Theoretical analysis of the motion of a dense gas which interacts with a wall during velocity-selective excitation

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A theory is derived for the drift of a gas in a vessel with dimensions large in comparison with the mean free path. This drift arises when the gas is excited in a velocity-selective way (by virtue of the Doppler effect), as a result of a difference between the ways in which excited and unexcited particles, are scattered by the wall of the vessel. The drift velocity and the relative concentration of the resonant component are calculated. These quantities cannot decrease during the transition from a low-density gas to a dense gas, as the mean free path becomes much smaller than the dimensions of the vessel. Possible experimental manifestations of the effect and certain applications are evaluated.

1. INTRODUCTION

The drift of a low-density single-component gas during velocity-selective excitation has been described in some recent papers[1)] (Refs. 1–3). This drift arises when the particles (atoms or molecules) which are resonant with the radiation are scattered in different ways by the wall of the vessel, depending on whether the particles are excited (e) or unexcited (g). The fractions of the e and g particles scattered in a specular manner were not the same in Refs. 1 and 2. The drift during elastic scattering was studied in Ref. 3, and the collisions of the e and g particles with the wall differed in the "degree of inelasticity" (see Refs. 7–9, for example, for an analysis of inelastic scattering[2)]). The difference in the scattering which can be used may be significant[5,7,8]; in principle, the drift velocity can reach values on the order of the thermal velocity v_T.

What will happen if the gas density is raised to the point that the mean free path l becomes much shorter than the tube radius R (Fig. 1)?

The particles which interact with the wall lie in a thin layer of thickness $\lesssim l$ beside the wall. The problem thus has the small parameter l/R. How would experimentally observable quantities depend on this parameter?

In order to focus on the prominent features we will ignore the "buffer" drift mechanisms (those which involve collisions of the particles with the buffer gas, not with the vessel wall).[10–13] We assume that the spectrum of the radiation is such that the excitation of the particles occurs asymmetrically with respect to the center of the Maxwellian velocity distribution. In the excited velocity interval, $|v_x - v_0| \lesssim \Delta v_0/2$, the relation between the numbers of excited and unexcited particles is different from that in the symmetric interval $|v_x + v_0| \lesssim \Delta v_0/2$, so that particles from the first interval are scattered by the wall in a different way than particles from the symmetric interval, and on the average the ensemble of resonant particles will acquire from the lateral wall a tangential momentum[1] $p_x \neq 0$. As a result, a gas layer beside the wall begins to be accelerated until the ordinary friction force with the wall associated with the nonspecular scattering cancels the accelerating force. We see that, on the whole, the resonant particles perceive the fixed wall as a moving wall. The problem can thus be reduced to a classical problem of gas dynamics. Specifically, we are to determine the state of the gas in a vessel with a lateral wall which is moving along the axis. Although the wall interacts directly only with the adjacent gas layer, with a thickness on the order of l, it is clear that the viscosity cause the entire volume of the gas to move, and the steady-state velocity V in a vessel without end walls must not decrease with increasing R/l. Consequently, some of the effects which we will be discussing here may be completely independent of the parameter l/R. The question of a gasdynamic formulation of the problem in the case of a mixture of gases will be taken up below.

2. SINGLE-COMPONENT GAS

In principle, the derivation of exact results requires that solution of a system of kinetic equations with appropriate boundary conditions, a determination of the flow velocity near the surface, and then the use of these results as boundary conditions for the gasdynamic equations. Because of the mathematical difficulties of this approach and also the need to deal simultaneously with the viscosity and the compress-

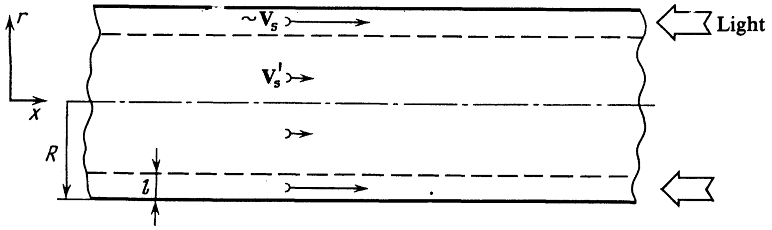

FIG. 1. Geometry of the problem of the drift of a dense gas in a vessel without ends.

ibility in the solution of the gasdynamic problem,[14] we will use some approximations.

