Surface light-induced drift caused by roughness

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A possible mechanism of surface light-induced drift (SLID) under velocity-selective excitation arising from the roughness of the cell wall surface is discussed here both qualitatively and quantitatively. Due to the backscattering from the facets of roughness SLID can arise even when scattering is completely locally diffusive. It provides significant widening of the scope of real physical situations where SLID can occur. This mechanism can basically explain the unexpected sign of SLID observed in recent experiments [Phys. Rev. Lett. **59**, 447 (1987); Phys. Rev. A **42**, 6471 (1990)]. As a method to study gas-surface interactions, SLID should be combined with some technique providing study of the surface topography.

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Surface light-induced drift [1–3] (SLID) is known to occur under velocity-selective excitation of a gas if molecules in the excited and the ground states are differently scattered by the cell wall surface. To describe the essence of SLID let us consider a one-component gas contained in a cell at the Knudsen regime (at low pressures where collisions with the walls dominate). A narrow-band laser beam travels along the cell. If the laser frequency ω is slightly detuned from the transition frequency ω_0, then due to the Doppler effect the only molecules that can be excited are those with an x component of the velocity near $v_0 = (\omega - \omega_0)/k$ (where x is the direction of propagation of radiation and k is the wave vector). Let the accommodation coefficient a_0 describing the transfer of parallel momentum to the wall be more (less) for excited molecules than for nonexcited ones, then the molecules in the excited velocity group around v_0 will be attenuated by the cell walls more (less) efficiently than molecules in the opposing velocity group (around $-v_0$), thus giving rise to a net flux. The flux direction coincides with the initial direction of molecules having smaller accommodation [Fig. 1(a)]. Recently [4,5] SLID was observed by Hoogeveen, Spreeuw, van der Meer, and Hermans in quartz cell for a vibrational-rotational transition of $^{13}CH_3F$, as well as for other species and surfaces. The geometry of the experiments [4,5] and the direction of drift observed are as shown in Fig. 1(a).

A commonly used explanation [1,5] for the accommodation effect is the Maxwell model of surface scattering. In this model only specular and diffusive scattering are taken into account. In the case of a flat wall, the coefficient a_0 is equal to the probability of diffusive scattering a_0. Thus, to explain the sign of the observed effect [4,5] one evidently is to assume $a_{0e} > a_{0g}$ (indices g and e here and below refer to the molecules in the ground and excited state, respectively). It looks natural to associate diffuse scattering mainly with adsorption and subsequent desorption, which leads to the conclusion that the adsorptivity in this case is larger in the excited state. In the CH_3F experiment the vibrotational transition $(v, J, K) = (0, 4, 3) \rightarrow (1, 5, 3)$ has been used. Comparing with other transitions, it was shown that the effect depends very little on the change in the vibrational quantum number,

but much more strongly on the change ΔJ of rotational number J. As $\Delta J = +1$, one would be led to the expectation that the adsorption probability should increase with J. This statement, however, was found [4] to be in contradiction to experimental evidence and physical arguments [6,7] that predict a decrease of the trapping probability with increasing J. A recent paper [8] attempts to explain this inconsistency by predicting an unmonotonous dependence of the value of a_0 on J. Such an assumption is in line with the result of a computer simulation [9], claiming that the adsorptivity increases with J at small J values but decreases at larger values.

It is, however, possible to suggest another, and perhaps more simple, explanation of the above apparent contradiction. The surface of the cell wall is generally not flat but rough. It was mentioned in Ref. [3] (in which SLID of a dense gas was studied) that wherever there is surface roughness SLID can arise even if all molecules are scattered in a locally diffuse manner. The origin of the drift in this case is illustrated in Fig. 1(b). Suppose the laser excites molecules in the velocity group near v_0, where $v_0 > 0$. Naturally, the molecules fall mostly onto those facets of the roughness which fact the direction of incidence. Hence, excited molecules will scatter primarily on facets of one orientation [facets labeled + in Fig. 1(b)], whereas ground-state molecules will scatter on facets of the oppo-
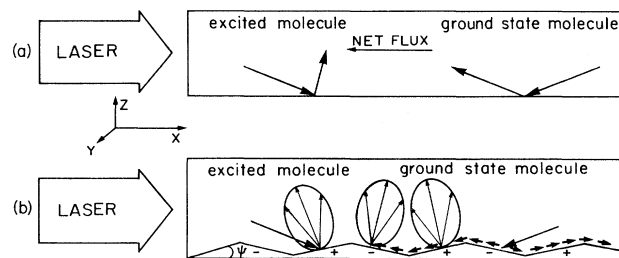

