Kinetic theory of light-induced drift in a channel

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A method is proposed for calculating the light-induced drift velocity, as well as the diffusive and thermal fluxes in a channel, treating both bulk and wall effects using a general kinetic approach. The light-induced drift velocity in a channel is calculated by means of a variational approach using the Barnett approximation for the distribution function. This is compared with the experimentally observed light-induced drift velocity as a function of pressure in the intermediate Knudsen-number range for $^{12}CH_3F$ molecules that absorb radiation at several distinct rotational-vibrational transitions.

1. INTRODUCTION

The phenomenon of light-induced drift and related effects due to laser-induced nonequilibrium in the velocity distribution function in a gas has received detailed scrutiny in previous publications.[1–4] This is true mainly of the so-called "bulk" light-induced drift,[3] where a necessary condition for the light-absorbing particles to drift is that the mixture contain a buffer gas such that the cross sections (frequencies) for collisions of the excited and unexcited gas with buffer particles are different ($\nu_{eb}\neq\nu_{gb}$). Directed particle transport can also occur in a one-component absorbent gas due to the surfaces bounding the gas (the channel walls). The theoretical analysis of this effect given in Refs. 5–7 only relates the motion of the gas in the channel to the difference in the accommodation rates of the tangential momentum on the channel wall for the excited and unexcited particles ($\kappa_e\neq\kappa_g$).

There a method of calculation is used which is based on using a Maxwell distribution in the shifted velocities as the zeroth-order approximation. This approach, which is quite suitable for free-molecular gas flow in a channel (Kn $=\lambda/d\gg 1$) turns out to be far from adequate for treating the other limiting regime (Kn$\ll$1), which corresponds to no-slip gasdynamic flow. As shown in Refs. 8–10, the use of more rigorous methods for solving the kinetic equation, which allow one to take into account the change in the distribution function of the Knudsen layer, implies that there is a slip velocity at the wall (and the related effect of "wall" light-induced drift) even when $\kappa_e=\kappa_g$, provided that $\nu_{eg}\neq\nu_{gg}$. Another reason for drift, noted by Hoogeveen *et al.*,[11] may be variation in the light intensity over the channel cross section, whose influence is only manifested if $\nu_{eg}\neq\nu_{gg}$ holds.

In the present work a theoretical treatment of light-induced drift is proposed in which bulk and wall effects are treated simultaneously by means of a general kinetic approach involving an average of the system of linearized kinetic equations over the channel cross section. This enables us to express the mass flow velocity and the diffusive and thermal fluxes of interest averaged over the cross section in terms of a few moments of the distribution function at the walls of the channel. The latter can be evaluated using familiar variational techniques.[12,13] By applying the Barnett approximation to the distribution function we can take into account the next-higher-order terms in the Knudsen number in the corresponding macroscopic fluxes, along with the slip effect. New terms related to wall effects also occur in the expression for the drift velocity of the excited gas when a buffer component is present. We conclude by comparing the calculated values of the drift velocity (or the related pressure drop in the channel) with the experimentally observed dependence of the light-induced drift on the pressure (Knudsen number) for $^{12}CH_3F$ molecules when light is absorbed at several distinct rotational-vibrational transitions.[11]

2. BASIC EQUATIONS

The system of equations describing light-induced drift in a system close to equilibrium excited by laser radiation whose intensity is uniform over the channel cross section was treated by Gel'mukhanov *et al.*[3,14] A system is close to equilibrium when the homogeneous half-width of an absorption line is much larger than the Doppler broadening ($\Gamma\gg k\bar{v}_\alpha$).

For a gaseous mixture consisting of an excited gas of two-level particles and a buffer gas, the relevant equations take the form

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\nabla+\Gamma_e\right)f_e=J_e+\frac{1}{2}\kappa(\mathbf{v})\Gamma_e(f_g-f_e),$$

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\nabla\right)f_g=J_g+\Gamma_e f_e-\frac{1}{2}\kappa(\mathbf{v})\Gamma_e(f_g-f_e), \qquad (1)$$

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\nabla\right)f_b=J_b.$$

Here the subscript e indicates the excited component, g indicates the component in the ground state, and b indi-

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cates the buffer component; Γ_e is the radiative decay constant of the excited state; and J_i is the Boltzmann collision integral.

The quantity $\kappa(\mathbf{v})$ is defined by

$$\kappa(\mathbf{v})=4\left|\frac{E_m d_{eg}}{2\hbar}\right|^2 \frac{\Gamma}{\Gamma_e}\frac{1}{\Gamma^2+(\omega-\omega_0-\mathbf{kv})^2}, \tag{2}$$

where E_m is the electromagnetic wave amplitude, ω is the frequency, $\mathbf{k}$ is the wave vector, d_{eg} is the dipole moment of the $e\rightarrow g$ transition, ω_0 is the transition frequency, Γ is the homogeneous radiation line width, and $\mathbf{v}$ is the particle velocity.