We assume that no collisions between particles occur in a layer of gas of thickness l besides the wall, while outside this wall layer the particle velocity distribution in the volume, $f_{e,g}(\mathbf{v})$, from the kinetic equations in the model of strong collisions:

$$\frac{df_{e,g}}{dt}=\nu\left\{\left(\frac{\alpha}{\pi}\right)^{3/2}N_{e,g}\exp[-\alpha(\mathbf{v}-\mathbf{V}_s)^2]-f_{e,g}\right\}$$

$$\pm Q(\mathbf{v})(f_g-f_e)\mp\gamma f_e=0, \tag{1}$$

$$Q(\mathbf{v})\equiv\int\{1+[(\omega-\omega_0-\mathbf{kv})\Gamma^{-1}]^2\}^{-1}BM(\omega)\,d\omega.$$

Here $\nu\sim v_T/l$ is the rate of Maxwellizing collisions in the volume, $\alpha\equiv0.5v_T^{-2}$, $N_{e,g}$ are the densities of e and g particles, γ is the relaxation rate of the excited state, $M(\omega)$ is the radiation power density, B is the Einstein coefficient, ω_0 is the transition frequency, and Γ is the homogeneous line width. We restrict the analysis to the case of continuous irradiation. The condition for a steady state is that the force exerted on the wall layer of gas vanish:

$$a_e\int v_x v_\perp f_e d^3v+a_g\int v_x v_\perp f_g d^3v=0. \tag{2}$$

Here, as in Refs. 1–3, we are using Maxwell's model for scattering by the wall, $a_{e,g}$ are diffuse-scattering coefficients, and the subscripts e and g specify the resonant particles in the corresponding states. The coefficient a is actually a measure of the extent of accommodation of the tangential momentum of the particle during its scattering by the wall. Using (2), we find V_s in (1), i.e., the gas velocity in the layer directly adjacent to the surface layer:

$$V_s=-\left[b\frac{\psi}{2(1+\psi\theta)+(1+\theta)/\varkappa_0}v_0\right]$$

$$\left[1+b\frac{\psi\theta}{2(1+\psi\theta)+(1+\theta)/\varkappa_0}\right]^{-1}, \tag{3a}$$

or

$$V_s=-b\frac{n}{N(\nu+\gamma)}v_0\left[1+b\frac{n}{N(\nu+\gamma)}\frac{\nu}{\gamma}\right]^{-1}. \tag{3b}$$

Here $b\equiv a_e/a_g-1$; ψ is given in the case $\Delta v_0\ll v_T$, $|V_s|\ll|v_0|$, by

$$\psi=\frac{1}{\sqrt{2\pi}}\frac{\Delta v_0}{v_T}e^{-\alpha v_0^2};$$

$\theta\equiv\nu/\gamma$, $\varkappa_0\equiv Q_0/\gamma$, $Q_0\equiv Q(v_0)$, and $N\equiv N_e+N_g$ is the density of the resonant gas; n is the number of photons which are absorbed in the wall layer per unit volume per unit time; and

$$v_0=\int v_x Q(\mathbf{v})(f_g-f_e)d^3\mathbf{v}\left[\int Q(\mathbf{v})(f_g-f_e)d^3\mathbf{v}\right]^{-1}=\varphi v_T,$$

where φ is a function introduced in Ref. 16. In deriving (3) we have ignored the viscous friction between the wall layer and the rest of the gas. This simplification is legitimate for a vessel without ends or with infinitely remote ends, in which case there can be a steady-state free gas flow along the axis, with a velocity independent or $\mathbf{r}$: $V(\mathbf{r})=V_s$. According to (3b), in the limit $a_g\to0$, $\nu/\gamma\to0$, $v_0\neq0$ we have $V_s\to\infty$. The physical meaning of the singularity which arises in the equation is that the "drag" force exerted by the wall acts in this case only on particles which are in the excited velocity interval. No matter how high the gas velocity becomes, the force exerted by the wall does not change the direction. When real factors are taken into account, V_s remains finite. For example, a radial gradient of V changes expression (3), since the viscous friction changes the balance of forces acting on the wall layer of the gas [see (2) and the discussion below].

As in many problems involving a velocity-selective excitation, it may prove convenient to express the result in terms of the radiation power absorbed per unit volume, (3b), instead of the microscopic parameters of the problem (3a). Expression (3b) remains valid when the excited and unexcited states have a rotational structure. The form of (3b) does not change when various models of rotational relaxation are used (Refs. 4, 16 or 17); it suffices that the rates of translational, vibrational, and rotational relaxation of all the sublevels of the given vibrational state agree.

