Theory of nonequilibrium phenomena at a gas-solid interface

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A new (multiphase) approach to the description of nonequilibrium phenomena in a gas-adsorbate-solid system is proposed. The approach is based on the simultaneous solution of the Boltzmann equation for the gas and the kinetic equation for the ensemble of all the particles within the range of the surface forces. A kinetic equation for such particles is introduced and justified, and describes not only the molecules trapped in the potential well on the surface (adsorbed, in the traditional understanding) but also the particles that are, at the given time, in the interaction region "above the potential well." The equation obtained incorporates a molecule-phonon collision integral, describing the relaxation of the ensemble of particles in the region of their interaction with the surface, and also includes terms that take into account the arrival of particles and their departure into the gas phase. In the framework of this approach a kinetic theory is constructed which describes from unified microscopic standpoints various transport processes in the gas and on the gas-solid interface, and also the scattering of molecular beams by the surface in conditions with and without physical adsorption. With the use of the τ-approximation for the molecule-phonon collision integral a number of new effects are described—in particular, the recently discovered nonequilibrium distribution of desorbing (after complete relaxation on the surface) molecules. A new interpretation is given of certain familiar processes on a gas-solid interface—in particular, the adsorption and accommodation of a gas on the surface.

1. INTRODUCTION

In recent years a number of new physical phenomena in gas-solid systems have been discovered—in particular, the nonequilibrium polarization of polyatomic molecules reflected from a surface,[1,2] the non-Maxwellian desorption of particles from a surface,[3,4] and the entrainment (drag) of molecules by phonons of a nonequilibrium solid.[5,6] In the framework of currently familiar ideas concerning the interaction of particles with a surface it has not proved possible either to construct a consistent microscopic theory of these delicate effects or even to describe from unified standpoints such well known surface processes as the adsorption and accommodation of a gas and the scattering of molecular beams. For example, from the results of investigations on beam scattering, which give the most direct information on the interaction of molecules with a solid, it has not proved possible to predict features of the transport processes—in particular, properties of the coefficients of accommodation of energy or momentum on the surface; different approaches are usually used in the description of nonequilibrium phenomena in conditions with and without adsorption of particles. The reason for this lies in the fundamental difficulties that arise in attempts to give a correct description of the complicated pattern of the evolution of the ensemble of molecules within the range of the surface forces. Microscopically justified approaches exist today in only two cases (very special cases, from the point of view of the broad class of observable phenomena). These are the fast scattering of particles by a surface, describable in the framework of the dynamical scattering theory of Ref. 7, and the slow evolution of the state of a particle in a deep potential well on the surface of a solid (thermostat), describable in the framework of the theory of random walks.[8] In the general case, either simple models of the interaction of the molecules with the surface are used, e.g., the specular-and-diffusive reflection model of Maxwell,[9] or the problem is reduced simply to formal mathematic modeling.[10]

In the present paper we develop a systematic kinetic theory of a nonequilibrium system consisting of a solid, a gas, and an ensemble of (gas) molecules within the range of the surface forces. This model makes it possible to describe from unified microscopic standpoints transport processes and the scattering of molecular beams by a surface in conditions with and without physical adsorption. A fundamental aspect of the theory being developed is the idea that the ensemble of all the molecules within the range of the surface forces should be regarded in the general case as a separate statistical subsystem, for which a special kinetic equation is introduced. The latter contains terms which describe the arrival of particles and their departure into the gas phase, which occur with conservation of the energy of the molecules (in levels of the continuous spectrum), while transitions between states with different energies, accompanied by the emission or absorption of phonons of the solid, and, in particular, transitions of molecules into bound states (adsorption), are taken into account in the molecule-phonon collision integral.

The resulting picture of the interaction of the particles with the surface differs substantially from conventional concepts, which speak of "fast" reflection of molecules by a surface and trapping of molecules. Such concepts presuppose the possibility of determining the probability of a transition of particles from the gas phase directly into bound states. This probability can be calculated using dynamical arguments (see, e.g., Ref. 11) for light or heavy particles, when the statistical properties of the ensemble of surface molecules are unimportant. In the general case, however, a statistical feature of the system—the relaxation of the ensemble of particles during the time in which they interact with the surface—is of fundamental importance. In this case, obviously,

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it is necessary to use a kinetic equation. As shown below in Sec. 2, the approach being developed can be justified "from first principles," and the proposed kinetic equation of the surface particles is obtained by averaging the exact kinetic equation for the one-particle distribution function over the region within the range of the surface forces.

The possibility of arbitrary relative magnitudes of the three characteristic times of the process of the interaction of the molecules with the surface [the relaxation time τ of the ensemble of surface particles, the relaxation time τ_s of the phonon system, and the time of flight t_f of the molecule through the region within the range of the surface forces] is taken into account in a natural manner within the proposed approach. As a consequence, the possibility arises of describing within a single theory both transport phenomena in a rarefied gas and on a surface, and the scattering of molecular beams by a surface when physical adsorption is either present or absent. In particular cases the approach being developed can be reduced to the above-mentioned known theories of the interaction of particles with a surface.

The solution of the kinetic equation for the surface phase makes it possible to obtain (Sec. 3) a boundary condition for the distribution function of the gas. When the simplest, relaxation-time approximation (τ-approximation) is used for the molecule-phonon collision integral the resulting boundary condition coincides in form with the well known specular-and-diffusive reflection model of Maxwell, widely used in applied work. However, the "diffusivity" α is found in this case to be not a constant but a known function of the state of the molecule, and has the meaning of the relaxation probability for particles flying from the gas into the surface region. Another new result is the fact that the boundary condition retains its form even when the interaction potential of the particles with the surface is purely repulsive and adsorption is impossible. This implies that the cause of the thermalization and "diffuse" escape of particles from the surface lies not in the trapping of molecules by the surface, as assumed by Maxwell himself[9] and repeated in practically all the literature published on this question, but in the relaxation, in interaction with the phonon subsystem, of the ensemble of particles moving within the range of the surface forces.

