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Nonequilibrium Kinetics: Exact and Approximate Solutions[1]

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The relaxation of an internal state distribution in the presence of an excess of an inert gas is considered. The explicit time dependence of the nonequilibrium contributions to the transition rate coefficients is approximated using the Kapral–Hudson–Ross method. The resulting solution contains cross-correlation terms which do not appear when a single reaction is considered. It is shown that the first term of a perturbation expansion of an exact formal solution gives the Kapral–Hudson–Ross solution for short times, and the Chapman–Enskog solution at long times if there is a wide separation in time scales. The Kapral–Hudson–Ross, Chapman–Enskog, and exact solutions are compared for a two-state, hard-sphere model system.

KEY WORDS: Chemical kinetics; nonequilibrium statistical mechanics; correlation functions; Boltzmann equation; Chapman–Enskog solutions; inelastic relaxation; projection operator.

1. INTRODUCTION

In a dilute gas, bimolecular reaction rates are found by averaging reactive cross sections over the velocity and internal state distributions. Usually it

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is assumed that these are Maxwellian distributions, which yields the equilibrium rate coefficients. Away from chemical equilibrium, however, the reaction perturbs the Maxwellian distributions. The more reactive parts of the distribution are relatively depleted for the reactants and enriched for the products when the reaction is going in the forward direction. Nonreactive collisions tend to restore the Maxwellian distributions, but the distributions will always be somewhat perturbed, and the actual rate will be smaller than that calculated using the equilibrium rate coefficients. Much of the work treating the nonequilibrium contributions to the rate has been based on a modification of the Chapman–Enskog (CE) perturbation theory.(1–7) In a previous paper(8),[5] it was shown that for isothermal systems the first CE nonequilibrium contribution to the reaction rate coefficients can be expressed as an autocorrelation function expression. This method, denoted as the KHR method, considers the explicit time dependence of the perturbed distributions, in contrast to the CE theory, which considers only the variation on the time scale of the chemical reaction. The KHR solution asymptotically approaches the CE correction on the microscopic time scale characterizing momentum relaxation. A crucial assumption made in both treatments is that momentum relaxation is much faster than chemical relaxation.

In this paper we apply the KHR method to the relaxation of an internal state distribution in the presence of an excess of an inert gas. It is assumed that a generalized Boltzmann equation (the Wang-Chang–Uhlenbeck equation) may be used to describe the time evolution of the system. If this is true, the transitions between different energy levels can be considered to be a set of coupled reactions. The expression derived for the nonequilibrium contribution to the transition rates contains cross-correlation terms which do not appear when only a single reaction is considered. An exact formal solution to this problem can be obtained easily because the equations are linear in the perturbed distribution functions, unlike the general reaction problem. We show that if the exact solution is expanded in a perturbation series, and if the assumption that there is a wide separation of time scales can be made, then the first term of the perturbation series yields the KHR and CE solutions. In Section 4, the exact, KHR, and CE solutions are compared for a model two-state, hard-sphere system.

2. THE KHR SOLUTION

The system we consider is a spatially homogeneous gas-phase mixture of molecules with internal structure dilutely dispersed in a structureless gas X. The presence of an excess of species X simplifies the problem in two ways.

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[5] Equations (2.31) and (2.32) in Ref. 8 do not, as stated, hold in general, but only when the reaction does not affect the temperature of the system.

First, it keeps the temperature of the system nearly constant during the relaxation of the internal state distribution, and second, since almost all collisions suffered by any molecule are with an X molecule, the collision operators are linear. The velocity distribution of the X molecules is not appreciably perturbed by the internal relaxation, and therefore can be assumed to be a Maxwell–Boltzmann distribution

$$f_x{}^0(\mathbf{v}_x, t) = n_x(m_x/2\pi kT)^{3/2} \exp(-m_x v_x{}^2/2kT) \tag{1}$$