All of the gas is entrained in the motion at a velocity $V=V_s$ following the wall layer by virtue of the viscosity. Clearly, the velocity V of the flow $J\equiv NV$ is no smaller than for a low-density gas (the only change is an increase in the time for relaxation to a steady state). Consequently, the drift flow increases with an increase in the number of resonant particles which are "sorted" by the wall per unit time, and thus with an increase of the momentum transferred to these particles.

If the vessel is bounded by lateral ends the gas will accumulated at one of these ends until the drift is balanced by the oppositely directed convection caused by the pressure drop which arises (Fig. 2). Taking the viscous friction on the wall layer of gas into account in a force balance equation analogous to (2), we find the following boundary conditions on the gasdynamic equations:

$$V|_{r=R}+c(\partial V/\partial r)_{r=R}=V_s, \tag{4}$$

where the coefficient c is proportional to the viscosity η. This coefficient is determined from this balance of forces acting on the wall layer:

$$c\approx\sqrt{2\pi}l\left[a_g+(a_e-a_g)\frac{n}{N(\nu+\gamma)}\frac{\nu}{\gamma}\right]^{-1}.$$

Solving the Navier-Stokes equation for a long tube with boundary conditions (4) and $(\partial V/\partial r)_{r=0}=0$, ignoring the compressibility, we find an expression for $V(\mathbf{r})$ and for the density drop between the ends of the tube, $\Delta N\equiv N|_{x=L}-N|_{x=0}$. ($L$ is the length of the tube):

$$V(\mathbf{r})\approx V_0\left[2\left(\frac{r}{R}\right)^2-1\right],\qquad V_0\equiv V_s\left(1+\frac{4c}{R}\right)^{-1}; \tag{5a}$$

$$\Delta N\approx8\frac{V_0}{v_T}\frac{\eta L}{mNv_TR^2}N=8\frac{V_0}{v_T}\frac{lL}{R^2}N=8\frac{V_0}{v_T}\frac{L}{\sigma R^2}; \tag{5b}$$

where $\sigma\equiv(lN)^{-1}$ is the cross section of the Maxwellizing collisions. Velocity distribution (5a) is seen to be characteristic of a Poiseuille flow,[18] "displaced" in such a manner that we have a boundary velocity $V(R)=V_0\neq0$ and such that the total gas flow through a cross section of the vessel is

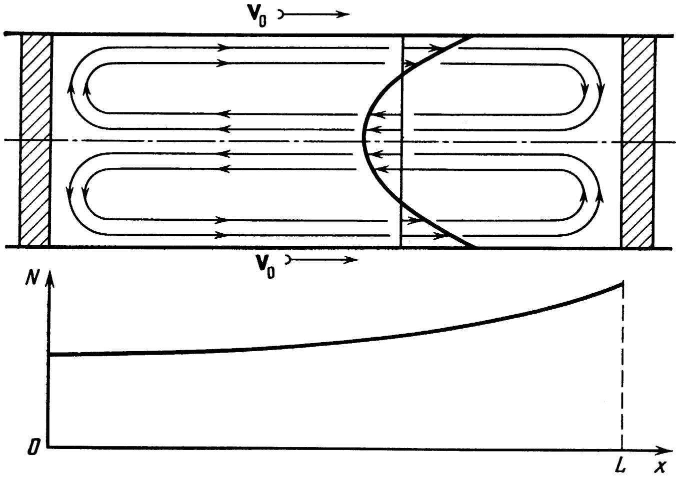

FIG. 2. Flows in a vessel with ends.

$$J=2\pi N\int V(r)\,r\,dr=0 \tag{6}$$

(Fig. 2). Expressions (5) are derived under the assumption $N(r)=\text{const}$ [see (6)]. Generally speaking, the compresibility of the gas will change the form of (6), while (5a) will contradict the continuity equation. However, Eq. (6) remains approximately correct at least for $\Delta N\lesssim N$. Over a distance $\sim R$, the length scale for a change in the vicinity profile $V(r)$ [see (5a) and Fig. 2], the gas density varies only slightly, according to (5b): $\Delta N/N\approx 8(V_0/v_T)(l/R)\ll 1$. The violation of the continuity equation is relatively small. We see that solution (5) can be used as an approximation. The exact solution of the problem of the flow of a viscous, compressible gas is considerably more complicated.[14]

If the velocity of the drift flow, V_0, and the tube radius are sufficiently large (if the Reynolds number is[18] $\mathrm{Re}\equiv 2V_0R/v_Tl\sim 10^3$), a turbulent regime in which the drift is cancelled may be established. Because of the pronounced nonuniformity of the transverse velocity profile, we do not rule out the possibility (especially in the case of a multicomponent medium, as discussed below) that vortex motions of the gas will arise even at a comparatively small value of V_0 (see Ref. 19, for example).