When the overdependence of the probability α on the energy of the molecule is taken into account it becomes possible for the first time to describe a number of new effects—in particular, the non-Maxwellian desorption of physically adsorbed molecules (Sec. 6) discovered recently in experiments with molecular beams,[4] and also features arising from this effect in heat transfer in a gas-solid system in strongly nonequilibrium conditions (Sec. 5). The phenomenon of non-Maxwellian desorption of (completely relaxed) particles from the surface, i.e., the departure of the distribution function from its equilibrium form with respect to the speeds and with respect to the directions of escape, is interesting by virtue of its apparent (at first sight) contradiction of the principles of statistical physics.[3] An analogous phenomenon had been observed previously for chemisorbed particles.[3] We note that in the case of chemisorption the physical cause of this phenomenon can be understood in terms of the presence of a potential barrier, which can be surmounted only by molecules with a sufficiently large energy. For physical adsorption there is no such barrier, and the mechanism of non-Maxwellian desorption turns out to be more subtle. In the conditions of the experiments of Ref. 4 it is connected, as shown below, with how the time of flight through the region within the range of the surface forces depends on the velocity of the molecule.

In the framework of the theory being developed it is also possible to obtain a microscopic interpretation of such familiar phenomena on a gas-solid interface as the accommodation of the energy and momentum of the gas molecules and their trapping by the surface (Sec. 4). In particular, from unified microscopic considerations we obtain expressions for various accommodation coefficients. It is shown that the observed low-temperature increase of the energy-accommodation coefficient with decrease of T is due not to the trapping of particles into bound states, as has been assumed *a priori* in the literature (see, e.g., Ref. 7), but to the way the particles relax at the surface (as the effective region of interaction of the molecules with phonons increases).

It should be stressed that the experimental data enumerated above can be described in a closed manner within the theory developed below. For example, non-Maxwellian desorption and heat transfer in strongly nonequilibrium conditions are described without the use of free parameters if the values of a characteristic parameter of the theory, equal to the ratio of the mean relaxation time of particles on the surface to the mean time of flight through the region within the range of the surface forces, are determined from an independent experiment to measure the energy-accommodation coefficient.

The present approach also makes it possible to construct a theory of a number of other nonequilibrium phenomena in a gas-solid system. These results, described briefly in Sec. 7, require a more detailed analysis in separate publications.

2. THE KINETIC EQUATION FOR THE SURFACE PARTICLES

We shall consider a solid occupying the half-space $z < 0$, and an ensemble of molecules forming a gas phase in the region $z < 0$. Going over, with the aid of familiar methods,[12] from the Liouville equation for the density matrix of the whole system to the equation for the one-particle distribution function $F(\mathbf{v},\mathbf{r},t)$ of the molecules in the quasiclassical limit, it is not difficult to obtain

$$\frac{\partial F}{\partial t}+\mathbf{v}\frac{\partial F}{\partial \mathbf{r}}-\frac{1}{m}\frac{dV^{(1)}}{d\mathbf{r}}\frac{\partial F}{\partial \mathbf{v}}=I_{\text{ph}}\{V^{(2)},\mathcal{P}_{1S}\}+J_m\{U,\mathcal{P}_{12}\}, \quad (1)$$

where $\mathbf{v}$ and $\mathbf{r}$ are the velocity and coordinate of a molecule (for simplicity, the gas is assumed to be monatomic), m is its mass, $V^{(1)}(\mathbf{r},\{\mathbf{r}_j\})$ is that part of the interaction potential of the molecule with the solid that depends on the coordinates $\mathbf{r}_j$ of the sites of the crystal lattice, $V^{(2)}(\mathbf{r},\{\delta\mathbf{r}_j\})$ is the other part of this potential, associated with the thermal fluctuations $\delta\mathbf{r}_j$ of the coordinates of the atoms of the solid, U is the energy of interaction of two molecules $\mathcal{P}_{1S}$ is the density matrix of the molecule-solid system, and $\mathcal{P}_{12}$ is the two-particle density matrix of the gas. The quantity J_m in (1) describes the interaction of the gas molecules with each other, and I_{ph} describes the interaction of the molecules with the thermal fluctuations of the solid and, obviously, has the meaning of the molecule-phonon collision integral. For

$z \gg L$, where L is the characteristic size of the region within the range of the surface potential, we have $I_{\mathrm{ph}} = 0$, and J_m is reduced by the standard *B–B–G–K–Y* hierarchy procedures to the Boltzmann collision integral; for $z \lesssim L$, assuming that the pressure of the gas is not too high and neglecting the interaction of the gas particles in the narrow region within the range of the surface forces, we can set $J_m \approx 0$.

At the present time two microscopically justified ways of describing the interaction of particles with a solid are known. The first, which originates from the work of Kramers,[13] is applicable to the description of the slow evolution of the state of a particle inside a deep potential well on the surface of a thermostat, in which case the equation of the form (1) refers from the outset only to the adsorbed particles, and I_{ph} takes the Fokker-Planck form (see, e.g., Ref. 8). In this case it is assumed that (for the case of interaction with phonons) the potential well has depth $V_m \gg T_D$, where T_D is the Debye temperature of the solid, and the particle relaxation time $\tau \gg \tau_s$, where $\tau_s \sim 10^{-11}$–10^{-10} sec is the phonon-relaxation time. The exchange of particles between the adsorbate and the gas phase is not described correctly by such an approach.

Another approach—the dynamical theory of scattering of particles by a surface[7]—turns out, as is well known, to be experimentally justified for light particles, such as He atoms, at not too low temperatures, when quasielastic reflection from the surface is observed and the probability of energy exchange is small. It is not difficult to convince oneself that Eq. (1) leads to results equivalent to the results of scattering theory, to first order in the parameter t_{fl}/τ, where $t_{\mathrm{fl}} \sim L/\bar{v} \sim 10^{-12}$ sec is the mean free time of flight of a molecule through the region within the range of the surface forces [t_{fl}^{-1} gives an estimate of the left-hand side of Eq. (1)], and $\tau^{-1} \sim I_{\mathrm{ph}}$ is the characteristic frequency of collisions of molecules with phonons. On the other hand, the scattering theory[7] does not make it possible to explain, e.g., the temperature dependence of the energy-accommodation coefficient α_E of heavy particles (Ar,Xe) when α_E is not small in comparison with unity. In fact, a value of, say, $\alpha_E \sim 0.5$ (i.e., such that the value of the average probability of collision of the molecules with phonons is ~ 0.5) implies that the flight frequency t_{fl}^{-1} and the mean frequency τ^{-1} of collision between phonons and particles moving with the range of the surface forces are comparable: $\tau \sim t_{\mathrm{fl}} \sim 10^{-12}$ sec, while for $\tau \ll t_{\mathrm{fl}}$ we have, obviously, $\alpha_E \approx 1$.