The time dependence of the velocity distribution $f_i(\mathbf{v}_i, t)$ for molecules in internal state i is governed by a Boltzmann equation

$$\begin{aligned} \frac{\partial f_i(\mathbf{v}_i, t)}{\partial t} = & \int [f_i(\mathbf{v}_i{}', t) f_x{}^0(\mathbf{v}_x{}') - f_i(\mathbf{v}_i, t) f_x{}^0(\mathbf{v}_x)]\sigma_i(|\mathbf{v}_i - \mathbf{v}_x|, \Omega) \\ & \times |\mathbf{v}_i - \mathbf{v}_x| \, d\Omega \, d\mathbf{v}_x + \gamma \sum_{j \neq i} \int [f_j(\mathbf{v}_j{}', t) f_x{}^0(\mathbf{v}_x{}') - f_i(\mathbf{v}_i, t) f_x{}^0(\mathbf{v}_x)] \\ & \times \sigma_{ij}^*(|\mathbf{v}_i - \mathbf{v}_x|, \Omega)|\mathbf{v}_i - \mathbf{v}_x| \, d\Omega \, d\mathbf{v}_x \end{aligned} \tag{2}$$

Here σ_i is the elastic scattering cross section for molecules in internal state i, σ_{ij}^* is the inelastic scattering cross section for the transition of molecules from the ith to the jth internal state, and γ is a formal ordering parameter, which is used to indicate that the inelastic collision operator is being treated as a perturbation to the elastic collision operator. The distribution functions are normalized to the number densities for the various internal states at time t

$$\int f_i(\mathbf{v}_i, t) \, d\mathbf{v}_i = n_i(t) \tag{3}$$

and can be written in the form

$$f_i = f_i{}^0(1 + \gamma\varphi_i^{(1)} + \gamma^2\varphi_i^{(2)} + \cdots) \tag{4}$$

where

$$f_i{}^0(\mathbf{v}_i, t) = n_i(t)(m/2\pi kT)^{3/2} \exp(-mv_i{}^2/2kT) \tag{5}$$

and m is the mass of the molecules with internal structure. The rate at which transitions from the ith to the jth internal state occur is given by

$$n_i(t)k_{ij}(t) = \gamma \int f_i(\mathbf{v}_i, t) R_{ij}(\mathbf{v}_i) \, d\mathbf{v}_i \tag{6}$$

with R_{ij} defined by

$$R_{ij} \equiv \int f_x{}^0(\mathbf{v}_x)\sigma_{ij}^*|\mathbf{v}_i - \mathbf{v}_x| \, d\Omega \, d\mathbf{v}_x \tag{7}$$

The rate coefficients can be expanded in powers of γ,

$$k_{ij} = \gamma k_{ij}^{(0)} + \gamma^2 k_{ij}^{(1)} + \gamma^3 k_{ij}^{(2)} + \cdots \tag{8}$$

The first term is the equilibrium transition rate coefficient,

$$k_{ij}^{(0)} = (1/n_i)\int f_i{}^0 R_{ij}\, d\mathbf{v}_i \tag{9}$$

and the remaining terms are nonequilibrium corrections, which are given by

$$k_{ij}^{(n)} = \langle \varphi_i^{(n)} R_{ij} \rangle_i \tag{10}$$

where $\langle\ \rangle_i$ represents the equilibrium average of a function of v_i,

$$\langle g \rangle_i \equiv (1/n_i)\int f_i{}^0(v_i) g(v_i)\, d\mathbf{v}_i \tag{11}$$

Keeping only terms linear in γ in Eq. (2), we obtain the following equation for the time dependence of $\varphi_i^{(1)}$,[8]

$$\partial\varphi_i^{(1)}/\partial t = -\mathscr{L}_i\varphi_i^{(1)} + \sum_{j\neq i} \delta R_{ij}(v_i)[\exp(-\beta\mathscr{A}_{ij}) - 1] \tag{12}$$

where

$$\mathscr{L}_i\varphi_i^{(1)} = \int f_x{}^0(\varphi_i^{(1)} - \varphi_i^{(1)\prime})\sigma_i|\mathbf{v}_i - \mathbf{v}_x|\, d\Omega\, d\mathbf{v}_x \tag{13}$$

and

$$\delta R_{ij}(\mathbf{v}_i) \equiv R_{ij}(\mathbf{v}_i) - \langle R_{ij}\rangle_i = R_{ij}(\mathbf{v}_i) - k_{ij}^{(0)} \tag{14}$$