FIG. 1. (a) The origin of SLID flux, with laser frequency shifted to the blue, and with surface accommodation in the excited state larger than the corresponding one in the ground state. (b) Cell with rough walls: SLID arises even if the scattering of all the molecules is diffusive.

site orientation (facets labeled $-$). Let us denote by A the probability for a molecule to be adsorbed and subsequently to travel along a few facets (or be chemisorbed [10]), and by a the probability for the molecule to be diffusively scattered without adsorption, or to be adsorbed and subsequently desorbed at the same facet. Evidently, the fraction a_e (a_g) or incident e (g) molecules will give rise to backscattering, while the fraction A_e (A_g) of incident e (g) molecules will "forget" the orientation of the facet which adsorbed them and desorb on the average in normal direction with respect to the x axis. If $A_e \ne A_g$ then a drift will occur [3], with a direction similar to that of the backscattering of molecules having smaller values of A. As one can see from Fig. 1(b), the direction of drift observed [4,5] is obtained if $A_e < A_g$, in line with the data of Refs. [6] and [7]. The resulting change of sign of the SLID flux emerges from the observation that the simple rule "more adsorption—more accommodation" which holds for a flat surface, is broken in the case of rough one. Due to backscattering locally diffusive scattering provides greater accommodation for the parallel momentum than scattering accompanied by adsorption and subsequent traveling over the surface.

The sign of SLID can change due to roughness, so in order to draw conclusions from the observed SLID data about the value (and even the sign) of a change of the coefficient of adsorption during excitation, one should first study the microscopic structure of the surface of the cell wall.

"Ordinary" mechanisms of SLID [1,2] show up only if there is an appreciable part $1 - a_0$ of molecules scattered in a (locally) nondiffusive way with state-dependent scattering lobes. Considering that quite commonly [11] (for surfaces which were not specially prepared) $a_0 \sim 1$ (in other words, scattering is locally diffusive), and that no information is available on state dependence of the local scattering, one should be rather skeptical about the probability of SLID being widely met. Unlike above, the condition $A_e \ne A_g$ can be provided by state dependence of adsorption probability (and, in principle, of length l_e (g) of a molecule traveling over the surface before desorption). Since adsorption probability is generally accepted to be state dependent [7], the new mechanism provides a wide extension of the scope of real physical situations where SLID can occur.

The quantitative treatment is based on that carried out in Ref. [2] for SLID arising due to direct inelastic scattering. Let us restrict ourselves to a simple model of regular zigzag-shaped corrugation having a small angle of roughness ($\psi \ll 1$), and facets of two possible orientations, labeled $+$ and $-$ [Fig. 1(b)]. (A similar model was recently [11] used to study the transmission probabilities in capillaries.) We do not take into consideration the double collisions of a molecule with the neigboring facets. Using the polar system for two-dimensional treatment and denoting by ϕ the angle between the x axis and the particle velocity vector, we get the following set of steady-state kinetic equations for velocity distribution functions $f_e(\phi,v)$ of excited and $f_g(\phi,v)$ of the ground-state molecules in a flat channel with rough walls:

$$v a_e (1 - \zeta)(n_e^+ W^+ + n_e^- W^-) + s_e[v^+ p^+(\phi^+) f_e(\phi^+,v) + v^- p^-(\phi^-) f_e(\phi^-,v)] - v f_e = -Q(\phi,v)(f_g - f_e) + \gamma f_e,$$

$$(1a)$$

$$v[A_g(n_g^+ + n_g^-) + A_e(n_e^+ + n_e^-)]W + v[a_g(n_g^+ W^+ + n_g^- W^-) + \zeta a_e(n_e^+ W^+ + n_e^- W^-)]$$

$$+ s_g[v^+ p^+(\phi^+) f_g(\phi^+,v) + v^- p^-(\phi^-) f_g(\phi^-,v)] - v f_g = Q(\phi,v)(f_g - f_e) - \gamma f_e. \quad (1b)$$

In (1a) and (1b) the left-hand sides contain collision integrals; in the right-hand sides the first term describes the molecule-field interaction and the second one takes into account spontaneous relaxation, γ being its rate. Here s_e (g) are the probabilities of specular scattering of molecules in corresponding states (so that $A + a + s = 1$), $v(\phi,v) \equiv v|\sin\phi|/d = |v_z|/d$ is the inverse time of flight of molecule between the walls (that is, the frequency of velocity-changing collisions), and d is the distance between the walls of the cell. In treating the quenching of the excited particles we assume that all collisions of A type are accompanied by quenching, and ζ is a fraction of quenching collisions during scattering of a type.