We assume that the radiation is in the z direction, parallel to the surfaces bounding the gas. The gas is assumed to be in steady state and the radiation intensity to be low ($\kappa(\mathbf{v})\ll 1$) and uniform in the interior of the channel. In this case the distribution functions f_e, f_g, and f_b vary only over the channel cross sections (in the x direction). Making use of these assumptions, we look for $f_{e,g,b}$ in the form $f_i=f_i^{(0)}[1+\Phi_i(x,\mathbf{v})]$, where $f_i^{(0)}$ is a Maxwellian distribution function and Φ_i are small corrections to it. For the latter we have the following system of equations in vector notation (the ith component of the mixture corresponds to the ith element of the vector)

$$v_x\frac{\partial}{\partial x}\Phi=\hat{\Lambda}\{\Phi\}+\Pi,$$

$$\hat{\Lambda}=\hat{L}+\begin{pmatrix}-\Gamma_e & 0 & 0\\ \frac{n_g}{n_e}\Gamma_e & 0 & 0\\ 0 & 0 & 0\end{pmatrix}, \tag{3}$$

where n_i is the number density of the ith component, $\hat{L}$ is the linearized Boltzmann collision operator, and Π is the field term

$$\Pi=\frac{1}{2}\kappa(\mathbf{v})\Gamma_e(n_g-n_e)\begin{pmatrix}1/n_e\\ -1/n_g\\ 0\end{pmatrix}. \tag{4}$$

In addition to Eqs. (3) we must apply boundary conditions at the channel walls. For simplicity, we assume that the excitation of the gas particles does not quench at the walls, but the excited, unexcited, and buffer particles are scattered from the surface with different accommodation coefficients. The boundary conditions can then be written in the form

$$\Phi(-d/2,\mathbf{v})=\hat{H}\Phi(-d/2,\mathbf{v})$$
$$=\int_{v_x'<0}\mathbf{R}(\mathbf{v},\mathbf{v}')|v_x'|f^{(0)}(\mathbf{v}')\Phi$$
$$\times(-d/2,\mathbf{v}')d\mathbf{v}'. \tag{5}$$

Here the kernel $\mathbf{R}(\mathbf{v},\mathbf{v}')$ of the scattering operator is a diagonal matrix and its elements satisfy the usual reciprocity relations.[12]

3. MEAN GAS FLOW VELOCITY

We are interested in the mass-averaged flow velocity $\langle u_z\rangle$ of the mixture averaged over the channel cross section, defined by the expression

$$\rho\langle u_z\rangle=\langle\langle m v_z,\Phi\rangle\rangle=\langle m v_z,\mathbf{F}(\mathbf{v})\rangle, \tag{6}$$

where ρ is the mass density of the mixture, $\mathbf{F}(\mathbf{v})=d^{-1}\int_{-d/2}^{d/2}\Phi dx$ is the spatially averaged distribution function, and the double angle brackets indicate an average over the channel cross section of a scalar product in the form

$$\langle\psi(\mathbf{v}),\chi(\mathbf{v})\rangle=\sum_i\int\psi_i\chi_i f_i^{(0)}d\mathbf{v}_i. \tag{7}$$

The average of Eqs. (3) over the transverse spatial coordinate yields

$$\frac{v_x}{d}\left[\Phi\left(\mathbf{v},\frac{d}{2}\right)-\Phi\left(\mathbf{v},-\frac{d}{2}\right)\right]=\hat{\Lambda}\{\mathbf{F}(\mathbf{v})\}+\mathbf{P}, \tag{8}$$

where

$$\mathbf{P}=d^{-1}\int_{-d/2}^{d/2}\Pi dx.$$

We will find $\mathbf{F}(\mathbf{v})$ in the form $\mathbf{F}_0(\mathbf{v})+\psi(\mathbf{v})$, where $\mathbf{F}_0(\mathbf{v})$ is defined by

$$\hat{\Lambda}\{\mathbf{F}_0(\mathbf{v})\}+\mathbf{P}=0. \tag{9}$$

Let $v_z\Phi^f$ be a solution of Eq. (9) such that $\langle m v_z,v_z\Phi^f\rangle=0$; then

$$\rho\langle u_z\rangle=\langle m v_z,\psi\rangle. \tag{10}$$

We will now show that the desired quantity $\rho\langle u_z\rangle$ can be expressed through some simple transformations in terms of certain scalar products of the auxiliary functions $v_z\Phi^f$ and moments of the distribution function Φ at the channel wall. Note that $v_z\Phi^f$ represents a bulk solution, in the sense of being a correction to the distribution function which develops in the gas outside the Knudsen layers. The form of $v_z\Phi^f$ can be found if we solve Eq. (9) by one of the usual techniques (the Chapman–Enskog technique[15] or the Grad technique[16]). The structure of $v_z\Phi^f$ was examined in Refs. 3 and 14 for special cases; consequently, we will assume that the solution $v_z\Phi^f$ is known.

Substituting $\mathbf{F}(\mathbf{v})=\mathbf{F}_0(\mathbf{v})+\psi(\mathbf{v})$ into (8), we find

$$\frac{v_x}{d}\left[\Phi\left(\mathbf{v},\frac{d}{2}\right)-\Phi\left(\mathbf{v}-\frac{d}{2}\right)\right]=\hat{\Lambda}\{\psi\}. \tag{11}$$

We use the well-known integral relations[17,18]

$$\frac{m v_x v_z}{kT}=\hat{\Lambda}^*\{v_x v_z\Phi^P\}, \tag{12}$$

$$v_x^2 v_z\Phi^P+\frac{m}{\rho kT}\eta v_z=\hat{\Lambda}^*\{v_z\Phi^B\}, \tag{13}$$

where η is the viscosity of the mixture, $v_x v_z\Phi^P$ is an analog of the familiar Chapman–Enskog solution for the shear viscosity of a gas,[15] and $v_z\Phi^B$ is the Barnett correction to

the distribution function. Note that Λ^* is an operator adjoint to Λ with respect to the scalar product (7).