$\mathscr{A}_{ij}$ is the affinity for the transition of molecules from the ith to the jth internal state. In terms of the internal energies ϵ_i and ϵ_j and the number densities of these two states, $\mathscr{A}_{ij}$ is defined by

$$\exp(-\beta\mathscr{A}_{ij}) = (n_j/n_i)\exp[-\beta(\epsilon_i - \epsilon_j)] \tag{15}$$

If we assume that initially the system is in a state of local equilibrium so that $\varphi_i^{(1)}(v_i, t = 0)$ vanishes, then the solution to Eq. (12) is

$$\varphi_i^{(1)}(v_i, t) = \sum_{j\neq i} [\exp(-\beta\mathscr{A}_{ij}) - 1]\int_0^t \exp(-\mathscr{L}_i t')\, \delta R_{ij}(v_i)\, dt' \tag{16}$$

provided t is small enough that the number densities have not changed appreciably in this time. Defining

$$\delta R_{ij}(\mathbf{v}_i, t) = \exp[-\mathscr{L}_i t]\, \delta R_{ij}(\mathbf{v}_i) \tag{17}$$

and substituting $\varphi_i^{(1)}$ from Eq. (16) into Eq. (10), we obtain the KHR solution for $k_{ij}^{(1)}$,

$$k_{ij}^{(1)}(t) = \sum_{k \neq i} [\exp(-\beta \mathscr{A}_{ik}) - 1] \int_0^t \langle \delta R_{ij}\, \delta R_{ik}(t') \rangle_i \, dt' \tag{18}$$

This expression contains cross-correlation terms not found in the KHR solution for a single reaction. These arise because the $i \rightarrow k$ and $k \rightarrow i$ transitions perturb f_i, and therefore affect the rate at which transitions from the ith to the jth level occur.

If the momentum and internal relaxation times are well separated, $\langle \delta R_{ij}\, \delta R_{ik}(t') \rangle$ will decay to zero before there is any appreciable change in the number densities, and the upper limit t in Eq. (18) can be extended to infinity to give the CE solution.(8)

3. THE EXACT SOLUTION

In this section an exact solution for $k_{ij}(t)$ will be found using a projection operator method.(9–11) The projection operator P_{ii} is defined by

$$P_{ii} X(v_i) = [f_i^0(v_i)/n_i] \int X(v_i)\, d\mathbf{v}_i \tag{19}$$

The P_{ii} are the elements of a diagonal matrix of operators $\mathbf{P}$. Letting $\mathbf{f}$ be a vector whose components are the distribution functions f_i for the various internal states, we obtain

$$(\mathbf{Pf})_i = f_i^0(v_i) \tag{20}$$

and

$$[(1 - \mathbf{P})\mathbf{f}]_i = h_i(v_i) = f_i^0[\gamma\varphi_i^{(1)} + \gamma^2\varphi_i^{(2)} + \cdots] \tag{21}$$

It is convenient to rewrite Eq. (2) as

$$\partial\mathbf{f}/\partial t = -(\mathbf{L}_E + \gamma\mathbf{L}_I)\mathbf{f} \tag{22}$$

$\mathbf{L}_E$ and $\mathbf{L}_I$ are matrices of elastic and inelastic collision operators, respectively. $\mathbf{L}_E$ is a diagonal matrix whose elements are related to the previously defined collision operator $\mathscr{L}_i$ by

$$L_{E,ii}(f_i^0\psi_i) = f_i^0\mathscr{L}_i\psi_i \tag{23}$$

Equations for the time dependence of $\mathbf{f}^0(t)$ and $\mathbf{h}(t)$ can be found using Eqs. (20)–(22). Solving for $\mathbf{h}(t)$, we obtain

$$\mathbf{h}(t) = -\int_0^t dt'\, \mathbf{G}(t')(1 - \mathbf{P})(\mathbf{L}_E + \gamma\mathbf{L}_I)\mathbf{f}^0(t - t') + \mathbf{G}(t)\mathbf{h}(0) \tag{24}$$

where

$$\mathbf{G}(t) \equiv \exp[-(1 - \mathbf{P})(\mathbf{L}_E + \gamma \mathbf{L}_I)t] \tag{25}$$