3. MULTICOMPONENT MIXTURE

Up to this point we have been talking about a single-component gas. If buffer particles are added to the vessel, they will become entrained in the flow of the resonant particles and will be slowed at the wall. The problem can also be formulated in the following way: We are to determine the state of a gas mixture in a vessel if we know that one of the components (the resonant component) perceives the side wall as moving, while the other (buffer) components perceive it to be at rest. The buffer gas therefore serves as a "volume" wall which creates a drag. Clearly, the flow velocities of the resonant and buffer components will become identical far from the wall (at distances $\gg l$). Writing the condition for a steady state analogous to (2), we find these velocities to be

$$V_s'=-b\frac{n}{N(\nu+\gamma)}v_0\left[1+\frac{a_b}{a_g}\frac{N_b}{N}\left(\frac{m_b}{m}\right)^{1/2}+b\frac{n}{N(\nu+\gamma)}\frac{\nu}{\gamma}\right]^{-1}. \tag{7}$$

Here m is the mass of a particle, and the subscript specifies the buffer gas. Since the velocities of the resonant and buffer components are identical throughout the vessel except in the wall layer, the total density $N+N_b$ evidently behaves in the same way as the density of a single-component gas, (5b). The role of V_0 here is played by the quantity

$$V_0'=-b\frac{n}{N(\nu+\gamma)}v_0\left[1+\frac{a_b}{a_g}\frac{N_b}{N}\left(\frac{m_b}{m}\right)^{1/2}+\frac{4\sqrt{2\pi}\,\eta}{a_gmv_TNR}\right.$$
$$\left.+b\frac{n}{N(\nu+\gamma)}\frac{\nu}{\gamma}\right]^{-1}. \tag{8}$$

In a wall layer with a thickness of order l, the resonant particles do not manage to undergo collisions with the buffer particles or to be slowed. Consequently, their flow in this layer remains comparatively fast. The flow of resonant particles in the wall layer is thus higher, and that of the buffer particles lower, than the average over the cross section. As a result, there is a separation of the gas components. Denoting by a the fraction of particles which are moving forward and backward with equal probabilities after scattering by the wall, we find the following expression for the flux densities of the resonant and buffer gases near the wall[3)]:

$$j=\left(1-\frac{a_g}{2}\right)V_0'N+\frac{a_g-a_e}{2}\int v_xf_e\,dv_x$$
$$=-\left[2+a_b\frac{N_b}{N}\left(\frac{m_b}{m}\right)^{1/2}+\frac{4\sqrt{2\pi}\,\eta}{mv_TNR}\right]$$
$$\times\left[1+\frac{a_b}{a_g}\frac{N_b}{N}\left(\frac{m_b}{m}\right)^{1/2}+b\frac{n}{N(\nu+\gamma)}\frac{\nu}{\gamma}\right.$$
$$\left.+\frac{4\sqrt{2\pi}\,\eta}{a_gmv_TNR}\right]^{-1}\frac{b}{2}\frac{n}{\nu+\gamma}v_0, \tag{9a}$$

$$j_b=(1-a_b/2)N_bV_0'. \tag{9b}$$

The difference between the particle flows j/N and j_b/N_b leads to an accumulation of the resonant particles at one end of the vessel and an accumulation of buffer particles at the other end. In the steady state, this effect is cancelled by diffusion and convection:

$$2\pi Rl\left[j-\left(j+\frac{l_b}{l}j_b+\frac{l-l_b}{l}N_bV_0'\right)\frac{N}{N+N_b}\right]+J_d+J_c=0, \tag{10}$$

where J_d and J_c are the flow components caused by diffusive and convective mixing, respectively; here $J_d\approx\pi R^2D\nabla N$. In estimating J_c we should taken into account the diffusion of resonant particles in the transverse direction; Eqs. (5a) and (8) give us (under the condition $L_d'\ll L$)

$$J_c\approx\frac{L_d'}{L}\Delta N\cdot 2\pi\int_0^{R/\sqrt{2}}V(r)r\,dr=-\frac{\pi}{4}\Delta N\frac{R^4V_0'^2}{DL},$$

where $L_d'\equiv V_0'(R^2/D)$. We see that under the condition $(RV_0'/2lv_T)^2\gg 1$ the convective equilibration outweighs the equilibration caused by diffusion in the longitudinal direction. From (9) and (10) we find the density drop beyond that in (5b):

$$\Delta N\approx-4\left\{a_b\left[\frac{l_b}{l}+\left(\frac{m_b}{m}\right)^{1/2}\frac{N_b}{N}\right]+\frac{4\sqrt{2\pi}\,\eta}{mv_TNR}\right\}\frac{v_T}{V_0'}\frac{Ll^2}{R^3}\frac{N_b}{N+N_b}N. \tag{11}$$

