_0\ (k)$ (also to second order in κ^{-1}). Finally, the exact long-time number density was used to predict the frequency-dependent rate coefficient $n_{\mathrm{B}}k_{\mathrm{rate}}\ (z)$ and the Rayleigh structure factor $S\ (k, \omega)$.

The results of applying the Chapman–Enskog and Hilbert approximation schemes to the model Boltzmann equation indicate that the exact distribution function cannot be analytically expanded in powers of κ^{-1} and that the assumed functional dependence of $\overline{f}$ on $\overline{n}$ does not hold. The CE–Hilbert distribution function agreed with the exact long-time $\overline{f}$, except for the replacement of the residue $R_0\ (k)$ by $\overline{n}\ (k, t = 0)$, which causes an error of order κ^{-2}. The number density and Rayleigh structure factor were also in error due to the difference between $R_0\ (k)$ and $\overline{n}\ (k, t = 0)$. The frequency-dependent rate coefficient in the CE–Hilbert approximation was found to be equal to the exact chemical rate coefficient, independent of frequency. The main conclusion to be drawn here is that the CE and Hilbert theories can be used to calculate the long-time number density and distribution function if one is satisfied with accuracy to first order in κ^{-1}.

The MTS and KHR formalisms were found to give the exact long-time distribution function for our model problem. Of course, the long-time number density, Rayleigh structure factor, and frequency-dependent rate coefficient were also exact. However, the short-time components of the MTS–KHR results possess a time constant κ which is not a solution of the dispersion relation in eq. (20). This implies that the analytic expansion of $f_{\mathrm{A}}\ (r, v, t)$ in powers of λ, which is assumed in both the MTS and KHR theories, cannot be carried out for the exact distribution function. The MTS and KHR procedures seem to offer the possibility of going beyond the CE–Hilbert results in calculating the long-time behavior of a chemically reacting system. They do not, however, allow prediction of the exact short-time dependence of $f_{\mathrm{A}}\ (r, v, t)$.

The results presented in section 6 give us some indication of the magnitude of the non-equilibrium terms which arise in the expansion of $f_{\mathrm{A}}, n_{\mathrm{A}}, n_{\mathrm{B}}k_{\mathrm{rate}}$, and D_{A} in powers of κ^{-1}. For the hard-sphere model reactive cross section, it was found that these non-equilibrium corrections can be significant if two conditions are met. First, the threshold energy $\frac{1}{2}\,\mu\overline{u}^2$ of the reaction must be small with respect to the thermal energy kT. Secondly, the amplitude of the reactive cross section σ must be of the same order of magnitude as the velocity-relaxation cross section $\overline{\kappa}$. Prime candidates for displaying such non-equilibrium effects are very fast ion–molecule reactions.

Although it is difficult to generalize from results of a specific model problem, we can be certain that our *negative* conclusions regarding the Hilbert–CE and MTS–KHR theories are valid. Moreover, we feel that the model calculations presented here can be of some intuitive use in understanding how non-equilibrium corrections to $n_{\mathrm{B}}k_{\mathrm{rate}}$ and D_{A} can arise and under what circumstances they become non-negligible.

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