We will assume, as in the previous section, that $\mathbf{h}(t = 0) = 0$, and comment on this assumption later. Since elastic collisions conserve the number density in any internal state, and do not alter Maxwell–Boltzmann velocity distributions,

$$\mathbf{PL}_E = \mathbf{L}_E\mathbf{P} = 0 \tag{26}$$

Therefore, Eq. (24) can be simplified to

$$\mathbf{h}(t) = -\gamma \int_0^t dt' \, \mathbf{G}(t')(1 - \mathbf{P})\mathbf{L}_I\mathbf{f}^0(t - t') \tag{27}$$

The nonequilibrium contribution to the rate coefficient is given by

$$k_{ij}(t) - \gamma k_{ij}^{(0)} = [\gamma/n_i(t)] \int R_{ij}(v_i)h_i(v_i, t) \, d\mathbf{v}_i \tag{28}$$

Using Eqs. (2), (7), (14), and (19), it can be shown that

$$-[(1 - \mathbf{P})\mathbf{L}_I\mathbf{f}^0(t - t')]_k = f_k{}^0(t - t') \sum_{l \neq k} \delta R_{kl}(v_k)\{\exp[-\beta\mathscr{A}_{kl}(t - t')] - 1\} \tag{29}$$

When this expression is used in Eq. (27) and the resulting expression for h_i is substituted into Eq. (28), we have

$$\begin{aligned} k_{ij}(t) - \gamma k_{ij}^{(0)} = \frac{\gamma^2}{n_i(t)} \sum_k \sum_{l \neq k} \int d\mathbf{v}_i \int_0^t dt' \, R_{ij}G_{ik}(t')f_k{}^0(t - t') \, \delta R_{kl} \\ \times \{\exp[-\beta\mathscr{A}_{kl}(t - t')] - 1\} \end{aligned} \tag{30}$$

This equation provides us with a formal solution for $k_{ij}(t) - \gamma k_{ij}^{(0)}$ in terms of the elastic and inelastic collision operators, and the number densities in the time interval $(0, t)$.

Comparing Eqs. (18) and (30), we see that both the exact and the KHR solutions for the nonequilibrium contributions to the rate coefficients contain similar factors $[\exp(-\beta\mathscr{A}_{kl}) - 1]$. These are a measure of how far removed the internal state distribution is from complete equilibrium. Their presence ensures that the nonequilibrium contributions to the transition rates are small when the system is close to equilibrium, and vanish at complete equilibrium. Each term on the right-hand side of Eq. (30) also contains a factor δR_{kl} [see Eqs. (7), (9), and (14)]. This is the difference between the velocity-dependent $k \rightarrow l$ inelastic collision frequency and its equilibrium average. These factors are a measure of how much the inelastic relaxation perturbs the Maxwell–Boltzmann velocity distributions. The δR_{kl} will be small if the inelastic collision frequencies are either small or do not depend strongly on velocity. The presence of a comparable factor in the CE solution has been noted and discussed by Shizgal and Karplus.(7)

The propagator G [Eq. (25)] can be expanded in powers of γ by repeatedly applying the operator identity

$$\exp[-(A+B)t] = \exp(-At) - \int_0^t \exp[-A(t-t')]B\exp[-(A+B)t']\,dt' \tag{31}$$

with $A = (1-\mathbf{P})\mathbf{L}_E = \mathbf{L}_E$ and $B = \gamma(1-\mathbf{P})\mathbf{L}_I$. Substituting the expanded form of G in Eq. (30) and keeping only the lowest order term in γ, we obtain