Thus, in the general case, if we are interested in a unified description of the elastic and inelastic scattering of light ($V_m \lesssim T_D$) and heavy ($V_m \gg T_D$) particles by a surface, including their possible trapping by the surface (physical adsorption), it is necessary, first, to allow for arbitrary relative magnitudes of t_{fl} and τ, and, second, to allow the characteristic value of τ to be much smaller than τ_s. The latter, at first sight, casts doubt on the possibility of decoupling the correlations of the state of the particle and the solid in the expression for I_{ph}. Nevertheless, it is obvious that such correlations can be neglected. If the energy of a particle incident on the surface is not too large, the creation (annihilation) of phonons by the particle as it evolves within the range of the surface forces will not appreciably change the state of the solid, which has an enormous number of vibrational modes, and will have no effect on the subsequent evolution of the particle. As is usually done in gas kinetics, we shall assume that the solid is in an equilibrium state. (Simultaneous allowance for the nonequilibrium character of the gas and the solid leads to interphase nonlocal kinetic effects[5]; we shall not be interested in such phenomena in the present paper.) In accordance with this, we shall assume that

$$I_{\mathrm{ph}} = I_{\mathrm{ph}}\{V^{(2)}, F\} \tag{2}$$

in (1). Below we shall show that a whole series of important results can be obtained using the simplest, relaxation-time approximation for the molecule-phonon collision integral.

The main idea of the proposed approach is to go over from the exact (but intractably complicated) Eq. (1), which applies in the entire region $0 < z < \infty$, to an approximate description by means of a system of kinetic equations that includes the Boltzmann equation for the particles outside the range of the surface forces and equations for the particles within the range of the surface potential [including particles that are adsorbed in the usual sense (i.e., in discrete energy levels in the well) and particles with energies in the continuous spectrum]. To simplify the account we shall confine ourselves to the case when $V^{(1)}$ depends only on z (i.e., at $T = 0$ the surface is smooth). To realize this idea we shall proceed as follows. We draw the plane $z = L$, where L is the characteristic range of the surface forces (see Fig. 1). We define the distribution function f of the gas as

$$f(\mathbf{v}, \mathbf{r}, t) = F(\mathbf{v}, \mathbf{r}, t)\big|_{z \geq L}. \tag{3}$$

For f, by the standard method we obtain from (1) the Boltzmann equation

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{r}} = J\{f\}, \qquad z \geq L. \tag{4}$$

To obtain the kinetic equation for the particles in the region $0 < z < L$ we take into account that the "total energy of the normal motion"

$$E_z = \frac{m v_z^2}{2} + V^{(1)}(z) \tag{5}$$

is a constant of the motion of a molecule if one ignores the emission or absorption of phonons by the molecule; we shall

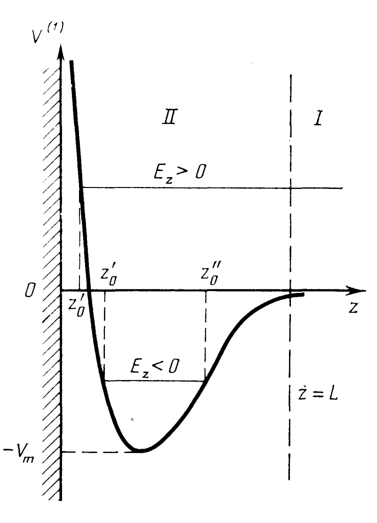

FIG. 1. Division of the particles into an ensemble of gas molecules ($z \geq L$, region I) and a surface ensemble ($0 < z, L$, region II). The distribution functions corresponding to regions I and II are $f(\mathbf{v},\mathbf{r},t)$ and $\rho(v_x, v_y, E_z, x, y, t)$.

trace the distribution of the particles with respect to their values of E_z without regard to the values of the rapidly varying quantities z and v_z. We define the distribution function ρ of the particles in the region $0<z<L$ as

$$\rho(v_x, v_y, E_z, x, y, t)=\frac{1}{l}\int_0^L dz\,\tilde{F}(v_x, v_y, E_z, x, y, z, t), \tag{6}$$

where the function $\tilde{F}$ is obtained from F by replacing the variable v_z by E_z with the aid of the equality (5), and the quantity l is equal to $L-z_0'$ for $E_z>0$ and $z_0''-z_0'$ for $E_z<0$; here z_0' and z_0'' are the turning points of a molecule with energy E_z (see Fig. 1). For the equilibrium function ρ_0, to within a normalization factor we have, in accordance with (6),

$$\rho_0 \propto \exp\left(-\frac{E_z}{T}-\frac{m(v_x^2+v_y^2)}{2T}\right). \tag{7}$$

Since the distribution function F is normalized to the total number N of particles in the system under consideration, as $\int d\mathbf{r}\int d\mathbf{v}F=N$, the function ρ is normalized to the number N_L of particles in the surface region $0<z<L$, in accordance with the relation $\int dx\,dy\int d\gamma\, l\rho=N_L$, where $d\gamma=(2mE_z)^{-1/2}dv_x\,dv_y\,dE_z$ for $-V_m<E_z<\infty$. Other macroscopic quantities in the surface region can also be defined in an analogous way in terms of ρ.