Taking the scalar product of Eq. (11) with $v_z\Phi^B$, we find

$$d^{-1}\left\langle v_x v_z \Phi^B, \left[\Phi\left(\frac{d}{2}\right)-\Phi\left(-\frac{d}{2}\right)\right]\right\rangle = \langle v_z\Phi^B, \hat{\Lambda}\{\psi\}\rangle. \tag{14}$$

Because the operators $\hat{\Lambda}$ and $\hat{\Lambda}^*$ are adjoint we have $\langle\Phi,\hat{\Lambda}\varphi\rangle = \langle\varphi,\hat{\Lambda}^*\Phi\rangle$, so the right-hand side of (14) can be written as $\langle\varphi,\hat{\Lambda}^*\{v_z\Phi^B\}\rangle$. As a result we can use (13) to write Eq. (14) in the form

$$d^{-1}\left\langle v_x v_z \Phi^B, \left[\Phi\left(\frac{d}{2}\right)-\Phi\left(-\frac{d}{2}\right)\right]\right\rangle = \eta(kT)^{-1}\langle u_z\rangle + \langle v_x^2 v_z \Phi^P, \psi\rangle, \tag{15}$$

in terms of which $\langle u_z\rangle$ can be expressed. To find the last term in (15) we use Eq. (3). We multiply this by $\mathbf{m}v_z$ and integrate with a Maxwellian weighting function. Using the conservation of momentum when molecules collide with one another and when they interact with the resonant radiation, we find

$$\langle \mathbf{m} v_x v_z \Phi\rangle = \text{const}. \tag{16}$$

The left-hand side of (16) contains the momentum flux density $\mathbf{m}v_z$ transported by the molecules in the x direction. Taking into account the symmetry of the channel and the symmetric radiation intensity profile over the channel cross section, we can show that this quantity vanishes at the center of the channel, so that the constant can be set equal to zero.

Now we take the scalar product of Eq. (3) with $v_x v_z \Phi^P$. Noting the form of the field (4), we find

$$\frac{\partial}{\partial x}\langle v_x^2 v_z \Phi^P, \Phi\rangle = \langle v_x v_z \Phi^P, \hat{\Lambda}^*\{v_x v_z \Phi^P\}\rangle = (kT)^{-1}\langle \mathbf{m} v_x v_z, \Phi\rangle = 0. \tag{17}$$

This enables us to obtain for the last term in (15) the relation

$$\left\langle v_x^2 v_z \Phi^P, \Phi\left(-\frac{d}{2}\right)\right\rangle = \langle v_x^2 v_z \Phi^P, \psi\rangle + \langle v_x^2 v_z^2 \Phi^P, \Phi^f\rangle. \tag{18}$$

Using (15) and (18), we can express the average gas flow velocity in the channel in terms of moments of the distribution function at the wall:

$$\langle u_z\rangle = \frac{kT}{\eta}\left\{\langle v_x^2 v_z^2 \Phi^P, \Phi^f\rangle - \left\langle v_x^2 v_z \Phi^{P'}, \Phi\left(-\frac{d}{2}\right)\right\rangle - d^{-1}\left\langle v_x v_z \Phi^B, \left[\Phi\left(\frac{d}{2}\right)-\Phi\left(-\frac{d}{2}\right)\right]\right\rangle\right\}. \tag{19}$$

4. HEAT FLOW AND DIFFUSION VELOCITIES

We now show that expressions similar to (19) may be obtained for the heat flow and diffusive velocities of the components of the mixture averaged over the cross section. We use the equation

$$(\beta v^2 - 5/2)v_z = \hat{\Lambda}^*\{v_z\Phi_t\}, \tag{20}$$

where $v_z\Phi_t$ is an analog of the well-known Chapman–Enskog solution for the thermal conductivity of a gas.[15] Taking the scalar product of Eq. (11) and $v_z\Phi_t$ we find

$$\left\langle d^{-1}v_x v_z \Phi_t, \left[\Phi\left(\frac{d}{2}\right)-\Phi\left(-\frac{d}{2}\right)\right]\right\rangle = \langle v_z\Phi_t, \hat{\Lambda}\{\psi\}\rangle = \langle \psi, \hat{\Lambda}^*\{v_z\Phi_t\}\rangle. \tag{21}$$

Using (20) and the definitions of $\mathbf{F}(\mathbf{v})$ and ψ we can rewrite the right-hand side of Eq. (21) in the form

$$\langle \psi, \hat{\Lambda}^*\{v_z\Phi_t\}\rangle = \langle \psi, (\beta v^2 - 5/2)\rangle v_z\rangle = (kT)^{-1}\langle q_z\rangle - \left\langle \left(\beta v^2 - \frac{5}{2}\right)v_z, v_z\Phi^f\right\rangle, \tag{22}$$

where $\langle q_z\rangle$ is the heat flux averaged over the cross section. When we make use of the symmetry of the distribution function $\Phi(v,x)$, we obtain for $\langle q_z\rangle$ the representation

$$\langle q_z\rangle = kT\left\{\left\langle \left(\beta v^2 - \frac{5}{2}\right)v_z, v_z\Phi^f\right\rangle + \frac{2}{d}\left\langle v_x v_z \Phi_t, \Phi\left(\frac{d}{2}\right)\right\rangle\right\}. \tag{23}$$