$$\begin{aligned} k_{ij}(t) - \gamma k_{ij}^{(0)} &= \frac{\gamma^2}{n_i(t)} \sum_{k\neq i} \int d\mathbf{v}_i \int_0^t dt'\, R_{ij} \exp[-L_{E,ii}t'] \\ &\quad \times f_i^0(t-t')\,\delta R_{ik}\{\exp[-\beta\mathscr{A}_{ik}(t-t')] - 1\} + O(\gamma^3) \\ &= \frac{\gamma^2}{n_i(t)} \sum_{k\neq i} \int d\mathbf{v}_i \int_0^t dt'\, R_{ij} f_i^0(t-t') \exp[-\mathscr{L}_i t'] \\ &\quad \times \delta R_{ik}\{\exp[-\beta\mathscr{A}_{ik}(t-t')] - 1\} + O(\gamma^3) \\ &= \frac{\gamma^2}{n_i(t)} \sum_{k\neq i} \int_0^t dt'\, n_i(t-t') \langle \delta R_{ij}\, \delta R_{ik}(t')\rangle_i \\ &\quad \times \{\exp[-\beta\mathscr{A}_{ik}(t-t')] - 1\} + O(\gamma^3) \end{aligned} \tag{32}$$

If t is small enough that the number densities are still very close to their initial values, then this first term reduces to the KHR solution, Eq. (18). This first term also will asymptotically yield the CE solution at any time after the initial transient behavior provided that the correlation functions $\langle \delta R_{ij}\, \delta R_{ik}(t')\rangle_i$ decay to zero before there is any appreciable change in the number densities [i.e., $n_j(t-t') \sim n_j(t)$ for any t' small enough that $\langle \delta R_{ij}\, \delta R_{ik}(t')\rangle_i$ contributes significantly to the integral in the final expression of Eq. (32)]. This analysis indicates that the CE correction to the rate will be accurate only if $\gamma(1-\mathbf{P})\mathbf{L}_I(1-\mathbf{P})$ is a small perturbation to the elastic collision operator $\mathbf{L}_E$ and if the momentum relaxation time is much smaller than the internal relaxation time. These conditions may not be met simultaneously. For example, even when there is a fairly wide separation in the time scales, the internal relaxation might substantially perturb $\mathbf{L}_E$ if the inelastic collision frequencies $R_{ij}(v_i)$ depend very strongly on velocity. An effect of this type seems to occur in Widom's step-ladder model,(12) which was devised to study the effect that the disturbance to an internal state distribution caused by a reaction has on the rate of reaction. Even though the nonequilibrium correction is large, it is believed that there is a wide separation in time scales for this model. (The rate was not expanded in a perturbation series, but the nonequilibrium contribution can be so large that good convergence of such a series would not be expected.)

In obtaining solutions for $k_{ij}(t) - \gamma k_{ij}^0$ we have assumed that the velocity distributions are initially unperturbed so that $\mathbf{h}(t = 0) = 0$. In general, of course, this will not be true and we should include the $\mathbf{G}(t)\mathbf{h}(0)$ term in Eq. (24). $\mathbf{G}(t)$ can be expanded as before in powers of γ, using Eq. (31). For reasonable initial distributions, $\mathbf{h}(0)$ would be expected to be of the order of γ or smaller. If this is the case, then we need to keep only the first term in the expansion of $\mathbf{G}(t)$, namely $\exp[-\mathbf{L}_E t]$, in order to evaluate the rate coefficients through order γ^2. Since $\mathbf{f}^0(t)$ is characterized by the actual number densities and temperature at time t, $\mathbf{h}$ must be orthogonal to the eigenfunctions of $\mathbf{L}_E$ with zero eigenvalue. Therefore, to lowest order in γ, the decay of $\mathbf{G}(t)\mathbf{h}(0)$ is governed by the smallest nonzero eigenvalue of $\mathbf{L}_E$, $\lambda_1{}^0$, which characterizes the momentum relaxation rate. Provided $\gamma(1 - \mathbf{P})\mathbf{L}_I(1 - \mathbf{P})$ is a small perturbation to $\mathbf{L}_E$, $\mathbf{G}(t)\mathbf{h}(0)$ will affect only the initial transient behavior of $k_{ij}(t)$, and can be neglected for $t \gg 1/\lambda_1{}^0$. Therefore the CE solution will still be valid if the perturbation is small and if there is a wide separation in time scales.

