

Light-Induced Heat and Mass Transfer of Rarefied Gas in a Capillary

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Abstract. Heat and mass transfer processes of a one-component gas in a capillary due to the resonant interaction of molecules with optical radiation are studied. The theory is based on the solution of linearized kinetic models at arbitrary Knudsen numbers. Two mechanisms of transport phenomena are considered. The surface light-induced drift and heat flux are caused by the difference in the accommodation coefficients for excited and ground state molecules. The so-called bulk mechanism of light-induced heat and mass transfer are caused by the difference in the kinetic cross sections for the excited and unexcited molecules. Kinetic coefficients characterizing these phenomena are calculated depending on Knudsen numbers and the detuning of radiation frequency from the center of the absorption line. The comparison between the theory and experiment is performed.

INTRODUCTION

For the first time the phenomenon of light-induced drift (LID) in infinite gas was predicted in [1]. The velocity-selective excitation of the gas molecules by resonant optical radiation can cause drift of the gas (LID) and heat flux (light-induced heat flux, LIHF). The LID takes place only in gaseous mixture with a buffer-gas, whereas the LIHF is possible in a one-component gas. But a boundary surface can play the role of a buffer-gas, which reflects excited and unexcited molecules in different ways.

The theory of LID of a one-component gas in a capillary is developed for a free-molecular regime in Ref. [2]. The surface LID due to the difference in the accommodation coefficients of excited and unexcited molecules was predicted in this work. The so-called collision LID of a one-component gas takes place in the vicinity of the boundary surface [3]. This mechanism is caused by the difference in the kinetic cross sections of the molecules in the excited and ground states.

The moment-integral method for solution of the kinetic model equation at arbitrary Knudsen number (Kn) was used in [4]. A discrete ordinate technique was applied in [5] for calculation of the LID velocity depending on the Kn number. In both works [4, 5] the second-order model of the linearized collision integral was used. This approximation to the Boltzmann equation gives an incorrect Prandtl number.

In this paper the LID and LIHF in a capillary are calculated at arbitrary Kn numbers. The third-order McCormack model [6] for gaseous mixture is solved by the moment-integral method. The kinetic equation gives correct Prandtl number and accurately describes velocities of species, stress and partial heat fluxes in a gaseous mixture.

STATEMENT OF THE PROBLEM

Consider a one-component gas confined in cylindrical capillary of radius r_0 . A traveling light wave propagates along the channel axis (the z -axis). We assume that particles absorb radiation in the electronic or vibrational-rotational transitions from the ground state “ n ” to the excited state “ m ”. The radiation frequency ω is slightly detuned from the center of the absorption line ω_{mn} , i.e. $|\Omega| \ll \omega, \omega_{mn}$.

Due to the Doppler effect, the radiation is absorbed selectively by molecules that have velocities around $v_{z0} = \Omega/k$, where k is the magnitude of the wave-vector and v_{z0} the light-selected velocity component along the propagation direction of the light. Molecules that have absorbed radiation change the kinetic cross-section and accommo-

dation coefficient. Thus, the gas can be interpreted as a binary mixture consisting of the excited and nonexcited components. The excited and unexcited molecules have equal masses m_0 but the effective diameter of molecules in the ground-state, σ_n , differs from that in the excited state, σ_m . Stimulated transitions and radiative decay of the excited levels lead to the exchange of molecules between excited and non-excited components.

Resonant radiation disturbs the equilibrium in the gas. In the case of finite detuning $\Omega \neq 0$ this stimulates the drift of the light-absorbing gas (LID) and heat flux (LIHF) in parallel to the wave-vector direction [1].