Integrating Eq. (1) over z from 0 to L, we can obtain, with allowance for (6),

$$\frac{\partial\rho}{\partial t}+v_x\frac{\partial\rho}{\partial x}+v_y\frac{\partial\rho}{\partial y}=\theta(E_z)\frac{\zeta}{L}(f^- -\rho)-\frac{\rho-\rho_0}{\tau}, \tag{8}$$

$$f^+=\theta(E_z)\rho. \tag{9}$$

Here $f^-=f|_{z=L,v_z<0}$, $f^+=f|_{z=L,v_z>0}$, $\zeta=(2E_z/m)^{1/2}$, and $\theta(a)=1$ for $a\geqslant 0$ and $\theta(a)=0$ for $a<0$. In the first term of the right-hand side of (8), and below, we neglect z_0' in comparison with L. The molecule-phonon collision integral [the second term in (8)] is written in the τ-approximation, i.e., we have assumed that

$$\frac{1}{l}\int_0^L dz I_{\text{ph}}\{V^{(2)},F\}=-\frac{\rho-\rho_0}{\tau}. \tag{10}$$

The equations (4) and (8) and the boundary condition (9) are the required system of coupled kinetic equations for the description of the ensemble of the particles that form the gas phase and interact with (and may be adsorbed by) the surface of the solid. The first term in the right-hand side of (8) is nonzero for $E_z>0$ and describes both the "arrival" of particles and their "departure" from the surface ensemble $(0<z<L)$ into the gas phase $(z\geqslant L)$. The frequency of this process is equal to ζ/L and is determined simply by the characteristic time of flight of a molecule through the region L. The second term in the right-hand side of (8) takes account of the spreading of the particles over the energy levels in the surface potential, which occurs with a rate τ^{-1} and leads, in particular, to the transition of particles into bound states with $E_z<0$ (or to the emergence of particles from bound states). It should be stressed that the structure of Eq. (8) has been obtained rigorously, and rejecting the τ-approximation and refining the form of the molecule-phonon collision integral will give only the possibility (if this is necessary) of refining the dynamics of the motion of the particles over the levels E_z (the dynamics of the relaxation process). We note that this picture (obtained here from microscopic considerations) of the evolution of particles near the surface of a solid differs substantially from the phenomenological constructions usually employed, in which a transition probability for the transition of a molecule from the gas directly into bound states is introduced, the concept of adsorption is associated only with molecules trapped in the potential well (molecules with $E_z<0$), and the role of particles in energy levels in the continuous spectrum $(E_z>0)$ is tacitly neglected. This also applies to earlier attempts to analyze the interaction between molecules and a surface by means of kinetic theory,[14–18] in which the above *a priori* concepts were used to a greater or lesser degree.

Integrating Eqs. (8) and (9), we obtain equations describing the transport of particle number in the system under consideration:

$$\frac{\partial n_S}{\partial t}+\frac{\partial G_{Sx}}{\partial x}+\frac{\partial G_{Sy}}{\partial y}=G_V^- - n_S t_a^{-1}, \tag{11}$$

$$n_S t_a^{-1}=G_V^+, \tag{12}$$

where $n_S=\int d\gamma l\rho$ is the surface density of (all) the particles in the region $0<z<L$, $\mathbf{G}_S=\int d\gamma\,\mathbf{v}_\tau l\rho$ is the flux of these particles parallel to the surface ($\mathbf{v}_\tau$ is the tangential component of the velocity), and G_V^+ and G_V^- are the fluxes of the molecules moving in the gas phase away from and toward the surface, respectively. The quantity t_a in (11) and (12), which has, obviously, the meaning of the mean time the molecule remains in the surface region, is determined by the expression

$$t_a^{-1}=\int d\gamma\,\rho\zeta\theta(E_z)\bigg/\int d\gamma\, l\rho. \tag{13}$$

In equilibrium an approximate calculation of t_a (13) for $T\ll V_m$ gives $t_a^{(0)}=t_a^{(0)}=t_0\exp(V_m/T)$, where the time $t_0\propto m^{1/2}(d^2V^{(1)}/dz^2)^{-1/2}$ coincides, as is not difficult to see, with the period of the oscillations of a molecule near the bottom of the potential well [the dependence on $V^{(1)}$ arises here because of the normalization factor in (7)]. Thus, the equilibrium mean lifetime of molecules on the surface in the limit under consideration has the familiar Frenkel-Arrhenius form. In a nonequilibrium system the distribution function ρ and, consequently, the lifetime t_a (13) will also depend on the rate of wandering of the particle over the levels E_z (in our case, on τ^{-1}). A specific example will be considered below, in Sec. 6.

Equations (11) and (12) coincide in form with the usual equations[19] of the phenomenological theory of adsorption (in the present limit of low surface occupation) to within the trapping coefficient. The latter in our case is identically equal to unity, since each molecule incident on the surface from the gas goes into the surface ensemble $(0<z<L)$. If the depth V_m of the surface-potential well is large in comparison with the temperature, the number of particles in bound states $(E_z<0)$ is equal, with good accuracy, to the total number of particles in the surface ensemble. In this case, neglecting the particles with $E_z>0$, the number of which is exponentially small (although it is precisely these particles which are responsible for transport between the gas and the surface phase, which can be important!), the surface phase can be regarded as an adsorbate in the traditional sense of this word. On the other hand, for $T \sim V_m$ the numbers of particles with $E_z < 0$ and $E_z > 0$ turn out to be comparable. In this case the average lifetime (13) of particles on the surface is comparable to the time of free flight of a molecule through the region within the range of the surface forces, and it becomes meaningless to associate the concept of adsorption only with molecules in bound states. Therefore, in the general case the interaction of particles with the surface should be analyzed on the basis of Eqs. (8)–(13).