To find a similar relation for the diffusion velocities we use the relation[19]

$$v_{iz}\left(\delta_{ik}-\frac{\rho_i}{\rho}\right)\frac{n}{n_i} = \sum_j \hat{\Lambda}_{ij}^*\{v_z\Phi_d^k\}, \tag{24}$$

where δ_{ik} is the Kronecker tensor with $i, k = e,g,b$; ρ_i is the density of a component of the mixture; and $v_z\Phi_d^k$ is the analog of the familiar solution for ordinary diffusion in a mixture.[19]

Taking the scalar product of Eq. (11) and $v_z\Phi_d^k$, we find

$$\left\langle \frac{v_x v_z \Phi_d^k}{d}\left[\Phi\left(\mathbf{v}, \frac{d}{2}\right)-\Phi\left(\mathbf{v}, -\frac{d}{2}\right)\right]\right\rangle = \langle v_z\Phi_d^k, \hat{\Lambda}\{\psi\}\rangle = \langle \psi, \hat{\Lambda}^*\{v_z\Phi_d^k\}\rangle. \tag{25}$$

Equation (24) and the relation between $\mathbf{F}(\mathbf{v})$ and ψ enable us to rewrite the right-hand side of (25) in the form

$$\langle \psi, \hat{\Lambda}^*\{v_z\Phi_d^k\}\rangle = \sum_i \int d\mathbf{v}(F_i - v_z\Phi_i^f)v_{iz}\left(\delta_{ik}-\frac{\rho_i}{\rho}\right)\frac{n}{n_i} = n(\langle V_{kz}\rangle - \langle u_z\rangle) - n\langle V_{kz}^f\rangle, \tag{26}$$

where $\langle V_{kz}\rangle$ is the velocity of the kth component averaged over the cross section of the channel and $\langle V_{kz}^f\rangle$ is the velocity of the kth component due to the bulk distribution function $v_z\Phi^f$.

We thus arrive at the following representation of the diffusive velocity:

$$\langle V_{kz}\rangle-\langle u_z\rangle=\langle V_k^f\rangle\frac{2}{dn}\left\langle v_z\Phi_d^k,v_x\Phi\left(\frac{d}{2}\right)\right\rangle. \tag{27}$$

Here we have again made use of the symmetry of the distribution function and have replaced $\Phi(-d/2)$ by $\Phi(d/2)$ with a change of sign. Note that the use of (19) and (23) enables us to calculate the drift velocity of the excited component in the channel when a buffer gas is present. In what follows we only calculate the mass-averaged velocity of the mixture, since it determines the pressure drop across the ends of a capillary due to the action of the resonant radiation, which is what is measured in experiments.[11,20–22]

5. CALCULATION OF THE GAS FLOW VELOCITY

In order to calculate the average gas flow velocity in the channel we use a variational principle developed for nonself-adjoint operators.[12,13] The basic idea of this method is that for a system of equations

$$\hat{W}\mathbf{h}=\mathbf{B},\quad \hat{W}^*\mathbf{h}^*=\mathbf{B}^*, \tag{28}$$

where the operators $\hat{W}$ and $\hat{W}^*$ are adjoint to one another with respect to the scalar product $\langle\langle\mathbf{f},\mathbf{g}\rangle\rangle$ and $\mathbf{B}$ and $\mathbf{B}^*$ are arbitrary source terms, the functional

$$J(\mathbf{h},\mathbf{h}^*)=\langle\langle\mathbf{h}^*,\hat{W}\mathbf{h}-\mathbf{B}\rangle\rangle-\langle\langle\mathbf{h},\mathbf{B}^*\rangle\rangle \tag{29}$$

takes its stationary value at solutions of (28); that value is

$$J_{\rm st}=-\langle\langle\mathbf{h},\mathbf{B}^*\rangle\rangle. \tag{30}$$

Because of the arbitrariness permitted in the choice of $\mathbf{B}^*$, this variational method can be used to ascertain various gas characteristics.

Thus, for $\mathbf{B}^*$ in the form

$$\mathbf{B}^*=2d^{-1}v_xv_z\Phi^B\delta\left(x-\frac{d}{2}\right)-v_x^2v_z\Phi^P\delta\left(x+\frac{d}{2}\right), \tag{31}$$

where $\delta(x)$ is the Dirac delta function,and the gas flow velocity is determined in accordance with (19) by the expression

$$\langle u_z\rangle=kT\eta^{-1}[\langle v_x^2v_z^2\Phi^P,\Phi^f\rangle-J_{\rm st}]. \tag{32}$$

The solutions of Eqs. (28) must satisfy the boundary conditions. For these we can construct a functional whose constant values correspond to the boundary condition (5) for the distribution function of Ref. 12. For this reason it is convenient to represent J as a sum of two terms, an interior term and a wall term. For the former we can write

$$J_V=\langle\langle\mathbf{h}^*,\hat{P}(\hat{D}-\hat{\Lambda})\mathbf{h}-\hat{P}\mathbf{B}\rangle\rangle-\langle\langle\mathbf{h},\mathbf{B}^*\rangle\rangle, \tag{33}$$

where we have set $\hat{D}=v_x\partial/\partial x$, $\hat{P}$ is the inversion operator in velocity space $[\hat{P}\varphi(\mathbf{v})=\varphi(-\mathbf{v})]$, and $\mathbf{B}=\Pi$. By introducing the scalar products

$$\langle\mathbf{g},\mathbf{h}\rangle_B=\sum_i\int_{\partial R}\int_{\mathbf{vn}>0}g_ih_if_i^{(0)}|\mathbf{vn}|\,d\mathbf{v}dS, \tag{34}$$

where ∂R is the surface bounding the gas and $\mathbf{n}$ is the inward-pointing unit normal to this surface, we can represent the wall part of the functional as

$$J_B=\langle\hat{P}\mathbf{h}^*,(1-\hat{A}\hat{P})\mathbf{h}\rangle_B. \tag{35}$$

Here we have assumed that the solution of the adjoint equation also satisfies the boundary condition (5).