We use two-level approximation for the molecules. In the stationary case, the non-equilibrium state of the gas can be described by the distribution functions for the excited, f_m , and unexcited, f_n , molecules. These functions satisfy the following kinetic equations [7]

$$\begin{aligned}\vec{v}\vec{\nabla}f_n &= -\frac{1}{2}\Gamma_m\chi(\vec{v})(f_n - f_m) + \Gamma_m f_m + S_n, \\ \vec{v}\vec{\nabla}f_m &= \frac{1}{2}\Gamma_m\chi(\vec{v})(f_n - f_m) - \Gamma_m f_m + S_m, \\ \chi(\vec{v}) &= \frac{4|G_{mn}|^2\Gamma}{\Gamma_m[\Gamma^2 + (\Omega - \vec{k}\vec{v})^2]}, \quad G_{mn} = \frac{E d_{mn}}{2\hbar},\end{aligned}\tag{1}$$

where Γ_m is the rate of radiative decay of the excited level, Γ is the homogeneous half-width of the absorption line, $\chi(\vec{v})$ is the absorption probability per unit time for molecules with given velocity \vec{v} , d_{mn} is the dipole matrix element of m - n transition, E is the amplitude of the electrical field in the light wave, G_{mn} is the Rabi frequency, \hbar is the Planck constant, and S_i is the Boltzmann collision integral for molecules of the i -th species.

The boundary conditions associated with Eqs. (1) are defined by the distribution functions f_i for molecules reflected from the capillary surface. We assume that the interaction of molecules of i -th species with the surface can be described by Maxwell model. Neglecting the inelastic collisions of the molecules with the wall, one gets the boundary conditions in the following form

$$\begin{aligned}f_i^+(\vec{v}) &= \varepsilon_i f_{ir}(\vec{v}) + (1 - \varepsilon_i) f_i^-(\vec{v} - 2(\vec{v}\vec{n})\vec{n}), \quad \vec{v}\vec{n} > 0 \\ f_{ir} &= n_{ir} \left(\frac{m_0}{2\pi k_b T} \right)^{3/2} \exp\left(-\frac{v^2}{\bar{v}^2}\right), \quad \bar{v} = \left(\frac{2k_b T}{m_0} \right)^{1/2},\end{aligned}\tag{2}$$

where ε_i is the fraction of molecules of the i -th species which are reflected diffusely, \vec{n} is the inner normal to the capillary surface, n_{ir} is the number density of diffusely emitted particles, k_b is the Boltzmann constant, T is the gas temperature; the superscripts “+” and “-” label respectively reflected and incident on surface particles.

Molar flow of the gas and heat flux averaged over the capillary cross section are determined by the following expressions

$$\begin{aligned}I = n\langle U \rangle &= I_n + I_m = \frac{1}{\pi r_0^2} \int_{\Sigma} d\vec{r} \int v_z (f_n + f_m) d\vec{v}, \\ Q = Q_n + Q_m &= \frac{1}{\pi r_0^2} \int_{\Sigma} d\vec{r} \frac{1}{2} m_0 \int (v_z - U) (\vec{v} - \vec{U})^2 (f_n + f_m) d\vec{v}.\end{aligned}\tag{3}$$

We examine the case of small values of $\chi(\vec{v})$ that is quite typical for vibrational-rotational transitions and also for electronic transitions at low radiation intensity. In this case the gas is quite near the equilibrium and, thus, the distribution functions can be written in the form of the perturbed Maxwellian distributions

$$f_i = f_{i0} [1 + h_i(\vec{r}, \vec{v})], \quad f_{i0} = n_i \left(\frac{m_0}{2\pi k_b T} \right)^{3/2} \exp\left(-\frac{v^2}{\bar{v}^2}\right), \quad i = m, n,\tag{4}$$

where h_i is the correction to the Maxwell distribution function for i -th component, n_i is the equilibrium number density of molecules of i -th species.

Further simplification is obtained by assuming that the molecular collisions are elastic, and their frequencies, $\gamma_i = \gamma_{ii} + \gamma_{ij}$ ($i, j = m, n$; γ_{ij} is the effective collision frequency between the molecules of the i -th and j -th species), are much larger than the radiative decay constant Γ_m , i.e., $\Gamma_{mi} = \Gamma_m / \gamma_i \ll 1$. We assume in addition that the radiation intensity is uniform over the capillary cross section.

Under the above assumptions, the kinetic equations (1) are linearized with respect to the values h_i and Γ_{mi} .

Since only elastic collisions between molecules are considered, we can use the linearized collision integral of third order developed by McCormack [6] for gaseous mixture.