3. BOUNDARY CONDITION FOR THE DISTRIBUTION FUNCTION OF THE GAS

To describe nonequilibrium phenomena in the gas we can go over from the complete system of kinetic equations (4), (8), (9) to a system that includes the Boltzmann equation and the boundary condition for the distribution function of the gas at the surface. Nonequilibrium processes in the gas occur with characteristic times significantly greater than the times $t_{fl} \sim L/\bar{v}$ and τ of the surface processes. In this case, to determine the boundary condition it is sufficient to use the time-independent solution of the kinetic equation (8) for the surface phase. In the case of a system that is uniform in the tangential direction, we have

$$\rho = \begin{cases} [1+\tau\zeta L^{-1}]^{-1}\rho_0 + [1+\tau^{-1}\zeta^{-1}L]^{-1} f^-, & E_z \geqslant 0, \\ \rho_0, \quad E_z < 0. \end{cases} \tag{14}$$

In accordance with (14), molecules in the potential well ($E_z < 0$) are distributed in an equilibrium manner, while particles with $E_z > 0$ can be regarded as divided into two groups. Particles of the first group can be regarded as having relaxed fully, inasmuch as their distribution is uniquely determined by the temperature T_S of the solid and does not depend on the distribution function of the gas. The distribution of the particles of the second group, on the other hand, is uniquely determined by the state of the gas. The factors multiplying ρ_0 and f^- in (14), the sum of which is equal to unity, have, obviously, the meaning of the probabilities that the particles with $E_z > 0$ belong to the respective groups. The simple result obtained is obviously a consequence of the relaxation-time approximation used for the collision integral.

Substituting (14) into (9) and assuming that the fluxes of the molecules incident on and reflected from the surface are equal, we obtain a boundary condition relating the distribution f^- of the incident particles and the distribution f^+ of the departing particles for an arbitrary lifetime on the surface:

$$f^+(\mathbf{v}) = (1-\alpha) f^-(\mathbf{v}_R) + \alpha f_0,$$

$$f_0 = \exp(-E/T) \left[\int\limits_{v_z<0} |v_z| \alpha \exp(-E/T)\, d\mathbf{v} \right]^{-1} \left[\int\limits_{v_z<0} |v_z| \alpha f^-\, d\mathbf{v} \right], \tag{15}$$

$$\alpha = [1+\tau\zeta L^{-1}]^{-1} = [1+\beta(E_z/T_S)^{1/2}]^{-1}, \qquad \beta = \frac{\tau^*}{L^*}\left(\frac{2T_S}{m}\right)^{1/2}. \tag{16}$$

Here $\mathbf{v}_R = (v_x, v_y, -v_z)$, $\mathbf{v} = (v_x, v_y, v_z)$, $E_z = mv_z^2/2$, and $E = mv^2/2$. In accordance with (15) the boundary condition obtained coincides in form with the well known Maxwell specular-and-diffusive reflection model widely used in gas kinetics; the calculations given above can be regarded as a microscopic justification of this model. However, the "diffusivity" α in (15) is not a constant but a known function (16) of the state (E_z) of the particle. [Previously, a possible dependence of α in a boundary condition of the type (15) on the velocity[20] or rotational angular momentum[1] of the molecule has been taken into account in the framework of formal mathematical modeling.] In the present theory α has the meaning of the probability that the evolution of a particle incident on the surface will proceed along the relaxation channel, or [see the expression (14)] the probability of trapping of the molecule into the subsystem of completely relaxed surface particles. In writing the second equality in (16) we have taken into account that the interaction of the molecule with phonons is important only over a certain part L^* of the range L of the surface forces, and, in accordance with (10), the relaxation time can be represented as $\tau = \tau^* L/L^*$, where $(\tau^*)^{-1}$ is the average (over this region) frequency of emission (absorption) of phonons by the molecule. The dependence of α on E_z in (16) is related to how the time of flight of the molecule through the region within the range of the surface forces depends on the velocity (energy E_z) of the molecule. The dimensionless parameter β in (16) is the ratio of the average relaxation time τ^* to the characteristic time $t^*_{fl} = L^*(m/2T_S)^{1/2}$ of flight of the molecule through the region L^* of interaction with the phonons.

We note that, as it should be, α is independent of the position $z = L$ ($L > L^*$) of the plane separating the gas phase from the surface phase (see Fig. 1). Since L is always much smaller than the mean free path of the molecules in the gas phase, the boundary condition (15) obtained for the distribution function of the gas, which is defined, strictly speaking, at $z = L$, can be regarded as defined simply on the surface ($z = 0$).

Although the calculation of τ^*/L^* from microscopic considerations raises serious difficulties, estimates of these quantities and their qualitative dependences on T_S (which we need later for the analysis of the experimental data) can be established from intuitive physical considerations. In accordance with Eq. (14), for not-too-large departures from equilibrium the relaxation of particles of the gas in the surface region is associated with spreading of the molecules over the energy levels $E_z > 0$ with E_z comparable to T_S. Therefore, below we shall be interested in those values of E_z that are in this relaxation region. If T_S (and, consequently, the width of the relaxation region) does not appreciably exceed the (surface) Debye temperature T_D, the relaxation of particles at the surface proceeds principally as a result of one-phonon processes. The interaction of molecules with phonons is due to the thermal perturbation $V^{(2)}$ of the interaction potential, which can be estimated roughly as $|V^{(2)}| \propto |dV^{(1)}/dz|\bar{\delta}r$, where $\bar{\delta}r$ is the mean displacement of the element of the solid, including the atoms drawn into interaction with the given gas molecule. At minimal distances from the surface ($z \sim z_0'$), when the interaction of the molecule is principally with one atom of the solid, the quantities $V^{(2)}$ and $V^{(1)}$ can be comparable. However, in the entire remaining region within the range of the surface forces it is obvious that $|V^{(2)}| \ll |V^{(1)}|$ (see Fig. 2).

First we shall consider the case $T_S \gtrsim V_m$ (which includes, e.g., the interaction between light molecules (He,Ne) and a surface at room temperatures). In this case, for $E_z \sim T_S$ we have $E_z \gg V_m^{(2)} \sim (V_m/L)\bar{\delta}r$, and $V^{(2)}$ (the "interaction potential with the phonons") becomes comparable to the energy of the particles only at the minimal distances from the surface—in the region of repulsion (see Fig. 2a); therefore, the size of the region of interaction with phonons is $L^* \ll L$. Setting $L^* \sim 0.1$ Å, $m \sim 10$, and $T_S \sim 300$ K, for the time of flight of a molecule through the region of interaction with the phonons we obtain $t_{\text{fl}}^* \sim L^* T_S^{-1/2} m^{1/2} \sim 10^{-14}$ sec. Since this quantity is considerably smaller than the period ($\sim 10^{-13}$ sec) of vibrations of atoms of the solid, the probability of emission (absorption) of phonons by the molecule in the time t_{fl}^* is small and we can write $\tau^*/t_{\text{fl}}^* = \beta \gg 1$. Here, as follows from (15) and (16), the probability α of scattering with relaxation is small and the scattering is close to elastic, and this has indeed been observed in experiment for light particles at room temperatures. In the case under consideration it is obvious that L^* has a negligible weak dependence on T_S (inasmuch as $L^* \sim z_0'$). On the other hand, the quantity τ^* should be a decreasing function of temperature, since the probability of emission or absorption of Bose particles is proportional to their number.