Finally, the functional can be represented in the form

$$J=\langle\langle\mathbf{h}^*,\hat{P}(\hat{D}-\hat{\Lambda})\mathbf{h}-\hat{P}\mathbf{B}\rangle\rangle-\langle\langle\mathbf{h},\mathbf{B}^*\rangle\rangle+\langle\hat{P}\mathbf{h}^*,(1-\hat{A}\hat{P})\mathbf{h}\rangle. \tag{36}$$

Since the original equation for φ is inhomogeneous, it is convenient to take as a test function the solution of the equation

$$\hat{\Lambda}\{\mathbf{h}\}+\Pi=0, \tag{37}$$

i.e., to include the corresponding solution of the inhomogeneous equation in it ahead of time. The simplest choice of a test function, in analogy with the solution for the gas flow in a channel when no radiation is present,[17] is to write it in the form

$$\mathbf{h}=\mathbf{m}av_z+v_z\Phi^f,\quad \mathbf{h}^*=\mathbf{m}a_1v_z. \tag{38}$$

By using these expressions in (36) and varying with respect to the parameters a and a_1 we can find a closed system for a and a_1. Substituting these values of a and a_1 into (38) and the functions $\mathbf{h}$ and $\mathbf{h}^*$ into the functional (36) yields the following expression for the average gas flow velocity in the channel:

$$\langle u_z\rangle=\frac{kT}{\eta}\{\langle v_x^2v_z\Phi^P,\Theta(v_x)(1-\hat{A}\hat{P})v_z\Phi^f\rangle+\frac{\langle\mathbf{m}v_xv_z^2,\Theta(v_x)(1-\hat{A}\hat{P})\Phi^f\rangle\langle\mathbf{m}v_xv_z^2\Phi^P,\Theta(v_x)(1-\hat{A}\hat{P})v_x\rangle}{\langle\mathbf{m}v_xv_z,\Theta(v_x)(1-\hat{A}\hat{P})\mathbf{m}v_z\rangle}+2d^{-1}\langle v_xv_z^2\Phi^B,\Theta(v_x)(1-\hat{A}\hat{P})\Phi^f\rangle-\frac{d^{-1}\langle\mathbf{m}v_xv_z^2,\Theta(v_x)(1-\hat{A}\hat{P})\Phi^f\langle\mathbf{m}v_xv_z\Phi^B,\Theta(v_x)(1-\hat{A}\hat{P})v_z\rangle}{\langle\mathbf{m}v_xv_z,\Theta(v_x)(1-\hat{A}\hat{P})\mathbf{m}v_z\rangle}. \tag{39}$$

We can find expressions for the heat flux and diffusive velocities in the channel similarly.

Further calculations require knowledge of the functions Φ^P, Φ^B, and Φ^f. The Appendix gives a calculation of Φ^P and Φ^B for components with identical masses ($m_e=m_g=m_b$); the method of calculation and specific form of Φ^f for various special cases are given in Refs. 8 and 14. Using these results and adopting the well-known specular diffusion model for particle scattering at a wall,[12] we arrive at the following expression for the gas flow velocity:

$$\langle u_z\rangle = -\frac{1}{2}\frac{n_e}{n}v_0\Big\{(\kappa_e-\kappa_g)$$
$$\times\Big[R_u\Big(1+\frac{(2-\kappa_g)n_g+(2-\kappa_b)n_b}{\kappa_g n_g+\kappa_b n_b}\Big)$$
$$+\frac{2}{5}R_h\Big(1+\frac{(2-\kappa_g)n_g+(2-\kappa_b)n_b}{2(\kappa_g n_g+\kappa_b n_b)}$$
$$-\frac{14\eta}{3pd}(\pi\beta)^{-1/2}\Big)\Big]-\kappa_g\frac{2}{5}R_h\frac{\Delta\nu}{\nu}$$
$$\times\Big(1+\frac{(2-\kappa_g)n_g+(2-\kappa_b)n_b}{2(\kappa_g n_g+\kappa_b n_b)}$$
$$-\frac{76\eta}{15}(\pi\beta)^{-1/2}\Big)$$
$$-\kappa_e\Big[R_d\Big(R_u+\frac{2}{5}R_h-\frac{2(\pi\beta)^{-1/2}}{d(\Gamma_e+\nu^{(1)})}$$
$$\times\Big(R_u+\frac{1}{5}R_h\Big)-\frac{\eta}{pd}(\pi\beta)^{-1/2}\Big(R_u\Big(\frac{3}{10}R_b$$
$$+\frac{16}{15}R_s\Big)+R_h\Big(\frac{9}{25}R_b+\frac{16}{25}R_s\Big)\Big)\Big]+(\kappa_g-\kappa_b)$$
$$\times\frac{n_b}{n}\Big[\frac{2}{5}DR_h\Big(1+\frac{(2-\kappa_g)n_g+(2-\kappa_b)n_b}{2(\kappa_g n_g+\kappa_b n_b)}$$
$$-\frac{14\eta}{3pd}(\pi\beta)^{-1/2}\Big)-\frac{\Delta\nu^{(1)}}{\nu^{(1)}}$$
$$\times R_u\Big(1+\frac{(2-\kappa_g)n_g+(2-\kappa_b)n_b}{\kappa_g n_g+\kappa_b n_b}\Big)\Big]\Big\}. \qquad (40)$$