Also, n_e^+ (g) and n_e^- (g) are the effective concentrations of particles scattered by the $+$ and $-$ facets, respectively,

$$n_{e,g}^{\pm} \equiv \int p^{\pm} f_{e,g}(\phi,v) d\phi \, dv . \quad (2)$$

$p^{\pm}(\phi)$ are the probabilities for the molecule to incident to $+$ or $-$ facets, respectively. A simple geometrical analysis yields $p^{\pm} = 0.5(1 \pm \psi \operatorname{ctg}\phi)$ for $\psi \le \phi \le \pi - \psi$. Scattering under very small angle ($\phi < \psi$ or $\pi - \psi < \phi < \pi$), which often leads to double collisions with neighboring facets, will be neglected here. $W(v) \equiv (\alpha/\pi) \times \exp(-\alpha v^2)$ is the Maxwellian. $W^{\pm}(\phi,v)$ are the distributions of molecules being diffusively scattered by $\pm$ facets. Since the probability for the particle to leave the surface after diffuse scattering is proportional to the cosine of the angle of its velocity to the surface normal $\mathbf{n}$ (Knudsen cosine law), the ejection from $\pm$ facets

$$v W^{\pm} \sim \mathbf{v} \cdot \mathbf{n} W = v(\sin\phi \mp \psi \cos\phi) W .$$

Note that $W^+ + W^- = 2W$, which is reflected in the term containing $A_{e,g}$. Then $v^+ \equiv v(\phi^+,v)$, $\phi^+ \equiv \phi - 2\psi$, $v^- \equiv v(\phi^-,v)$, and $\phi^- \equiv \phi + 2\psi$. Using the obvious symmetry of f_e (g) with respect to ϕ, f_e (g)$(\phi,v) = f_{e,g}(-\phi,v)$, one can see that specular scattering of a particle by the $+$ facet leads to its turn over the angle $+2\psi$, and specular scattering by the $-$ facet leads to its turn over -2ψ, which is taken into account by the terms with shifted ϕ. $Q(\phi,v) \equiv \int d\omega B M(\omega)[1 + (\Omega - \mathbf{k} \cdot \mathbf{v})^2/\Gamma^2]^{-1}$ is the rate of excitation of particles moving with the given velocity v under the given direction ϕ, M is the radiation intensity, $\Omega \equiv \omega - \omega_0$, and Γ is the homogeneous width of the absorption line. Using the condition $\psi \ll 1$, one can present

$f_{e,g}(\phi \pm 2\psi, v)$ as $f_{e,g}(\psi, v) \pm 2\psi \partial f_{e,g}(\phi,v)/\partial\phi$. Taking into account (2) we see that (1a) and (1b) are a set of integro-differential equations, the solution of which is rather complicated. To simplify calculations let us treat the case $s_e = s_g = 0$, when the contribution of the ordinary [1,2] mechanisms of SLID is absent. We will neglect spontaneous relaxation, since its rate is exceedingly small for rovibrational transitions of molecules [3,5]. We will consider the case of excitation of the half-infinite velocity group $v_x \geq 0$, that is, $-\pi/2 \leq \phi \leq \pi/2$. We suppose saturated absorption of radiation $Q \gg v_t/d$ [where $v_t \equiv (2\alpha)^{-1/2}$ is the mean thermal velocity]. In order to obtain $f_{e,g}$, we restrict ourselves by the first-order approximation, substituting the zeroth-order approximation (that is, the values of $f_{e,g}$ at $\psi=0$) to calculate $n_{e,g}^{\pm}$. We come to the following expression for SLID flux $j \equiv \iint d\phi\, dv\, v \cos\phi f(\phi,v)$ along the x axis (where $f \equiv f_e + f_g$ is the net velocity distribution):

$$j \simeq \frac{2}{\pi}(A_e - A_g)(\psi^2 \ln^2\psi)\frac{\Delta I}{\hbar\omega L}d . \tag{3}$$

Here we have assumed the case of an optically thin system, L is the cell length, and $\Delta I \equiv \hbar\omega L \int d\phi\, dv\, Q(\phi,v) \times (f_g - f_e)$ is the absorbed radiation power density. The proportionality of the flux to ψ^2 is a result of the multiplication of two quantities: (i) the difference of scattering probabilities on the $+$ and on the $-$ facets, and (ii) the asymmetry of diffusive ejection from each facet, both (i) and (ii) being proportional to ψ. The slight ($\sim \ln^2\psi$) deviation from ψ^2 is caused by particles moving at tangent angles $\phi \ll 1$ for which the difference in p^+ and p^- is not small.