In the case $|J_d|\gg|J_c|$, on the other hand, which corresponds to $(RV_0'/2lv_T)^2\ll 1$, we find from (9) and (10)

$$\Delta N\approx\frac{\Delta S}{\hbar\omega(\nu+\gamma)R}\frac{v_0}{v_T}A\sim\frac{V_0}{v_T}\frac{N}{R}L, \tag{12}$$

where $\Delta S\equiv n\hbar\omega L$,

$$A\equiv-\frac{N_b}{N+N_b}b\left\{\left[\frac{l_b}{l}+\frac{N_b}{N}\left(\frac{m_b}{m}\right)^{1/2}\right]a_b+\frac{4\sqrt{2\pi}\,\eta}{mv_TNR}\right\}$$

$$\times\left[1+\frac{a_b}{a_g}\frac{N_b}{N}\left(\frac{m_b}{m}\right)^{1/2}+b\frac{n}{N(\nu+\gamma)}\frac{\nu}{\gamma}+\frac{4\sqrt{2\pi}\eta}{a_gmv_TNR}\right]^{-1}.$$

Equations (11) and (12) can be used in the case $l=l_b$ for an arbitrary relation between N and N_b, and in the case $l\gg l_b$ they can be used if $N_b\gg N$. The reason for this restriction is that at distances from the wall greater than a mean free path the distribution function is assumed to be Maxwellian, and the established of such a distribution required that the particles collide predominantly with a gas in equilibrium.

It can be seen from (12) that in a two-component mixture the quantity ΔN may be considerably larger (by a factor R/l) than the value of ΔN for a single-component gas, (5b). The reason is that a cancellation of the drift by the diffusion requires a higher value of ΔN than would be required for a cancellation by convective mixing. Figure 3 shows a typical solution for the conditions corresponding to (12).

Using (11) and (12), we can find the dependence of ΔN on the drift velocity. For small values of V_0' in (12) we have $\Delta N\propto V_0\propto V_0'$, while at larger values of V_0' we find that ΔN begins to decrease with increasing V_0', as can be seen from (11). Finally, at V_0' large enough to satisfy the condition $L_d'\gtrsim L$ the dependence $\Delta N(V_0')$ becomes a constant, as can be seen by using (9), (10), and the expression for J_c without allowance for transverse diffusion (the factor L_d'/L drops out).

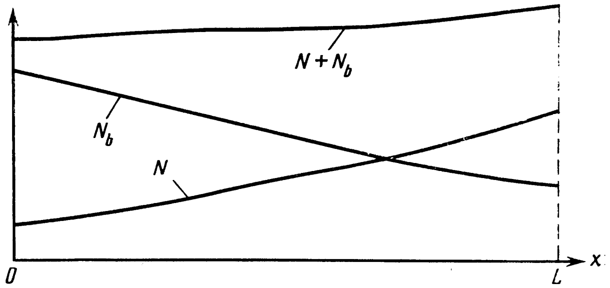

FIG. 3. Gas mixture in a vessel with ends. The drop in the total density, $N+N_b$, is small; the partial drops of the densities of the resonant (N) and buffer (N_b) components are directed oppositely and may be large.

In the case

$$\frac{N_b}{N}\left(\frac{m_b}{m}\right)^{1/2}\gg\max\left\{\frac{l_b}{l},\frac{a_g}{a_b},\frac{4\sqrt{2\pi}\,\eta}{mv_TNRa_b},\quad b\frac{a_g}{a_b}\frac{n}{N(\nu+\gamma)}\frac{\nu}{\gamma}\right\}$$

we have, according to (12),

$$A=\frac{N_b}{N+N_b}(a_g-a_e).$$

In the case

$$b\frac{n}{N(\nu+\gamma)}\frac{\nu}{\gamma}\gg\max\left\{1,\ \frac{a_b}{a_g}\frac{N_b}{N}\left(\frac{m_b}{m}\right)^{1/2},\quad\frac{4\sqrt{2\pi}\,\eta}{mv_TNRa_g}\right\}$$

we have

$$A=-\frac{N_b}{N+N_b}\left\{\left[\frac{l_b}{l}+\frac{N_b}{N}\left(\frac{m_b}{m}\right)^{1/2}\right]a_b+\frac{4\sqrt{2\pi}\,\eta}{mv_TNR}\right\}$$

$$\times\frac{(\nu+\gamma)\gamma}{\nu}\frac{N}{n}.$$

We see that in the latter case the magnitude of the effect becomes independent of the parameter b.