Here we have written $v_0=2\Omega k k_b T/\Omega^2+\Gamma^2)m$, $\Omega=\omega=\omega_0$; k is the wave number, κ_e, κ_g, and κ_b are the accommodation coefficients of the molecules (excited, unexcited, and buffer gas), and $\nu^{(i)}=n\chi_{eg}^{(i)}/m$, $\Delta\nu^{(i)}=n(\chi_{eg}^{(i)}-\chi_{gg}^{(i)})/m$, $\chi_{\alpha\beta}^{(i)}$ are the familiar functions of kinetic theory, expressed in terms of Ω, the Chapman–Cowling integral.[15] The $\nu^{(i)}$ are analogs of the collision frequencies, $\nu=\nu^{(5)}+\nu^{(6)}$, $\eta=2p/3\nu$,

$$D=\frac{\Gamma_e+\nu^{(5)}}{\nu^{(5)}}\Big[\frac{\Delta\nu^{(2)}}{\nu^{(2)}}-\frac{\Delta\nu^{(1)}}{\nu^{(1)}}\Big]+\frac{\Delta\nu^{(6)}\nu-\Delta\nu\nu^{(6)}}{\nu\nu^{(5)}},$$

$$R_u=\frac{\Gamma_e}{\Gamma_e+\nu^{(1)}},\quad R^h=\frac{-5}{4}\frac{R\nu^{(2)}}{\Gamma_e+\nu^{(5)}},$$

and R_d,R_b,R_s are defined in the Appendix.

For a pure gas ($n_b=0$), expression (40) can be written in the form

$$\langle u_z\rangle = -\frac{1n_e}{2n}v_0\Big\{(\kappa_e-\kappa_g)\Big[R_u\Big(1+\frac{2-\kappa_g}{\kappa_g}\Big)+\frac{2}{5}R_h$$
$$\times\Big(1+\frac{2-\kappa_g}{2\varkappa_g}-\frac{14}{3}\mathrm{Kn}\Big)\Big]-\frac{2}{5}\kappa_g R_h\frac{\Delta\nu}{\nu}\Big(1$$
$$+\frac{2-\kappa_g}{2\kappa_g}-\frac{76}{15}\mathrm{Kn}\Big)-\kappa_e R_d\Big[R_u+\frac{2}{5}R_h-3\mathrm{Kn}\frac{\Gamma_e}{\nu}$$
$$\times\Big(R_u+\frac{1}{5}R_h\Big)\Big]-\kappa_e\mathrm{Kn}\Big[R_u\Big(\frac{3}{10}R_b+\frac{16}{15}R_s\Big)$$
$$+R_h\Big(\frac{9}{25}R_b+\frac{16}{25}R_s\Big)\Big]\Big\}, \qquad (41)$$

where $\mathrm{Kn}=(\pi\beta)^{-1/2}\eta(pd)^{-1}=\lambda/d$ is the Knudsen number (here λ is the mean free path).

Note that for $\mathrm{Kn}=0$, the result (41) is the same as the expression for the slip velocity obtained by Roldugin using an integral variational technique.[8] The quantity $\langle u_z\rangle$ depends both on the difference in the accommodation coefficients and on the relative difference in the collision frequencies of the excited and unexcited particles. This conclusion differs sharply from the results of Ref. 11, which disregarded the presence of slipping at the wall, and the dependence of $\langle u_z\rangle$ on $\Delta\nu/\nu$ is seen only when we retain the variation of the radiation intensity over the channel cross section.

Analysis of the expressions for the coefficients R_u,R_h,R_d,R_b,R_s reveals that $\langle u_z\rangle$ is very sensitive to the ratio $\Gamma_e/\nu^{(i)}$. The quantity Γ_e is defined as the reciprocal of the lifetime of the excited state, which in turn depends on the probabilities for spontaneous, stimulated, and collisional relaxation. Two cases are of primary interest: $\Gamma_e\gg\nu^{(i)}$ and $\Gamma_e\sim\nu^{(i)}$. It is easy to see that for $\Gamma_e\gg\nu^{(i)}$ we have $R_u\sim 1$, whereas all other coefficients vanish. Expression (41) in this case assumes the form

$$\langle u_z\rangle = -\frac{h_e}{n}v_0\frac{\kappa_e-\kappa_g}{\kappa_g}. \qquad (42)$$

It is noteworthy that (42) coincides with the expression of Ref. 20 to within a factor of order unity; the latter expression was obtained in the limit of free molecular gas flow ($\mathrm{Kn}\gg 1$), which occurs at relatively low pressures (for the experimental conditions,[20,21], e.g., where $d\sim 1$ mm holds at pressures $p\lesssim 10^{-1}$ torr). Although the coefficients R_i become comparable to the contribution from R_μ as the pressure rises, this increase in the pressure in experiments on light-induced drift is meaningful only up to the point where collisional broadening becomes comparable to Doppler broadening; for a typical rotational-vibrational transition resonant with CO_2 laser radiation, this occurs at pressures ~ 1 torr. In principle, this implies that (42) is valid in many cases even for intermediate Knudsen numbers.