The linearized expressions (3) for the mass flow and heat flux in a capillary have the form

$$I = \frac{n}{2\sqrt{\pi}} \Gamma_m r_0 (G\chi_1 + \tilde{G}\chi_3), \quad Q = \frac{p}{2\sqrt{\pi}} \Gamma_m r_0 (S\chi_1 + \tilde{S}\chi_3), \quad (5)$$

$$\chi_k = \int_{-\infty}^{+\infty} c_z^k \chi(c_z) \exp(-c_z^2) dc_z, \quad n = n_n + n_m, \quad p = p_n + p_m.$$

Here $G, \tilde{G}, S,$ and \tilde{S} are the dimensionless kinetic coefficients depending on the Knudsen number Kn , accommodation coefficients ε_i , and effective diameters of the excited, σ_m , and unexcited, σ_n , molecules; n and p are the number density and pressure of the gas, respectively.

METHOD OF SOLUTION

Kinetic equations, taking into account linearized boundary conditions (2), are formally integrated and transformed into a set of integral equations for the dimensionless velocities (u_i), stresses (π_{iz}) and heat fluxes (H_i). These equations are Fredholm integral equations of the second kind. They were solved by the Bubnov-Galerkin method [8]. The method is effective because it allows one to calculate the LID (I), and LIHF (Q) with high accuracy by using only approximation for profiles of the macroparameters u_i, π_{iz}, H_i . In N -approximation we have

$$u_i^{(N)} = \sum_{k=0}^{N-1} a_k^{(i)} r^{2k}, \quad \pi_{iz}^{(N)} = \sum_{k=1}^{N-1} b_k^{(i)} r^{2k-1}, \quad H_i^{(N)} = \sum_{k=1}^{N-1} c_k^{(i)} r^{2(k-1)}. \quad (6)$$

Substitution of approximations (6) into the set of integral equations and the requirement of the orthogonality of residual to each of the basic functions make it possible to obtain the set of linear algebraic equations for quantities $a_k^{(i)}, b_k^{(i)}, c_k^{(i)}$. We used the second approximation ($N = 2$). In this case the results for the velocity of LID have satisfactory accuracy at all values of the Knudsen number [4].

The theory is linear in $\chi(\vec{v})$. Therefore we can assume that $n_m \ll n_n$, i.e. $n_n \approx n$. In addition, we assume that the molecules are hard elastic spheres. In this case it is convenient to introduce into the theory the rarefaction parameter δ which is inversely proportional to the Knudsen number

$$\delta = \frac{\sqrt{\pi}}{2} Kn^{-1}, \quad Kn = \frac{l}{r_0}, \quad (7)$$

where l is the mean free path of the molecules.

Let the relative difference between the effective diameters of excited (σ_m) and ground-state (σ_n) particles is small. Besides let the accommodation coefficients ε_i are close to unity, i.e. we assume the almost complete accommodation. Thus, the theory acquires two small parameters

$$\frac{|\Delta\sigma|}{\sigma_n} \ll 1, \quad \Delta\sigma = \sigma_m - \sigma_n, \quad (1 - \varepsilon_i) \ll 1, \quad \Delta\varepsilon = \varepsilon_n - \varepsilon_m \neq 0. \quad (8)$$

Linearization with respect to the small parameters (8) makes it possible to separate the surface and collision mechanisms of the LID and LIHF. For the kinetic coefficients we obtain

$$G = G_1 \Delta \varepsilon + G_2 \frac{\Delta \sigma}{\sigma_n}, \quad \tilde{G} = G_3 \Delta \varepsilon + G_4 \frac{\Delta \sigma}{\sigma_n}, \quad S = S_1 \Delta \varepsilon + S_2 \frac{\Delta \sigma}{\sigma_n}, \quad \tilde{S} = S_3 \Delta \varepsilon + S_4 \frac{\Delta \sigma}{\sigma_n}. \quad (9)$$

Analytic expressions for the G_k and S_k can be obtained only for large and small values of the Kn number.