4. MODEL TWO-STATE HARD-SPHERE CALCULATION

In this section the KHR, CE, and exact solutions are compared for the internal relaxation of a two-state system (or, equivalently, for an isomerization reaction) in the presence of an excess of inert gas. This supplements similar comparisons published by Shizgal(13,14) and Simons.(15) The present model includes the effects of the reverse reaction, which were neglected in these previous treatments.

The elastic cross sections for this model system were chosen to be hard-sphere cross sections

$$\sigma_1 = \sigma_2 = \tfrac{1}{4}d_E{}^2 \tag{33}$$

The inelastic cross section for the conversion of molecules from state 1 to state 2 was taken to be a modified hard-sphere cross section,

$$\begin{aligned} \sigma_{12}^* &= \tfrac{1}{4}d_I{}^2(1 - E^*/E), \qquad && E > E^* \\ &= 0, && E < E^* \end{aligned} \tag{34}$$

Here the reduced relative kinetic energy E is given by

$$E = \mu|\mathbf{v}_1 - \mathbf{v}_x|^2/(2kT) \tag{35}$$

where μ is the reduced mass. E^* is a reduced activation energy below which the reaction does not occur. As a consequence of detailed balance(16) the inelastic collision cross section for the conversion of molecules from state 2 to state 1 must have the same form as σ_{12}^{*} given in Eq. (34) with E^* replaced by $E^{*\prime} = E^* - (\epsilon_2 - \epsilon_1)/kT$. In all of the calculations the mass of the molecules with internal structure was restricted to be the same as the mass of an X molecule, and the initial number densities were related to their equilibrium values by $n_1(t = 0) = 0.9n_1^{\text{eq}}$ and $n_2(t = 0) = n_2^{\text{eq}} + 0.1n_1^{\text{eq}}$. The activation energies E^* and $E^{*\prime}$ were varied, as was the ratio of the inelastic and elastic hard-sphere diameters.

The rate coefficients will be written

$$k_{ij}(t) = k_{ij}^{(0)}[1 - \eta_{ij}(t)] \tag{36}$$

where $k_{ij}(t)$ is defined by Eq. (6). From Eqs. (15) and (18) it can be seen that the only dependence that the KHR and CE approximations for η_{ij} have on the number densities is through the factor $[1 - \exp(-\beta\mathscr{A}_{ij})]$. The KHR solution is valid only for very short times, so that the initial number densities were used to calculate this factor for η_{ij}^{KHR}. The CE solution, however, is valid on the slow time scale of the internal state relaxation (or chemical reaction), and depends on time only implicitly through its dependence on the hydrodynamic variables, which for this problem are the number densities and the temperature.(17) It seemed most consistent with this interpretation of the CE solution to use the exact number densities at time t in calculating the factor $[1 - \exp(-\beta\mathscr{A}_{ij})]$ for $\eta_{ij}^{\text{CE}}(t)$, and this is the convention used in this paper. Although the theoretical rate coefficients k_{12} and k_{21} are conceptually convenient quantities, the net rate of the appearance or disappearance of molecules in one of the internal states is more accessible experimentally. If we write

$$\eta_{ij}(t) = \eta_{ij}'(t)\{1 - \exp[-\beta\mathscr{A}_{ij}(t)]\} \tag{37}$$

then the net rate can be written as

$$dn_1/dt = -n_1k_{12} + n_2k_{21} = (k_{12}^{(0)} + k_{21}^{(0)})(n_1^{\text{eq}} - n_1)(1 - \eta_{12}' - \eta_{21}') \tag{38}$$

Since $(k_{12}^{(0)} + k_{21}^{(0)})(n_1^{\text{eq}} - n_1)$ is the net rate predicted using the equilibrium rate coefficients, $-(\eta_{12}' + \eta_{21}')$ is the fractional nonequilibrium contribution to the net rate. In the CE approximation $\eta_{12}' + \eta_{21}'$ is constant, while for the exact solution $\eta_{12}' + \eta_{21}'$ asymptotically approaches a quantity η_A' which is related to the smallest nonzero eigenvalue of $\mathbf{L}_E + \mathbf{L}_I$, λ_1, by

$$\lambda_1 = (k_{12}^{(0)} + k_{21}^{(0)})(1 - \eta_A') \tag{39}$$

The approximate and exact solutions were calculated by expanding the distribution functions in Sonine polynomials $S_{\frac{1}{2}}^{(N)}$ and truncating the expansion at $N = 3$. With one exception, which is noted, the uncertainty in