We now consider the other limiting case, when $T_S \ll V_m$ (see Fig. 2b). Here the interaction of the molecules with phonons can be important in almost the entire region within the range of the surface forces, i.e., $L^* \sim L$. The time of motion of a molecule in this region ($L^* \gtrsim 1$ Å) amounts to $t_{\text{fl}}^* \sim 10^{-13}$–$10^{-12}$ sec and exceeds the period of vibration of the surface atoms ($\sim 10^{-13}$ sec). Therefore, the probability of the creation (annihilation) of phonons can be large. Then, estimating τ^* as 10^{-13} sec, we obtain $\tau^*/t_{\text{fl}}^* = \beta \lesssim 1$. In this case, in accordance with (15) and (16), there is appreciable thermalization of the particles on the surface ($\alpha \lesssim 1$), and this corresponds to the experimental data for heavy particles at room temperatures or for light particles at low temperatures. The temperature dependence of τ^* in the present limit of strong interaction with phonons, when the relaxation time is close to its limiting value (10^{-13} sec), should be weak. However, the effective size L^* of the relaxation region should now decrease with increasing T_S. In fact, the ratio of the occupations of the long-wavelength and short-wavelength vibrational modes of the solid changes with change of the temperature. The long-wavelength modes make a contribution to the perturbation potential $V^{(2)}$ even at large distances from the surface. The short-wavelength modes, which are high-energy modes and, consequently, make a large contribution to the relaxation of the particle, come into play only at short distances from the surface.

By generalizing the theory under development to the case of a nonsmooth wall, i.e., by taking into account a weak dependence of $V^{(1)}$ on x and y in (1), it is possible to show that the boundary condition (15) retains its form except that the specular-scattering term [the first term in the right-hand side of (15)] is replaced by

$$v_z^{-1} \int\limits_{v_z<0} |v_z'|\, W_{\text{el}}(\mathbf{v}' \to \mathbf{v}) f^-(\mathbf{v}')\, d\mathbf{v}' \tag{17}$$

and describes the elastic (without exchange of energy) scattering

$$\int\limits_{v_z<0} W_{\text{el}}(\mathbf{v}' \to \mathbf{v})\, d\mathbf{v} = 1 - \alpha(\mathbf{v}');$$

the expression for α in (15) is in this case somewhat more complicated than in (16). We shall not need these expressions below. We note that the boundary condition obtained, in the form of a superposition of elastic scattering [the first term in (15) or (17)] and departure of molecules from the surface after complete relaxation [the second term in (15)] is a direct consequence of the τ-approximation used for the molecule-phonon collision integral in Eq. (8).

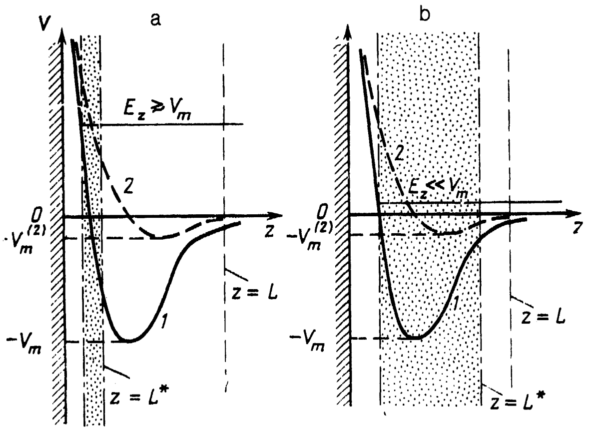

FIG. 2. Regions of effective interaction with phonons (the dotted regions) for light (a) and heavy (b) particles; the curves 1 and 2 correspond to $V^{(1)}(z)$ and $V^{(2)}(z)$.

To conclude this section we shall make an important methodological remark. The fundamentally new result of the theory being developed is the fact that for the derivation of the boundary condition (15), (16) it does not matter whether there is a potential well near the surface or not; in particular, the interaction potential of the molecules with the surface can be purely repulsive. Thus, the *a priori* idea that holds sway in the literature,[7,9,14,16,21] that the diffusive departure of particles from a surface is due to desorption of trapped particles, is by no means necessary. In particular, for light particles (He,Ne) at room temperatures, when $T \sim V_m$ and the lifetime on the surface is $t_a \sim t_{\text{fl}} \ll \tau$ (the latter inequality also follows from the experimental fact that $\alpha_E \ll 1$; for more detail, see Sec. 4), such a statement is simply untrue. The result obtained makes it possible to understand the well known fact that the specular-diffusive boundary condition in the kinetics of rarefied gases works just as well for light molecules as for heavy molecules, when $T \ll V_m$ and practically all the surface particles are indeed concentrated in the potential well.