For the near free-molecular regime ($\delta \ll 1$) we obtain

$$\begin{aligned} G_1 &= \frac{16}{3\sqrt{\pi}} + 6\delta \ln \delta + 3,24\delta, \quad G_2 = \delta \ln \delta + 0,6158\delta - 1,6048\delta^2, \\ G_3 &= G_4 = 0, \quad S_1 = -\frac{32}{3\sqrt{\pi}} - 15\delta \ln \delta - 11,1\delta, \\ S_2 &= -2,5\delta \ln \delta - 2,0395\delta + \frac{128}{15\sqrt{\pi}}\delta^2, \quad S_3 = G_1, \quad S_4 = G_2. \end{aligned} \quad (10)$$

In case of slip-flow regime ($\delta \gg 1$) we have

$$\begin{aligned} G_1 &= \frac{1}{\varphi_{nn}^{(1)}} \frac{1+0,75\alpha_1}{1-2,5\alpha_1\alpha_2} \frac{1}{\delta} + \dots, \quad G_2 = \frac{1}{2\varphi_{nn}^{(1)}} \frac{1+0,5\alpha_1}{1-2,5\alpha_1\alpha_2} \frac{1-\alpha_3}{\delta} + \dots, \\ S_2 &= \frac{1}{2\varphi_{nn}^{(1)}} \frac{5\alpha_1+3\alpha_4}{1-2,5\alpha_1\alpha_2} \frac{1}{\delta} + \dots, \quad S_4 = -\frac{1}{\varphi_{nn}^{(1)}} \frac{\alpha_4}{1-2,5\alpha_1\alpha_2} \frac{1}{\delta} + \dots, \\ G_3 &= O(\delta^{-2}), \quad G_4 = O(\delta^{-2}), \quad S_1 = O(\delta^{-2}), \quad S_3 = O(\delta^{-2}), \\ \alpha_1 &= v_{nn}^{(2)}/v_{nn}^{(5)}, \quad \alpha_2 = v_{nn}^{(2)}/v_{nn}^{(1)}, \quad \alpha_3 = v_{nn}^{(4)}/v_{nn}^{(3)}, \quad \alpha_4 = v_{nn}^{(1)}/v_{nn}^{(5)}, \quad \varphi_{nn}^{(k)} = v_{nn}^{(k)}/\gamma_{nn}. \end{aligned} \quad (11)$$

The expressions for the rates $v_{nn}^{(k)}$ in terms of the Chapman-Cowling integrals are given in [6].

Numerical calculations were carried out at intermediate Kn numbers. The results are shown in Figs. 1–3.

DISCUSSION

The solution of the kinetic equation substantiates the known qualitative conclusion that the LID of a one-component gas is possible only in bounded systems, while the LIHF takes place in a boundless gas additionally. In the latter case we obtain for the LIHF

$$Q = -\frac{p\bar{v}\Gamma_m}{2\sqrt{\pi}} \frac{(\chi_3 - 1,5\chi_1)v_{nn}^{(1)} - 2,5v_{nn}^{(2)}\chi_1}{v_{nn}^{(1)}v_{nn}^{(5)} - 2,5(v_{nn}^{(2)})^2} \frac{\Delta \sigma}{\sigma_n}. \quad (12)$$

Note that the same expression follows immediately from the Eqs. (5), (9), and (11) in the slip-flow regime.

Inhomogeneous broadening of the absorption line ($\Gamma \ll k\bar{v}$) is typical for rarefied gases. In this case neglecting terms proportional to the $v_{nn}^{(2)}$ (since $\alpha_1 \approx 0,07$, $\alpha_2 \approx 0,1$) we obtain

$$Q = \frac{3\sqrt{\pi}}{v_{nn}^{(5)}} p\bar{v}\Omega \left(\frac{G_{mn}}{k\bar{v}} \right)^2 \frac{\Delta \sigma}{\sigma_n}. \quad (13)$$

In the case of homogeneous broadening ($\Gamma \gg k\bar{v}$) we have $\chi_3 = 1,5\chi_1$. Thus, the LIHF is proportional to the rate $v_{nn}^{(2)}$, i.e. this is the second order effect (identical with the Dufour effect). It follows that the second-order kinetic model for gaseous mixture does not describe the LIHF because does not contain terms of the order of $v_{nn}^{(2)}$.

