

Solution of the Fokker-Planck equation for reactive Rayleigh gas

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A Rayleigh model of heavy molecules diluted in a thermal bath of light molecules is extended to include a chemical reaction between both species. The solution of the appropriate Fokker-Planck equation for the distribution function is obtained from the corresponding solution for the nonreactive mixture. In the hydrodynamic regime the shape of the velocity distribution of heavy molecules is Maxwellian, but with a temperature different from that of the carrier gas. Exact results are derived for the reaction rate constant and diffusion coefficient.

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A number of kinetic theory studies of reactive gaseous systems were concerned with effects related to a deformation of the equilibrium Maxwellian velocity distribution by a chemical reaction. This generic name denotes corrections to the quasiequilibrium reaction rate constant [1–3] and to the linear transport coefficients [4–7], which both can be calculated by means of the Boltzmann equation. Due to difficulties in treating the collisional integral, it is inevitable to resort to approximate methods of solution, like perturbation technique [1,2,6,7], limited moment expansion [4,5], or numerical simulation [3]. The results obtained in this way are applicable to chemical reactions relatively slow compared with a relaxation process. The complex Boltzmann integral can be transformed to a much simpler Fokker-Planck (FP) form in the case of the Rayleigh model system, which consists of a foreign gas A diluted at a very low concentration in a carrier C (a thermal bath) with the essential condition $(m_A/m_C)^{1/2} \gg 1$ for the ratio of molecular masses of the species. This paper presents a solution of the kinetic equation for the reactive Rayleigh gas; in particular, exact results for the reaction rate constant and diffusion coefficient are derived.

In the Rayleigh system complemented by the chemical process, the species are mutually involved in an irreversible reaction $A + C \rightarrow P$, where the product is neglected because of its low concentration. It should be emphasized that the reactive system is constructed from the nonreactive one in such a way that a part of originally elastic collision is switched to become reactive. Under this procedure, the original cross section σ_0 in the nonreactive system is divided in the reactive system into a part σ_e for elastic collisions and a part σ^* for reactive collisions, with the constraint $\sigma_0 = \sigma_e + \sigma^*$. For concreteness, the molecules are treated in the following as reactive hard spheres of diameters d_A and d_C , respectively. In this system the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ of position \mathbf{r} and velocity \mathbf{v} of molecules A obeys the following Boltzmann equation [6(b)]:

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} = n_C \int (f' \psi_C^M - f \psi_C^M) |\mathbf{v} - \mathbf{v}_C| d\sigma_0 d\mathbf{v}_C - n_C \int f' \psi_C^M |\mathbf{v} - \mathbf{v}_C| d\sigma^* d\mathbf{v}_C, \quad (1)$$

where n_C denotes the concentration of the carrier C , and

$$\psi_C^M(\mathbf{v}_C) = \left(\frac{m_C}{2\pi kT} \right)^{3/2} \exp \left[-\frac{m_C v_C^2}{2kT} \right] \quad (2)$$

is the Maxwellian distribution of velocity \mathbf{v}_C of molecules C at temperature T (k denotes the Boltzmann constant). The primed distribution functions are calculated for postcollisional velocities. The first term of the right side of Eq. (1) has the same form as the collisional integral for the nonreactive system. The respective second term accounts for the chemical reaction, and expresses a deficiency of molecules which appear with the postcollisional velocities, but instead are transformed into products in reactive collisions, after hitting the reactive part σ^* of the cross section.