Although all these results were derived in the Maxwell model, they remain valid for certain other models of the interaction of the gas particles with the wall. For example, the contribution of inelastic processes is described by the same equations with

$$b\approx\frac{1-a}{2a}\frac{1}{v_T}(d_eu_e+d_{eg}u_{eg}-d_gu_g-d_{ge}u_{ge}), \tag{13}$$

where $a_e=a_g\equiv a$, $u_{e,g}$ are the increments in the tangential velocity component of the e and g particles, $d_{e,g}$ are the probabilities for the inelastic scattering of these particles during quasispecular reflection without a change in internal state, u_{eg} and u_{ge} are the increments during scattering accompanied by transitions from the e state to the g state and from the g state to the e state, respectively, and d_{eg} and d_{ge} are the probabilities for inelastic reflection accompanied by these transitions. Expression (13) was derived for the case[4)] $a\gtrsim 1-a$, $u_{e,g,eg,ge}\ll v_T\sim\Delta v_0$.

For rough surfaces "antispecular" (back) scattering, with the particles being reflected backward along the direction of incidence, may also occur (see Ref. 20 and the experiments of Ref. 21). In terms of the accommodation of the tangential momentum of a particle, antispecular scattering corresponds to the value $a = 2$. Interestingly, antispecular scattering is possible even in the case of scattering which is completely a locally diffuse scattering.[20] If the scattering is locally diffuse for both the unexcited and excited particles, the difference in the probabilities for adsorption upon collisions with the wall assumes primary importance. According to certain data (see Refs. 5 and 22, for example), the probability for the adsorption of a particle can be changed dramatically by radiation. Because of the comparatively high rate of surface diffusion,[23] adsorbed particles are distributed essentially uniformly over the surface relief, and they do not contribute to the antispecular scattering, in contrast with the particles which are scattered in a locally diffuse manner, but without adsorption. Accordingly, when there is a surface roughness a drift can arise even if all the particles are scattered in a locally diffuse manner by the surface. The same conclusion follows from an analysis of inelastic scattering by a rough surface (for different degrees of inelasticity of the e and g particles) and of scattering accompanied by chemisorption (for which the probabilities are different for e and g particles; see the review by Zhdanov and Zamaraev[24]). It thus appears that the effects discussed in the present paper can be seen in a broader range of actual physical situations.

The physics of this mechanism for the separation of the components of a mixture is different from that for a buffer mechanism. For a buffer mechanism the reason for the separation is the mutual "repulsion" of the resonant and buffer gases. In our case, the separation results from a difference (caused by the wall layer) in the velocities at which the gases are entrained by the wall. The value of ΔN in our case does not decrease with decreasing size of the region irradiated over the cross section of the vessel, provided that a narrow layer near the wall of thickness $\lesssim l$ remains irradiated[5),6)] (Fig. 1). This circumstance may prove extremely important.

Since the effect under consideration can in principle be large, there is the question of whether it can be seen under the conditions typical of experiments with velocity-selective excitation of optical transitions in atoms (Refs. 26 and 27, for example) and of vibrational and rotational transitions in molecules (Ref. 17, for example). It follows from (12) that for optical transitions in atoms values $A \sim -10^{-2}$ with $R = 0.3$ mm, $N \sim 10^{11}$ cm^{-3}, $N_b \sim 10^{17}$ cm^{-3}, $\Delta S \sim 2$ W/cm^2 and $v_0 \sim -v_T$ lead to $\Delta N \sim 0.3N$. For infrared excitation of molecules, values $A \sim -10^{-1}$ with $R = 1$ mm, $N \sim 10^{15}$ cm^{-3}, $N_b \sim 10^{16}$ cm^{-3}, $\Delta S \sim 100$ W/cm^2, and $v_0/v_T \sim -0.3$ lead to $\Delta N \sim N$. It can be seen from (12) that even if there are only elastic processes [specular, diffuse, and antispecular (back) scattering], the values of $|A|$ may exceed unity. In principle, inelastic processes may lead to even larger values of $|A|$. Analyzing the available data on the interaction of particles with surfaces (see Refs. 5, 7, 8, and 21–24, for example), we conclude that values $|A| \gtrsim 1$ are possible but unlikely, while values $|A| \sim 10^{-1}$–10^{-2} seem completely realistic.[7)]