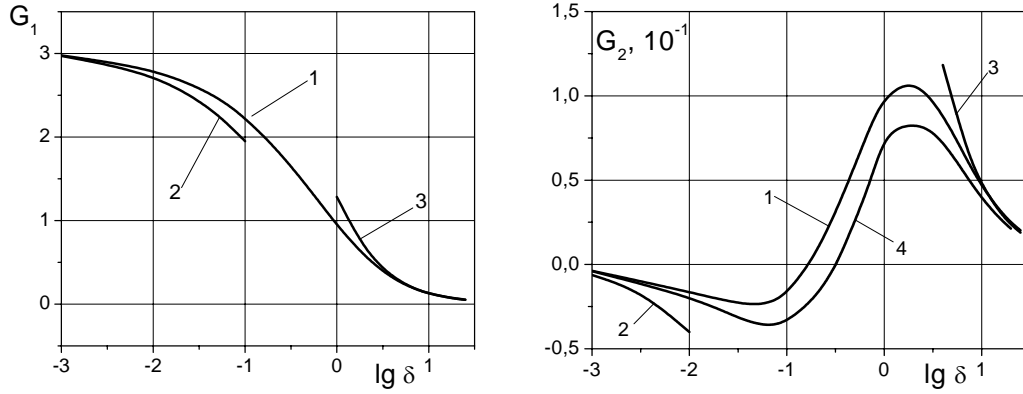


FIGURE 1. The dependences G_1 and G_2 of δ ; 1 – numerical calculation, 2 – Eqs. (10), 3 – Eqs. (11), 4 – results of [4].

The kinetic coefficients G_1, G_3, S_1, S_3 , characterizing the surface mechanism of light-induced transport phenomena, have the constant signs at all values of the Kn. Thus, the directions of the surface LID and LIHF are determined by the signs in the difference of the accommodation coefficients for the unexcited and excited particles, $\Delta\epsilon$,

and the frequency detuning Ω . In the case when $\Delta\epsilon > 0$, the direction of the surface LID coincides with the direction of light propagation at $\Omega > 0$, and it is opposite to the direction of light propagation at $\Omega < 0$. The surface LIHF is directed opposite to the surface LID at any values of Kn.

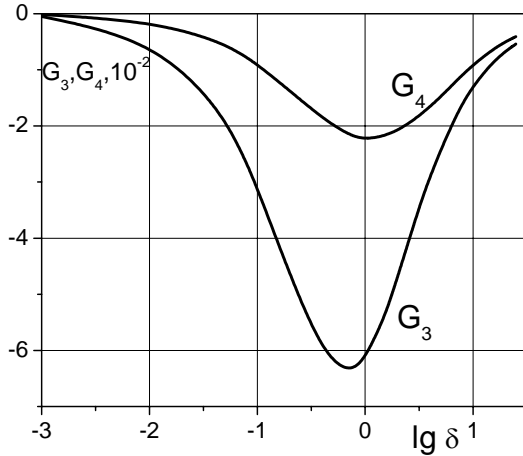


FIGURE 2. G_3 and G_4 as functions of the δ .

The kinetic coefficients G_2, G_4 and S_2, S_4 characterize the collision LID and LIHF respectively. The dependence of G_2 on the rarefaction parameter δ is shown in Fig.1. At intermediate Knudsen numbers (at $\delta = \delta_{inv} \approx 0,195$) the coefficient G_2 reverses sign. Hence it follows that the velocity of the LID reverses direction at intermediate regime. In addition, the direction of the collision LID is determined by the difference of the effective diameters of particles in the ground-state and excited state, $\Delta\sigma$, and by the sign of the detuning Ω . In

case when $\delta < \delta_{inv}$ and $\Delta\sigma > 0$, the collision LID is aligned with the direction of the light propagation at $\Omega < 0$ and it is opposed to the direction of the light propagation at $\Omega > 0$. When $\Delta\sigma < 0$, the direction of the collision LIHF coincides with the direction of the light propagation at $\Omega > 0$, and it is opposite to the direction of light propagation at $\Omega < 0$ at any values of the δ .