For the whole spectrum of the molecular mass ratio, only the approximate solution of Eq. (1) has been obtained previously [6b] by means of the perturbation method. In the Rayleigh limit the collisional integrals can be approximated by the differential FP form. The transformation relies on the fact that a change of velocity in a single collision, $\mathbf{v}' - \mathbf{v}$, is scaled by the small parameter $(m_C/m_A)^{1/2}$. The well-known result for the nonreactive term has the form [8]

$$n_C \int (f' \psi_C^M - f \psi_C^M) |\mathbf{v} - \mathbf{v}_C| d\sigma_0 d\mathbf{v}_C = \xi_0 \frac{\partial}{\partial \mathbf{v}} \cdot \left[\mathbf{v} f + \frac{kT}{m_A} \frac{\partial f}{\partial \mathbf{v}} \right] + o(m_C/m_A). \quad (3)$$

The friction coefficient in (3) is

$$\xi_0 = \frac{4}{3} n_C \pi d^2 \left[\frac{8kT}{\pi \mu} \right]^{1/2} \frac{m_C}{m_A}, \quad (4)$$

where $d = (d_A + d_C)/2$ is a collisional diameter, and $\mu = m_A m_C / (m_A + m_C)$ is a reduced mass. Similarly, one can transform the integral for reactive collisions, either by calculating the transition probability kernel [9,10], or in the more traditional way proceeding with the expansion

$$\begin{aligned}
n_C \int f' \psi_C^M |\mathbf{v} - \mathbf{v}_C| d\sigma^* d\mathbf{v}_C &= n_C \frac{f}{\psi^M} \int \psi^M \psi_C^M |\mathbf{v} - \mathbf{v}_C| d\sigma^* d\mathbf{v}_C \\
&+ n_C \left[\frac{\partial}{\partial \mathbf{v}} \frac{f}{\psi^M} \right] \cdot \int (\mathbf{v}' - \mathbf{v}) \psi^M \psi_C^M |\mathbf{v} - \mathbf{v}_C| d\sigma^* d\mathbf{v}_C \\
&+ \frac{1}{2} n_C \left[\frac{\partial^2}{\partial \mathbf{v}^2} \frac{f}{\psi^M} \right] \int (\mathbf{v}' - \mathbf{v})^2 \psi^M \psi_C^M |\mathbf{v} - \mathbf{v}_C| d\sigma^* d\mathbf{v}_C + \dots, \quad (5)
\end{aligned}$$

where ψ^M is the equilibrium Maxwellian velocity distribution of molecules A [Eq. (2) with the obvious replacements]. Integral (5) is calculated for the line-of-centers model, which assumes that a collision is reactive with the probability s_f if it satisfies the condition

$$\mathbf{e} \cdot (\mathbf{v} - \mathbf{v}_C) > g. \quad (6)$$

\mathbf{e} is a unit vector along a line connecting centers of molecules at the instant of impact. According to inequality (6) it is a necessary condition for reactive collision that the relative energy of colliding molecules exceeds the definite threshold value, which in a dimensionless form can be written as

$$\varepsilon = \frac{\mu g^2}{2kT}. \quad (7)$$

For the above reaction model, integral (5) has the following form:

$$\begin{aligned}
n_C \int f' \psi_C^M |\mathbf{v} - \mathbf{v}_C| d\sigma^* d\mathbf{v}_C \\
\approx \xi^* \frac{\partial}{\partial \mathbf{v}} \cdot \left[\mathbf{v} f + \frac{kT}{m_A} \frac{\partial f}{\partial \mathbf{v}} \right] \\
+ \nu^* \left[1 + \left(\frac{1}{2} + \varepsilon \right) \left[1 - \frac{m_A v^2}{3kT} \right] \frac{m_C}{m_A} \right] f, \quad (8)
\end{aligned}$$

where $\xi^* = \xi_0 s_f \exp(-\varepsilon)(1+\varepsilon)$ is a contribution to the friction coefficient, and

$$\nu^* = n_C \pi d^2 \left[\frac{8kT}{\pi\mu} \right]^{1/2} s_f \exp(-\varepsilon) \quad (9)$$

is the frequency of reactive collisions calculated for the Maxwellian velocity distribution ψ^M . The factor $s_f \exp(-\varepsilon)$ controls the intensity of the chemical process. The terms up to the order m_C/m_A were retained in expansion (8) to adjust with the order of dissipative term (3). Using approximations (3) and (8) for the collisional integrals, the FP equation for the reactive Rayleigh gas can be written as