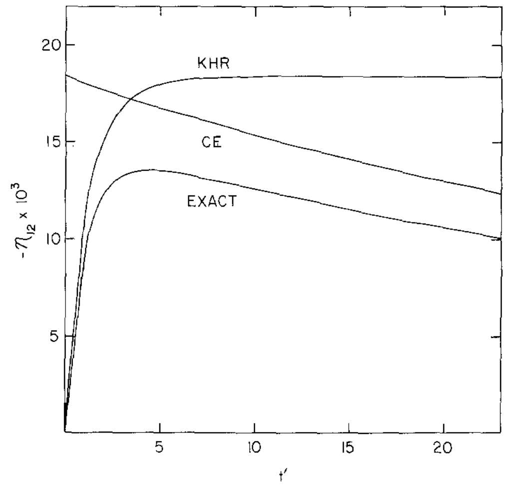

Fig. 1. The time dependence of η_{12} with $E^* = 5$, $E^{*\prime} = 4.5$, $d_I^2/d_E^2 = 1$.

the results is no more than two units in the third significant figure. The details of the calculations are similar to those in previous treatments.(8,15)

In Table I, $\eta_A{}'$ is compared to the CE value for $\eta'_{12} + \eta'_{21}$ for several values of E^*, $E^{*\prime}$, and d_I^2/d_E^2. Included in this table are the ratio of the $2 \rightarrow 1$ inelastic collision frequency to the elastic collision frequency (ν_{21}/ν_E) and the ratio of the two smallest nonzero eigenvalues of $\mathbf{L}_E + \mathbf{L}_I$, (λ_1/λ_2). The eigenvalues λ_1 and λ_2 approximately characterize the inelastic and elastic relaxation rates, respectively, so that the ratio λ_1/λ_2 will be much less than one when there is a wide separation in time scales. The results in this table bear out Shizgal's(13,14) conclusion that the ratio of the reactive and elastic collision frequencies must be very small in order for the CE method to be valid, although how small may well depend considerably on the nature of both the reactive and elastic cross sections. In Fig. 1 the KHR, CE, and exact values for η_{12} are shown as a function of time for the case $E^* = 5$, $E^{*\prime} = 4.5$, and $d_I^2/d_E^2 = 1$. In Fig. 2 the exact and KHR values of $(\eta'_{12} + \eta'_{21})/(\eta'_{12} + \eta'_{21})_{\mathrm{CE}}$ are plotted against time for the same set of parameters. In these two figures the time scale has been chosen so that one elastic collision occurs per unit t'. It can be seen from these figures that the KHR solution approximates the initial transient behavior, while the CE solution approximates the long-time hydrodynamic behavior.[6] Both of these approximations improve as the time

[6] The fact that the KHR and CE values for $\eta'_{12} + \eta'_{21}$ coincide at long times is due to the linear nature of this problem. In general the KHR solution approximates only the initial transient behavior and is not valid at long times.

Table I

E^*	$E^{*\prime}$	d_I^2/d_E^2	ν_{21}/ν_E	λ_1/λ_2	$(\eta'_{12} + \eta'_{21})_{\mathrm{CE}}$	η_A'	$\eta_A'/(\eta'_{12} + \eta'_{21})_{\mathrm{CE}}$
2	1.5	1	0.223	0.359	0.440	0.30[a]	0.68
2	1.5	0.04	0.893×10^{-2}	0.235×10^{-1}	0.0176	0.0173	0.98
5	4.5	1	0.111×10^{-1}	0.264×10^{-1}	0.142	0.116	0.82
5	4.0	1	0.183×10^{-1}	0.363×10^{-1}	0.163	0.130	0.80
5	4.0	0.04	0.733×10^{-3}	0.167×10^{-2}	0.00653	0.00646	0.99

[a] This result converged to only two figures probably because in this instance λ_1 is not well separated from the other nonzero eigenvalues of $\mathbf{L}_E + \mathbf{L}_I$.