If the side ends of the cell are closed then the light-induced flux is to be compensated by the diffusive one, $j - D\nabla N = 0$ (where N is molecule concentration, $D \simeq v_t d$ is the coefficient of diffusion). It leads to the expression of the relative pressure drop [12] along the cell as

$$\Delta p/p \simeq [j/(Nv_t)](L/d) \tag{4}$$

where the value of j is to be substituted from (3). The only observable quantity in the experiments [4,5] was $\Delta p/p$ (where it was found that $s_g - s_e = 1.9 \times 10^{-3}$). Equation (3) was derived under the assumption of strong saturation of the light absorption; unsaturated absorption should produce even greater effect (for a given ΔI). It can be shown that asymmetry and random behavior of the corrugation do not change essentially the value of the SLID flux. Note that even in the case of an arbitrary excitation spectrum, Eq. (3) can be used to estimate the flux which is now given by $(v_0/v_t)j$. We can conclude that in order to get the same observed $\Delta p/p$, when $s_e = s_g = 0$ and $\Delta A \equiv A_e - A_g = -\Delta a \sim -10^1 - -10^{-2}$, it is enough to assume [13] the existence of roughness with $\psi^2 \approx 0.1$ (i.e., $\psi \approx 19°$, the value derived [11] from comparison of the experimental and theoretical data for the transmittance of

the long capillaries for the gas flux).

Although when $\psi \ll 1$ the influence of roughness on specular collisions cannot change the sign of the drift, it is quite the opposite for $\psi \sim 1$. In this case, specular reflection from the facets leads to "antispecular" [3] (with respect to the macroscopic interface) scattering. For example, as qualitative treatment indicates, the results [4,5] can be provided if $\psi \sim 1$, $\Delta a = 0$, $s_e - s_g = -\Delta A \sim 10^{-2}$. Again, $\Delta A < 0$, which is in line with the results of Refs. [6] and [7].

Of course, if in experiments [4,5] roughness is very small $(\psi^2 \ln^2\psi \lesssim 10^{-2})$ then the calculation of $s_g - s_e$ carried out in Refs. [4] and [5] still holds.

The value of SLID arising due to roughness in the absence of specular reflection and chemisorption is maximal when the typical size of the facet is less than a characteristic diffusion length l of the molecule before desorption. At room temperatures l differs widely, at least [14] between 10^{-6} and 10^{-2} cm.

It is important to take the alternate mechanism of SLID into account, especially since the values of velocity of SLID flux (and of the drop of concentration of resonance molecules) cannot decrease during the transition from a rare gas to a dense gas, as the mean-free path becomes much smaller then the distance between cell walls [3].

Needless to say, in further treatments of the alternate mechanism, it remains to include a detailed examination of real physical systems, probably by means of a numerical solution of the kinetic equations of type (1) and a proper averaging over the angles of roughness, the values $l_{e(g)}$, etc.

In conclusion, we showed that surface light-induced drift arising due to roughness of the cell walls strongly differs from that in the case of a flat surface and extends the field of real physical situations where SLID can arise. Quantitative results were obtained for a model of small roughness. They indicate that when the roughness increases, its influence grows rapidly [$\sim \psi^2 \ln^2\psi$, where ψ is the typical angle of roughness, see Fig. 1(b)]. Hence, information about the surface structure is necessary in order to produce from SLID data any conclusion about the change in molecule-surface interaction by the excitation. The experimental data on SLID [4,5] can be reconciled basically with the results of Refs. [6] and [7] if we assume the existence of a suitable surface roughness.

One should note that SLID phenomenon provides a method of exceedingly high [4,5] sensitivity for studying the change of gas-surface interaction with excitation. As the above treatment indicates, this method should be combined with scanning tunneling microscopy [15] or another technique which allows the study of the surface topography.

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