6. COMPARISON WITH EXPERIMENT

Next we make a qualitative comparison of this behavior with experiments on light-induced drift in a one-component gas, performed at intermediate and small Knudsen numbers ($p=1$–10^2 Pa) by Hoogeveen *et al.*[11] Under the conditions of Ref. 11, this corresponds to the situation in which the primary mechanism for relaxation of an excited state is collisional ($\Gamma_e\sim\nu^{(i)}$). For estimates we use the simplest model of intermolecular interactions (elastic hard spheres). For this model we have

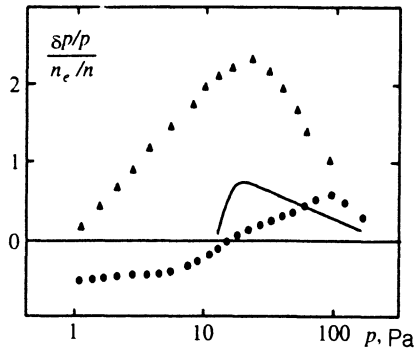

FIG. 1. Relative pressure difference across the ends of a capillary as a function of the mean pressure for the $R(4,3)$ and $Q(12,2)$ transitions: solid trace, calculated; ●—$R(4,3)$; ▲—$Q(12,2)$.

$$\nu^{(1)}=\frac{8}{3}\left(\frac{\pi kT}{m}\right)^{1/2}nd^2,\quad \nu^{(2)}=\frac{2}{5}\nu^{(1)},$$

$$\nu^{(3)}=\frac{16}{5}\nu^{(1)},\quad \nu^{(4)}=\frac{4}{5}\nu^{(1)},\quad \nu^{(5)}=\frac{59}{40}\nu^{(1)},$$

$$\nu^{(6)}=\frac{-27}{40}\nu^{(1)},\quad \nu=\frac{4}{5}\nu^{(1)},\quad A^*=D^*=1.$$

Here it is assumed that the diameters satisfy $d_{gg}\approx d_{eg}\approx d_{ee}=d$ and that their differences are retained only in those terms which vanish when the diameters are equal. Setting $\Delta=(d_{eg}^2-d_{gg}^2)/d_{gg}^2$, for $\Gamma_e\approx\nu^{(1)}$ we find

$$R_u=\frac{1}{2},\quad R_h=\frac{-10}{33},\quad R_d=\frac{-4}{21}\Delta,$$

$$R_b=\frac{34}{125}\Delta,\quad R_S=\frac{-1}{6}\Delta.$$

As a result, we arrive at the following simple expression for the gas flow velocity in a channel:

$$\langle u_z\rangle=\frac{-1}{2}\frac{n_e}{n}v_0[(\kappa_e-\kappa_g)(1+0.203\mathrm{Kn})+0.152\Delta(1-5.66\mathrm{Kn})]. \tag{43}$$

In experiments on light-induced drift,[11,22] the pressure drop δp was measured between the ends of a circular cylindrical capillary coupled to a flow of resonantly excited $^{12}CH_3F$ gas. The relative pressure drop as a function of the pressure p was found. Figure 1 shows the corresponding experimental behavior for different molecular transitions: the $Q(12,3)$ transition[11,22] and the $R(4,3)$ transition.[22]

Using the properties for the excited gas ($\kappa_e-\kappa_g=1.3\cdot10^{-3}$, $\Delta=1.1\cdot10^{-2}$) given in Refs. 11 and 22 for these transitions and the parameters of the experimental apparatus, we can find the following expression using (43):

$$\frac{\delta p/p}{n_e/n}=\frac{103.4}{p}\left(0.342-\frac{4.12}{p}\right), \tag{44}$$

where p is measured in Pa with $\mathrm{Kn}=5/p$.

Note that the slip velocity at the wall does not depend on the channel geometry, so that a difference in the numerical coefficient when we go from a planar to a cylindrical channel occurs only in the second term in parentheses in Eq. (44).

Figure 1 displays the experimental results and the behavior calculated in accordance with (44). It is evident that the behavior agrees qualitatively with the experimental dependence for the range $\mathrm{Kn}\lesssim0.25$. More satisfactory quantitative agreement in the results can probably be achieved by taking into account a correction factor associated with the finite ratio of the homogeneous and Doppler line broadening,[22,23] and also the variation in the radiation intensity over the channel cross section.[11]

APPENDIX

We present the scheme used to calculate the Chapman–Enskog functions for the adjoint operator $\hat\Lambda^*$. The adjoint operator $\hat\Lambda^*$ can easily be shown to be have the form

$$\hat\Lambda^*=\hat L+\begin{pmatrix}\Gamma_e & \Gamma_e & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix}. \tag{A1}$$

Taking into account the fact that n_e is small in comparison with n_g and n_b and the form of the operator $\hat\Lambda^*$, we can see that the nonself-adjoint character of the operator is manifested when the functions Φ_e^P and Φ_e^B for the excited molecules are evaluated, while $\Phi_{g,b}^P$ and $\Phi_{g,b}^B$ can be taken from the classical work of Refs. 15 and 19.