4. ACCOMMODATION OF MOLECULES ON THE SURFACE

To describe the transport processes in the gas in weakly nonequilibrium conditions, as is well known, it is sufficient to specify the interaction with the surface by means of accommodation coefficients α. These are defined[22] in terms of the fluxes ($G^{\pm}\{\varphi\}$) of the molecular characteristics φ associated with the incident molecules and the molecules reflected from the surface:

$$\alpha_\varphi = \lim \frac{G^-\{\varphi\} - G^+\{\varphi\}}{G^-\{\varphi\} - G^{(0)}\{\varphi\}}, \quad G^{\pm}\{\varphi\} = \int\limits_{v_z \gtrless 0} |v_z|\, \varphi f^{\pm}\, d\mathbf{v},$$

$$G^{(0)}\{\varphi\} = \int\limits_{v_z>0} v_z \varphi f_0\, d\mathbf{v}. \tag{18}$$

The limit operation in (18) refers to the approach of the system to equilibrium. With $\varphi = E, m\mathbf{v}_\tau$, and m, the expression (18) defines the energy-accommodation coefficient α_E, the tangential-momentum accommodation coefficient α_p, and the sticking probability α_m. Using the boundary condition (15) obtained above we can obtain, for the first time in the framework of unified microscopic arguments, expressions for the various accommodation coefficients:

$$\alpha_E = G^{(0)}\{\alpha E\}/G^{(0)}\{E\}, \tag{19}$$

$$\alpha_p = \alpha_p' + \alpha_p'', \quad \alpha_p' = G^{(0)}\left\{\alpha \frac{v_\tau^2}{v_z}\right\} \Big/ G^{(0)}\left\{\frac{v_\tau^2}{v_z}\right\}, \tag{20}$$

$$\alpha_m = G^{(0)}\{\alpha\}/G^{(0)}\{1\}. \tag{21}$$

Here the function α is given by the relation (16). The quantities α_p' and α_p'' in (20) describe the accommodation of the tangential momentum of the molecules on account of their interaction with phonons and in elastic scattering, respectively; α_p'' can be expressed in terms of W_{el} in (17); for a smooth surface, $\alpha_p'' = 0$. The expression (20) has been written for the case of free molecular flow of a gas in a plane channel; in the case of flow with slip it is necessary to replace v_z^{-1} in (20) by 1.

In accordance with the formulas (19)–(21) the accommodation coefficients α_E and α_m, and also α_p', are different average values of the probability α of relaxational scattering of molecules by the surface. Since α given by Eq. (16) depends on the state of the particle, the coefficients α_E, α_p, and α_m are different (in contrast to the specular-and-diffusive reflection model, in which $\alpha = \text{const}$ and all the accommodation coefficients coincide). When (16) is taken into account Eqs. (19)–(21) yield relations of practical importance between α_E, α_p', and α_m, and the inequalities $\alpha_p \geqslant \alpha_p' \geqslant \alpha_m > \alpha_E$ hold.

Unfortunately, there are currently no direct measurements of the various accommodation coefficients under identical conditions. However, we do have data concerning α_E and α_p, obtained by determination of these coefficients from experimental results for one of the following complicated effects: the absorption of sound in a rarefied gas[23] and the thermal polarization of macroscopic particles.[24] In both cases, for all the gases investigated, the inequality $\alpha_p > \alpha_E$ is indeed fulfilled. It is also not difficult to convince oneself that α_p' for a collisionless gas should be greater than in the regime of flow with slip. This statement also agrees with the data of Ref. 25, in which a corresponding difference of 3–6% in the values of α_p was observed.

In contrast to the coefficient α_E, for which a reliable experimental technique of measurement has been developed[26] and extensive experimental data have been gathered,[7] for α_p and α_m the available information is disconnected and not always sufficiently reliable. In the framework of the theory the quantities α_p' and α_m can be calculated without difficulty if the parameter β in (16) is determined from the experimental data for α_E with the aid of relation (19). Characteristic experimental data for different systems and values of the indicated parameter found as a function of the temperature with the aid of the data are presented in Fig. 3. The calculations of α_p' and α_m performed using (16), (20), and (21) show (for α_p' see the dashed curves in Fig. 3a) that, e.g., for argon gas and a tungsten surface at room temperatures the quantity α_p' is ~ 2 times greater than α_E, while for Ar and a Pt surface covered by chemisorbed oxygen the difference between α_p' and α_E amounts to $\sim 7\%$. The difference between α_m and α_E is somewhat smaller. The quantities $\alpha_p' - \alpha_E$ and $\alpha_m - \alpha_E$ decrease with decreasing the temperature and when we go over to heavier molecules.

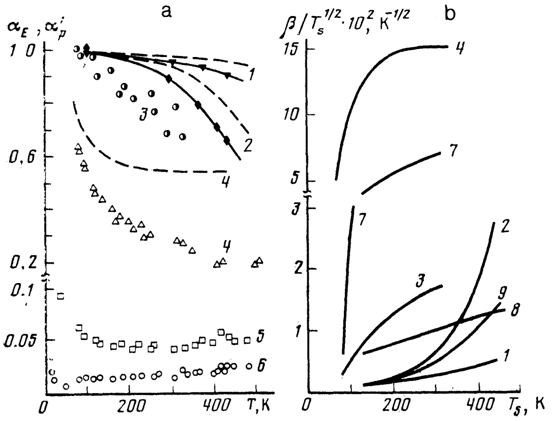

FIG. 3. a) Experimental data for the energy-accommodation coefficient α_E as functions of the temperature for inert gases interacting with a clean W surface (from Ref. 7) and with a Pt surface covered with chemisorbed oxygen (from Ref. 27). The dashed curves are the "phonon part" α_p' of the tangential-momentum-accommodation coefficient (for the flow of a Knudsen gas), calculated from Eq. (20) using data for α_E. Data are given for the systems 1) Xe/Pt(O), 2) Ar/Pt(O), 3) Xe/W, 4) Ar/W, 5) Ne/W, and 6) He/W; b) values of the parameter β as functions of the surface temperature, calculated from the experimental data of Refs. 7 and 27 for α_E. For the curves 1–6 see above; the curves 7, 8, and 9 correspond to the systems Kr/W, N_2/Pt(O), and CH_4/Pt(O).