We can use (12) to determine how the magnitude of the effect depends on the various parameters of the problem only if we know how the parameter b depends on them. For example, b may depend on the gas pressure P, since P determines the surface density of adsorbed particles. This density may in turn affect the depth of the adsorption potential, U (Ref. 5). There is the further possibility of an effect of the surface density of adsorbed particles on the extent to which the scattering is diffuse or antispecular. The adsorption of the component of the gas mixture which is at resonance with the radiation may vary with the density of the other components.[29] Consequently, an identification of the effect discussed here will require further study of the physics of the interaction of gases with surface and appropriate experiments.

The interaction of the field-induced dipole with its image in the wall material or with the dipole moments of particles at the surface changes the adsorption potential U (Ref. 5); this change may, along with other factors, cause a drift. If a drift arises because of the irradiation $a_e \neq a_g$, then at $\theta \equiv \nu/\gamma > 1$, the velocity of this drift decreases, as can be seen from (3a) and (3b), since collisions "scatter" the excited particles over the entire Doppler contour. At a fixed value of γ, the result is the imposition of an upper limit on the gas density in the vessel. In the case of a polarization mechanism, the scale time of this scattering is evidently determined not by the lifetime γ^{-1} but by the decay time of the dipole moment, Γ^{-1}. As a rule, the rate of depolarizing collisions of significantly higher than the rate of Maxwellizing collisions, so that at $\nu/\gamma > 1$ the extent of the scattering may be substantially smaller, and the effect may be a factor of ν/γ larger in this parameter than predicted by (3).

Even in the absence of a velocity-selective excitation, the longitudinal spatial nonuniformity of the radiation will cause a drift analogous to that which occurs for buffer mechanisms.[30] This question was discussed in Ref. 31 for the case of a low-density gas $(l \gg R)$. In our case, this effect is reminiscent of thermal creep.[32] An estimate carried out by analogy with the elementary derivation of the diffusion coefficient (Ref. 32, for example) for $\gamma \gtrsim \nu$ and $N_b \gg N$, shows that the corresponding density drop differs from the ΔN given by (12) for $v_0/v_T \sim 1$ by a factor of $v_T/L_a\gamma$, where L_a is the scale length of the linear optical absorption. Restrictions on the spectral width, the gas density, etc., are eliminated here.

Analogous effects can evidently occur in a solid as a result of an interaction of free carriers with its surface. According to Ref. 33, in film zones in thin films and in inversion layers at temperatures below the film quantum on the zone, the carriers corresponding to optical excitation are parallel, so that there is a pronounced velocity-selective excitation. It was also shown in Ref. 33 that in such systems, "the difference in momentum relaxation times is determined by the difference in the transverse structures of the wave functions, and apparently this difference may be seen particularly vividly when scattering by a surface is the dominant scattering mechanism."

Let us examine one possible application of phenomemon (see Ref. 6 for more details on these applications and regarding distinctive features of the effect for polyatomic molecules). According to Lyubitov,[7] "Quite soon there will be a need for beams of particles in given excited states, beams of metastable particles, and beams of polarized particles (in all senses: electric, magnetic, and spin polarizations). Analysis of the scattering of such particles by special targets will provide important information on surface states." There is the hope that the phenomenon described above will become the basis of a new method for studying the interactions of particles, especially excited particles, with surfaces. Using the conventional beam procedure (Ref. 34, for example), we can draw conclusions about the differences in the scattering of excited and unexcited paticles by comparing the scattering diagrams with and without irradiation. During the rapid relaxation of an excited state, it may be necessary to irradiate a region directly adjacent to a wall, including the surface itself. In this case the scattering diagram will be deformed by changes in the states of both the particles and the surface[5] (as a rule, the surface is covered by adsorbed particles of the same gas[34]). In the method proposed here, on the other hand, ΔN is related in a fundamental way to the difference in the scattering of excited and unexcited particles by the surface. At a fixed value of A, the frequency dependence of ΔN will be antisymmetric with respect to the center of the line; i.e., ΔN will change sign due to a relatively small change in the laser frequency. This circumstance also helps distinguish the effect described here from thermal effects[35,36] due to V-T relaxation and so forth. By measuring the actual dependence $\Delta N(\omega)$, we can obtain information on the absorption spectra of the adsorbed particles.