The functions Φ_e^P and Φ_e^B can be found using the moment technique.[16] A distinctive aspect of this case is that the operator $\hat\Lambda^*$ is nondegenerate, and there exist eigenfunctions proportional to v_z with nonvanishing eigenvalues. For this reason the function Φ_i^B is sought in the form

$$v_z\Phi_i^B=\frac{mA^0}{kT}v_z\delta_{ie}+\frac{4}{5}\beta^{1/2}p_i^{-1}c_z\left(c^2-\frac{5}{2}\right)B_i+2\beta^{1/2}p_i^{-1}mc_z\left(X_ic_x^2+Y_ic_y^2+\frac{1}{2}Z_ic_z^2\right),$$

$$\mathbf{c}=\beta^{1/2}\mathbf{v},\quad \beta=m/2kT. \tag{A2}$$

Simple calculations using the standard moment technique yield

$$\Phi_i^P=-\frac{m\eta}{pkT}[1-\delta_{ie}R_d],$$

$$\Phi_i^B=-\frac{\eta}{p}\frac{R_d}{\Gamma_e+\nu^{(1)}}\delta_{ie}+\frac{3}{5}\left(\frac{\eta}{p}\right)^2\left(\left(\beta v^2-\frac{5}{2}\right)\right)(1-\delta_{ie}R_b)+\frac{20}{9}\beta\left(v_x^2-\frac{v^2}{5}\right)(1-\delta_{ie}R_s)),$$

$$R_d=\frac{\Delta\nu^{(4)}}{\Gamma_e+\nu^{(3)}},$$

$$R_b=\frac{\nu R_d+\Delta\nu}{\Gamma_e+\nu^{(5)}}+\nu\frac{R_d R_h}{\Gamma_e},$$

$$R_s=\frac{\frac{3}{2}\frac{p}{\eta}R_d-\frac{4}{9}\Delta\nu}{\Gamma_e+\frac{4}{15}n\Omega^{11}\left(\frac{15}{2}+9A^*+\frac{24}{7}D^*\right)}, \tag{A3}$$

where Ω^{11}, A^*, and D^* correspond to the usual notation of kinetic theory.[19]

[1] F. Kh. Gel'mukhanov and A. M. Shalagin, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 773 (1979) [JETP Lett. **29**, 711 (1979)].
[2] F. Kh. Gel'mukhanov and A. M. Shalagin, Zh. Eksp. Teor. Fiz. **78**, 1674 (1980) [Sov. Phys. JETP **51**, 839 (1981)].
[3] F. Kh. Gel'mukhanov and A. M. Shalagin, Avtomet. **3**, 103 (1980).
[4] A. M. Dykhne and A. N. Starostin, Zh. Eksp. Teor. Fiz. **79**, 1211 (1980) [Sov. Phys. JETP **52**, 612 (1980)].
[5] M. A. Vaksman and A. V. Gainer, Zh. Eksp. Teor. Fiz. **89**, 41 (1985) [Sov. Phys. JETP **52**, 233 (1985)].
[6] A. V. Ghiner, M. I. Stockmann, and M. A. Vaksman, Phys. Lett. **96A**, 79 (1983).
[7] V. V. Levdanskii, Zh. Tekh. Fiz. **53**, 810 (1983) [Sov. Phys. Tech. Phys. **28**, 518 (1983)].
[8] V. I. Roldugin, Kolloid. Zh. **50**, 506 (1988).
[9] I. V. Chermyaninov and V. G. Chernyak, Inzh.-Fiz. Zh. **60**, 1015 (1991).
[10] A. É, Bazelyan and M. N. Kogan, Dokl. Akad. Nauk SSSR **308**, 75 (1979).
[11] R. W. M. Hoogeveen, G. J. van der Meer, L. J. F. Hermans *et al.*, Phys. Rev. A **39**, 5539 (1989).
[12] C. Cercignani, *Theory and Application of the Boltzmann Equation*, Elsevier-North Holland, New York (1976).
[13] B. I. M. ten Bosch, J. J. M. Beenaker, and I. Kuscer, Physica A **143**, 261 (1987).
[14] F. Kh. Gel'mukhanov and L. V. Il'ichev, Khim. Fiz. **3**, 1544 (1984).
[15] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases*, Cambridge University Press (1953).
[16] H. Grad, Comm. Pure Appl. Math. **2**, 331 (1949).
[17] H. Lang, Phys. Fluids **19**, 336 (1976).
[18] V. M. Zhdanov and V. I. Roldughin, Physica A **185**, 169 (1992).
[19] J. H. Fertsiger and G. Kaper, *Mathematical Theory of Transport in Gases*, Elsevier-North Holland, New York (1972).
[20] R. W. M. Hoogeveen, G. I. van der Meer, and L. J. F. Hermans, Phys. Rev. A **42**, 6471 (1990).
[21] A. V. Gainer, K. P. Komarov, and K. G. Folin, Zh. Eksp. Teor. Fiz. **82**, 1853 (1982) [Sov. Phys. JETP **55**, 1068 (1982)].
[22] R. Hoogeveen, *Light-Induced Kinetic Effects in Molecular Gases*, Huygens Laboratorium, Leiden (1990).
[23] V. R. Mironenko and A. M. Shalagin, Izv. Akad. Nauk SSSR Ser. Fiz. **45**, 995 (1981).

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