$$\begin{aligned}
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} \\
= J_{\text{FP}}(f) - \nu^* \left[1 + \left(\frac{1}{2} + \varepsilon \right) \left[1 - \frac{m_A v^2}{3kT} \right] \frac{m_C}{m_A} \right] f, \quad (10)
\end{aligned}$$

where the linear differential operator

$$J_{\text{FP}}(f) = \xi \frac{\partial}{\partial \mathbf{v}} \cdot \left[\mathbf{v} f + \frac{kT}{m_A} \frac{\partial f}{\partial \mathbf{v}} \right] \quad (11)$$

has the usual FP form, but the friction coefficient is modified by the chemical reaction and its effective value is

$$\xi = \xi_0 [1 - s_f \exp(-\varepsilon)(1+\varepsilon)]. \quad (12)$$

Equation (10) has a physical sense only if $\xi \neq 0$, otherwise there is no effective relaxation mechanism for f . In the latter case, condition $\xi = 0$ is satisfied only for $s_f = 1$ and $\varepsilon = 0$, meaning that every collision is reactive.

The solution of Eq. (10) is simplified considerably by elimination of the component of the reactive term proportional to v^2 . This can be done via substituting the distribution function in the form

$$f(\mathbf{r}, \mathbf{v}, t) = \exp \left[\delta \frac{m_A v^2}{2kT} \right] F(\mathbf{r}, \mathbf{v}, t), \quad (13)$$

in which the exponent δ is calculated as

$$\delta = \frac{1}{2} \left[\left[\frac{1 - s_f \exp(-\varepsilon)/2}{1 - s_f \exp(-\varepsilon)(1+\varepsilon)} \right]^{1/2} - 1 \right]. \quad (14)$$

The resulting equation for the function F has the form

$$\frac{\partial F}{\partial t} + \mathbf{v} \cdot \frac{\partial F}{\partial \mathbf{r}} = J'_{\text{FP}}(F) - (\nu^* - 3\xi\delta^2)F, \quad (15)$$

where the FP term is given by

$$J'_{\text{FP}}(F) = \xi(1+2\delta) \frac{\partial}{\partial \mathbf{v}} \cdot \left[\mathbf{v} F + \frac{kT}{m_A(1+2\delta)} \frac{\partial F}{\partial \mathbf{v}} \right]. \quad (16)$$

The form of Eq. (16) implies the use of renormalized friction coefficient ξ' and temperature T' ,

$$\xi' = \xi(1+2\delta), \quad T' = \frac{T}{1+2\delta}. \quad (17)$$

The second component on the right side of Eq. (15) is of purely chemical origin, and corresponds formally to a depletion of molecules A by the reaction proceeding at a rate α , independent of velocity,

$$\alpha = -(\nu^* - 3\xi\delta^2). \quad (18)$$

The well-known [11] fundamental solution F' of the part of Eq. (15) forming the ordinary FP equation (with ξ' and T' as effective parameters) provides the solution of the entire Eq. (15),

$$F(\mathbf{r}, \mathbf{v}, t) = \exp(\alpha t) F'(\mathbf{r}, \mathbf{v}, t). \quad (19)$$

Formally, the effect of chemical reaction consists in the change of the parameters of J'_{FP} according to Eq. (17), and introduction of the factor decaying exponentially

with time. The solution of Eq. (10) is then found from Eq. (13).