The dependences of coefficients G_3 and G_4 on the rarefaction parameter δ are shown in Fig. 2. Note that these coefficients arise due to usage of kinetic models in the higher approximations, beginning with third-order model [6]. They are proportional to the rate $v_{nn}^{(2)}$ and, as a rule, have the higher order of smallness in relation to values of coefficients G_1 and G_2 . In the case of the inhomogeneous broadening of absorption line ($\Gamma \ll k\bar{v}$) we have $\chi_3/\chi_1 \approx \Gamma/(k\bar{v})$, and the contribution of coefficients G_3 and G_4 to the magnitude of LID is negligible. The contribution of coefficients S_3 and S_4 to the magnitude of the LIHF is negligible too, of order $\Gamma/(k\bar{v})$. But in the case of the homogeneous broadening ($\Gamma \gg k\bar{v}$) the contributions of coefficients S_1, S_2, S_3 and S_4 to the magnitude of the LIHF are of the same order.

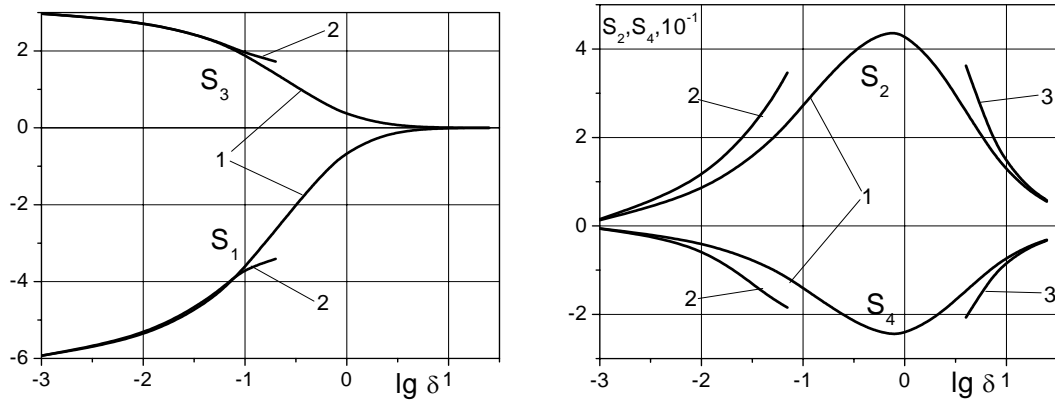
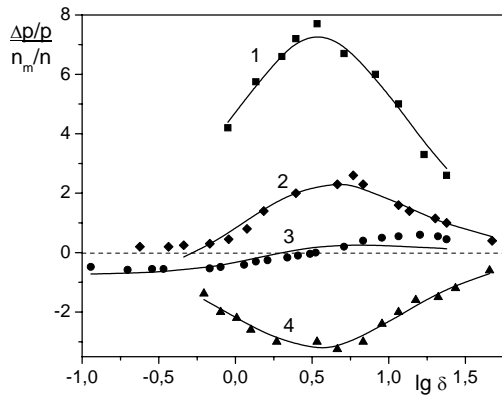


FIGURE 3. S_1, S_2, S_3, S_4 as functions of the parameter δ ; 1– numerical calculation, 2 – Eqs. (10), 3 – Eqs. (11).



The light-induced pressure difference between the ends of a closed capillary is studied in [9] for CH_3F molecules. This pressure difference, Δp , is aroused in the steady-state, where the light-induced drift is balanced by a Poiseuille flow [4]. For quantitative comparison of the theory with experiment [9] unknown parameters $\Delta\sigma/\sigma_n$ and $\Delta\epsilon$ are determined (table 1).

FIGURE 4. Comparison the theory (solid lines) with experiment [9]: 1-branch P (24,13) ; 2 - Q (12,3) ; 3 - R (4,3) ; 4 -R (31,9).

Table. 1. Experimental parameters for CH_3F molecules.

Branch	R(4,3)	R(31,9)	Q(12,3)	P(24,13)
$\Delta\epsilon, 10^{-3}$	-1.88	-(2.36-2.96)	4.71-4.97	-(2.17-3.33)
$\Delta\sigma/\sigma_n, 10^{-3}$	9.45	-(47.7-60)	-(99.5-105)	-(58.3-89.2)

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