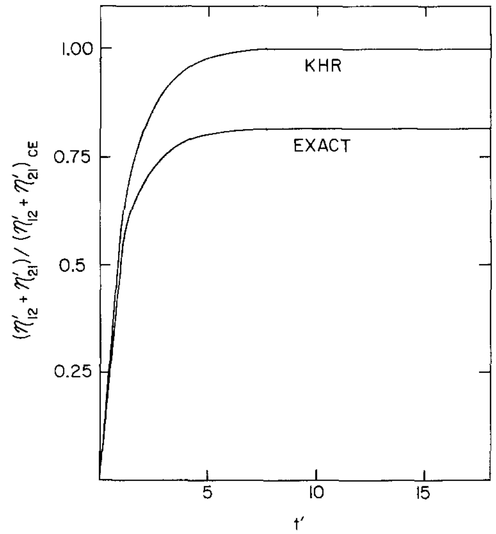

Fig. 2. The time dependence of $(\eta'_{12} + \eta'_{21})/(\eta'_{12} + \eta'_{21})_{CE}$ with $E^* = 5$, $E^{*\prime} = 4.5$, $d_I^2/d_E^2 = 1$.

scales become more widely separated, and as the nonequilibrium correction becomes smaller, as can be seen from Table II, where the exact and approximate values of $\eta_{12}/\eta_{12}^{CE}(t = 0)$ are compared for two cases both with $E^* = 5$ and $E^{*\prime} = 4$ but with $d_I^2/d_E^2 = 1$ in one instance and $d_I^2/d_E^2 = 0.04$ in the other. The separation in the time scales is wider, and the nonequilibrium

Table II. Time Dependence of the Approximate and Exact $\eta_{12}/\eta_{12}^{CE}(t=0)$ for $E^*=5$, $E^{*\prime}=4$

	$d_I^2/d_E^2 = 1$			$d_I^2/d_E^2 = 0.04$		
t'	KHR	CE	Exact	KHR	CE	Exact
1	0.582	0.974	0.507	0.582	0.999	0.578
2	0.814	0.950	0.658	0.814	0.998	0.806
3	0.913	0.927	0.703	0.913	0.997	0.902
4	0.957	0.905	0.711	0.957	0.996	0.944
5	0.979	0.883	0.705	0.979	0.994	0.964
6	0.989	0.862	0.693	0.989	0.993	0.973
8	0.997	0.822	0.664	0.997	0.991	0.978
10	0.999	0.784	0.635	0.999	0.989	0.978
15	1.000	0.697	0.564	1.000	0.984	0.974
20	1.000	0.620	0.502	1.000	0.978	0.968
30	1.000	0.492	0.398	1.000	0.967	0.958

correction smaller, for the smaller value of d_I^2/d_E^2, and the approximate solutions are correspondingly better.

The previous comparisons of the CE, KHR, and exact solutions considered only irreversible reactions,(13–15) while in this model problem both $1 \rightarrow 2$ and $2 \rightarrow 1$ transitions occur. Retaining the reverse reaction has two effects for this type of linear problem. First, at long times the exact η_{ij} drift downward rather than leveling off to a constant value. Second, the nonequilibrium contributions to the forward and reverse rates both decrease the net rate, so that the total nonequilibrium effect is larger than when the reverse reaction is neglected.

Another reason why the long-time behavior of our results differ from those Shizgal obtained(13,14) is because we chose to define the η_{ij} differently than he did. For the present problem Shizgal's nonequilibrium contribution to k_{12}, η_{12}^S, would be given by

$$n_1(t)k_{12}(t) = n_1^{(0)}(t)k_{12}^{(0)}[1 - \eta_{12}^S(t)] \tag{40}$$

where $n_1^{(0)}(t)$ is the value for n_1 at time t predicted using the equilibrium rate constants and $n_i^{(0)}(0) = n_i(0)$. We use $n_1(t)$ instead of $n_1^{(0)}(t)$ in Eq. (40). Therefore, Shizgal's values for the nonequilibrium contribution to the rate coefficients contain a cumulative effect not present in our results.

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