The hydrodynamic approximation is obtained from the kinetic description in the limit of long time and soft spatial inhomogeneities. The following treatment of the hydrodynamic regime is based on the perturbative method of Resibois [12]. Let us first consider Eq. (10) for a reactive but homogeneous system. As the FP operator (11) is self-adjoint in the scalar product defined by

$$\langle \phi | \varphi \rangle = \int \bar{\phi}(\mathbf{v}) \varphi(\mathbf{v}) [\psi^M(\mathbf{v})]^{-1} d\mathbf{v}, \quad (20)$$

the distribution function f can be expanded in a series of eigenfunctions of the operator of the right-hand side of Eq. (10). By means of Eq. (13) these eigenfunctions are generated by the eigenfunctions of the right side operator of Eq. (15), which in turn are exactly the familiar eigenfunctions of the FP term J'_{FP} itself [12], since the remaining (reactive) part introduces multiplication by the simple factor α . The corresponding eigenvalues for both equations are the same, and can be presented as $\lambda_n = \lambda_n^{\text{FP}} + \alpha$, where $\{\lambda_n^{\text{FP}}\}$ is the well-known spectrum of the FP term given in the form of J'_{FP} . The hydrodynamic solution is furnished by the eigenfunction associated with the largest eigenvalue, which provides the slowest decaying rate. This condition evidently selects $\lambda_0^{\text{FP}} = 0$, and the associated eigenfunction of J'_{FP} is the Maxwellian with the temperature T' , which yields the corresponding eigenfunction of Eq. (10) in the form

$$\begin{aligned} \psi_0(\mathbf{v}) &= N \exp \left[\delta \frac{m_A v^2}{2kT} - \frac{m_A v^2}{2kT'} \right] \\ &= N \exp \left[-(1+\delta) \frac{m_A v^2}{2kT} \right], \end{aligned} \quad (21)$$

where N is a normalization factor with respect to scalar product (20). Thus in the hydrodynamic limit the velocity distribution of molecules A has a Maxwellian shape with the effective temperature

$$T_A = \frac{T}{1+\delta}. \quad (22)$$

The eigenvalue $\lambda_0 = \alpha$ associated with ψ_0 determines the rate of decline of the hydrodynamic solution; that is, the rate constant for the irreversible, (pseudo) first order reaction consuming molecules A . As the separation of λ_0 from the next nearest eigenvalue is $|\lambda_1 - \lambda_0| = \xi'$, the hydrodynamic solution is valid for $t \gg 1/\xi'$.

In the analysis of the nonuniform system, inhomogeneities are treated as infinitesimally small spatial perturbations. This approach leads to exact results for diffusion, which is a linear response to the spatial inhomogeneities. Following Resibois [12], it is convenient to consider the spatial Fourier decomposition

$$\phi(q, \mathbf{v}, t) = \int \exp(-iqx) f(x, \mathbf{v}, t) dx, \quad (23)$$

assuming that the nonuniformity is only x dependent. Transformation (23) in Eqs. (10) and (15) changes only the term which accounts for the spatial inhomogeneity, and its resulting form $iqv_x \phi$ in the hydrodynamic regime,

$q \rightarrow 0$, can be treated by the perturbation technique adopted from the quantum theory. The perturbed hydrodynamic solution can be written as [12,6]

$$\phi_h(q, \mathbf{v}, t) = Q \exp((\alpha - Dq^2)t) \psi'_0(q, \mathbf{v}), \quad (24)$$

where Q is v and t independent, and $-Dq^2 = \Delta\lambda_0$ is the (second order) correction to the unperturbed eigenvalue $\lambda_0 = \alpha$. Calculation of $\Delta\lambda_0$ closely follows the standard method [12,6] with only minor modifications, and without going into computational details one can pass to the final result

$$D = -\langle v_x \psi_0 | (J_{\text{FP}} + R - \alpha)^{-1} (v_x \psi_0) \rangle, \quad (25)$$

where R is the reactive term of the operator of right side of Eq. (10) [so that $J_{\text{FP}} + R$ is the complete operator of the right side of (10)]. Calculation of (25) is easily performed, as $v_x \psi_0$ is the eigenfunction of $J_{\text{FP}} + R$,

$$D = \frac{kT'}{m_A \xi'}. \quad (26)$$

The hydrodynamic equation associated with FP equation (10) governs the concentration of molecules

$$n(x, t) = \int f(x, \mathbf{v}, t) d\mathbf{v}. \quad (27)$$

It is readily found that $n(x, t)$ calculated from the hydrodynamic solution (24) satisfies the equation

$$\frac{\partial n}{\partial t} = \alpha n + D \frac{\partial^2 n}{\partial x^2}. \quad (28)$$

Evidently, α is identified as the reaction rate constant, and D as the diffusion coefficient.