For estimates of the influence of the drift mechanism described above under specific experimental conditions, we would need to know the power density ΔS_{wall} absorbed near the wall, (12). In principle, we can draw conclusions about ΔS_{wall} by determining the traverse intensity distribution at the exit from the cell. When this approach is taken to estimate ΔS_{wall}, however, (see the Appendix), some caution must be exercised. For example, the fact that the intensity is low near the wall at the exit by no means automatically guarantees that ΔS_{wall} is small. In certain cases, this observation may be evidence of the opposite: At high power densities of the incident light, the light suffers almost no absorption in the volume because of saturation, and it is transmitted through the vessel, while a surface layer with a thickness of a few mean free paths [see (A.4)] will not be saturated (because of quenching at the wall) and will absorb strongly.

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APPENDIX

To derive the transverse distribution of excited particles and of the absorbed power density, taking into account the quenching of excited particles at the wall, we make use of the condition for a steady state:

$$D\frac{d^2N_e}{dy^2}+Q(N-2N_e)-\gamma_V N_e=0, \tag{A.1}$$

where y is the transverse coordinate, and γ_V is the relaxation rate of an excitation in the volume. For simplicity we assume that the excitation is not velocity-selective and that the total density N is constant over the cross section.[15] We take the quenching at the wall account through the boundary condition

$$DdN_e/dy-v_T\zeta N_e=0. \tag{A.2}$$

From (A.1) and (A.2) we find

$$N_e=\frac{Q}{2Q+\gamma_V}N\left[1-\frac{\zeta}{\beta+\zeta}e^{-\beta y/l}\right],$$
$$\beta=[(2Q+\gamma_V)/\nu]^{1/2}. \tag{A.3}$$

Using (A.3), we find the transverse distribution of the absorbed power density:

$$\Delta S(y)\propto N_g-N_e\propto\frac{\gamma_V}{2Q+\gamma_V}+\frac{2Q}{2Q+\gamma_V}\frac{\zeta}{\beta+\zeta}e^{-\beta y/l}. \tag{A.4}$$

Under the condition $R\gg l$, the power density absorbed near the wall and that absorbed in the volume form the following ratio, according to (A.4),

$$\frac{\Delta S_{\text{wall}}}{\Delta S_{\text{bulk}}}\approx 1+\frac{2Q}{\gamma_V}\frac{\zeta}{\beta+\zeta}. \tag{A.5}$$

For $Q=\nu$ we find from (A.5)

$$\frac{\Delta S_{\text{wall}}}{\Delta S_{\text{bulk}}}\approx 1+\frac{2\zeta}{\zeta'[(\zeta'+2)^{1/2}+\zeta]}\sim\frac{\zeta}{\zeta'},$$

where ζ is the fraction of quenching collisions which occur at the surface [see (A.2)], and ζ' is the same fraction in the volume. Typically, $\zeta\sim 0.1$–0.9 (see the bibliography in Ref. 6) and $\zeta'\sim 10^{-4}$ (Ref. 4) and thus $\zeta/\zeta'\sim 10^3$.

[1)] Dykhne and Starostin[4] raised the question of how the drift velocity of a gas would be affected by a difference between the interactions of excited and unexcited particles with walls.

[2)] A "polarization" mechanism for the interaction of particles with a wall[5] may also cause a drift[6] (more on this below).

[3)] Here we are ignoring the difference between the particle densities in the volume and near the walls and also the difference between the numbers of particles moving toward the wall and away from it in the wall layer.[15] This is one of the factors which can give rise to a separation of the components in the transverse direction. Also considering the convective longitudinal motion, we do not rule out the possibility of an increase in the degree of longitudinal separation of the components, by analogy with the effect in thermal diffusion. The latter circumstance was kindly pointed out by V. N. Panfilov.

[4)] Here it is assumed that no changes occur in the modulus of the normal component of the velocity during scattering by the wall; otherwise, expression (13) may become much more complicated.

[5)] The velocity u_V of the drift caused by buffer mechanisms may decrease by a factor of more than R/l. An additional reason for a decrease in this velocity here is a slowing of the drift by friction with the wall. The decrease in u_V was estimated in Ref. 4.

[6)] In this situation we should take into account the spatial nonuniformity of the light (Ref. 25, for example) and also, in some cases, the diffractive divergence of the light beam.

[7)] So far, no experiments have been carried out under the optimum conditions for the effect under discussion here. We are thus not in a position to confidently assert that the effect under discussion here has played a dominant role in comparison with other possible explanations in any of the experiments of which we are aware. In a recent paper reporting observation of a "semipermeable piston" in sodium vapor, Weij *et al.*[28] mentioned that surface effects were important in their experiments.

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