The corrections to the rate coefficients induced by the chemical reaction are related to the deviation of the velocity distribution from the equilibrium Maxwellian ψ^M . The relative correction to the quasiequilibrium reaction rate constant, $\alpha^M = -\nu^*$, is given by

$$\eta = \frac{\alpha - \alpha^M}{\alpha^M} = -\frac{4m_C}{m_A} \left[\frac{1}{s_f \exp(-\varepsilon)} - (1+\varepsilon) \right] \delta^2. \quad (29)$$

The corrections to the unperturbed diffusion coefficient, $D_0 = kT/m_A \xi_0$, and to the temperature of species A (related to the mean kinetic energy per molecule), are, respectively,

$$\gamma = \frac{D - D_0}{D_0} = \frac{s_f \exp(-\varepsilon)}{2 - s_f \exp(-\varepsilon)}, \quad (30)$$

$$\vartheta = \frac{T_A - T}{T} = -\frac{\delta}{1+\delta}. \quad (31)$$

It is only the correction η which vanishes as $m_C/m_A \rightarrow 0$. In the limit of slow reaction, $s_f \exp(-\varepsilon) \ll 1$, the above equations confirm the results derived by the perturbation method [6(b),13]:

$$\eta_p = -\frac{m_C}{4m_A} s_f \exp(-\varepsilon) \left(\frac{1}{2} + \varepsilon \right)^2, \quad (32)$$

$$\gamma_p = \frac{1}{2} s_f \exp(-\varepsilon), \quad (33)$$

$$\vartheta_p = -\frac{1}{4} s_f \exp(-\varepsilon) \left(\frac{1}{2} + \varepsilon \right). \quad (34)$$

It is interesting to note that the diffusion coefficient is increased in the reactive system, while the corrections to the temperature and reaction rate constant are negative. As discussed previously [6], the decrease of T_A and α can be explained by the fact that the studied reaction model preferably consumes molecules with a higher energy. However, Eq. (26) indicates that the diffusion coefficient is affected both by cooling of the reactant and by the modification of the friction coefficient, which according to Eq. (12) is smaller in the reactive system. As this second factor prevails, the resultant correction to D is positive. To find a physical explanation for the decrease of ξ , one can notice that only the elastic collisions contribute to the friction mechanism, and that the magnitude of the force is proportional to the frequency of collisions. In the system considered, introduction of the reactive col-

lisions reduces a number of the elastic collisions. Moreover, the reactive collisions preferably substitute the elastic collisions in which velocities of molecules are oppositely oriented (that is, $\mathbf{v} \cdot \mathbf{v}_C < 0$), because condition (8) for the reaction favors this configuration. This is the kind of collisions which oppose the motion of a molecule A , and actually form the friction force. With a significant deficiency of the appropriate elastic collisions, the effect of weakening of the dissipation mechanism can dominate the opposite influence of a lowering of the mean thermal velocity of molecules. While this relation between the both factors holds in the Rayleigh limit, it cannot span the whole range of the mass ratio. At least for the Lorentz range $m_A/m_C \ll 1$, the perturbative solution of Eq. (1) predicts the prominent negative correction for the diffusion coefficient [6].

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 [13] In Ref. [6(b)] there is a misprint in Eq. (68). It should read $K_{II} = 1 + \varepsilon - HM_C \dots$