We shall consider the temperature dependence of α_E. At the present time the only aspect that can be regarded as explained from a microscopic point of view is the observed increase of α_E with temperature for light gases at not-too-low temperatures; this qualitative result arises from calculation of α_E by means of scattering theory.[7] On the basis of the relations (19) and (16) obtained above it is easy to explain all the observed variations of α_E with temperature in different temperature ranges and for different gases, and also the corresponding characteristic magnitudes of α_E (see Fig. 3a). For example, for light gases at room temperatures we have $T_S \gtrsim V_m$ (as is well known, $V_m < 100$ K for He and $V_m \sim 100$ K for Ne). Since in this case $\beta \gg 1$, while τ^* decreases with increase of T_S (see Sec. 3), it follows from (19) and (16) that α_E should increase with the temperature, while remaining a small quantity ($\alpha_E \ll 1$). As we go over to heavier molecules their interaction (in particular, V_m) with the surface increases, and, consequently, the relaxation time τ^* decreases, so that the accommodation coefficient increases. For heavy particles, and also for light molecules at low temperatures, we have $T_S \ll T_m$ (e.g., $V_m \sim 1500$ K for Ar). In this case (see Sec. 3), the function α given by Eq. (16) decreases both with increase of T_S (on account of the narrowing of the effective region L^* of interaction of the molecules with phonons) and with increase of the particle energy E_z (on account of the decrease of the time of flight through this region). These causes explain the experimentally observed decrease of α_E with temperature, which occurs, as should be the case in accordance with $\beta \lesssim 1$, at values

$\alpha_E \lesssim 1$. We note that the statement that the variation of L^* has an important role in the temperature dependence of α_E also agrees with the fact that the parameter β for clear surfaces (see Fig. 3b) varies substantially in precisely the temperature range $T_S < T_D \sim 300$ K in which the variation of T_S gives rise to a strong variation of the relative occupation of the short-wavelength and long-wavelength vibrational modes of the solid.

The form of the dependence of the parameter β on T_S for an uncleaned surface (see Fig. 3b) indicates that, as one might have expected,[7] variation of the temperature is accompanied by change of the state (occupation) of the chemisorbed layer. Since for a fixed temperature the state of the adsorbate is fully determined, the formulas obtained above can be extended also to uncleaned surfaces (taking τ^* and L^* as effective quantities). As will be shown in the following sections, by using values of the parameter β obtained from experimental data for α_E it is possible to describe a number of other physical effects, both for clean and for uncleaned surfaces.

We note that in the literature[7,16] the growth of α_E with decrease of the temperature is usually attributed *a priori* to the trapping of molecules into bound states and associated with the idea of "complete accommodation of such molecules." In fact, although for $T \ll V_m$ the relative number of such molecules does turn out to be large, the quantity α_E as determined by (19) and (16) does not depend on the presence of bound states ($E_z < 0$) but is determined by features of the relaxation of particles with $E_z > 0$. The main reason for the growth of α_E at low temperatures is then the increase of the effective size L^* of the region of interaction of the molecules with phonons.

5. HEAT TRANSFER IN STRONGLY NONEQUILIBRIUM CONDITIONS

In the determination of transport processes in strongly nonequilibrium conditions it is not sufficient to know the accommodation coefficients (i.e., the average values of the function α) and it is necessary to use a boundary condition for the distribution function. Therefore, the analysis of experimental data for such conditions can serve as a more direct check on the theory constructed above. Figure 4 shows experimental curves[27] of the heat flux G_E in a collisionless gas between two surfaces with temperatures T_1 and T_2 as a function of T_2. From independent experiments the authors of Ref. 27 also determined the values of the energy-accommodation coefficient α_E at different temperatures; examples for Ar and Xe are given in Fig. 3a. The theoretical dependence $G_E(T_2)$ was determined after solution of the Eqs. (15) written for each of the two surfaces. Here the values of the parameter β in (16) for different T_S were determined from the experimental values of α_E (see Fig. 3b). The dependences obtained in this way (the solid lines in Fig. 4) agree with the experimental data for the gases Ar, Xe, N_2, and CH_4, not only in the limit of small $\Delta T = T_2 - T_1$, as should be the case, by construction, but also for $\Delta T \gtrsim T_1$.

For comparison the dashed curves in Fig. 4 give the dependences $G_E(T_2)$ obtained with the use of the specular-diffusive boundary condition, i.e., when the dependence of α on E_z is neglected and α is set equal to α_E in (15). For $\Delta T \gtrsim T_1$ the dashed curves diverge strongly from the solid curves and from the experimental points for the gases Ar and CH_4 (an analogous, but slightly less pronounced situation also obtains for Kr). This is direct evidence that the expression (16) correctly describes the dependence of α on E_z for heavy gases (inasmuch as allowance for such a dependence greatly changes the result and makes it possible to describe experiment). For Xe and N_2 the dashed curves lie close to the solid curves and also coincide with the experimental data within the error bars of the experiments. As the analysis performed has shown, this behavior is connected with the fact that for Xe the parameter β is quite small, while for N_2 it depends weakly on the temperature (see Fig. 3b).

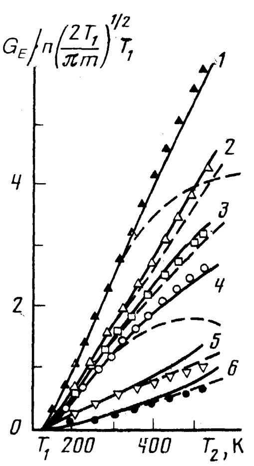

FIG. 4. Dependence of the heat flux G_E in a series of collisionless gases between two Pt(0) surfaces on the temperature of one of the surfaces (from Ref. 27). The solid curves are the result of calculation using the boundary condition (15) with allowance for (16), and the dashed curves correspond to the specular-and-diffusive reflection model (($\alpha = \alpha_E$ in (15)). The numbers alongside the curves correspond to different gases: 1) CH_4, 2) N_2, 3), Xe, 4) Ar, 5) HD, and 6) He.

For the light gases He and HD the dashed curves in Fig. 4 agree with experiment and the solid curves do not. Here, clearly, we have a manifestation of the inadequacy of the relaxation-time approximation used above for the molecule-phonon collision integral. The experimental data can be described if we assume that the quantity τ in the kinetic equation (8) and, consequently, the parameter β in (16) depend on the state of the particle and, in the case under consideration, decrease with energy at $E_z^{-1/2}$. In fact, such behavior might have been expected in advance, since for light particles (Fig. 2a) interaction with phonons occurs only at the minimum distances from the surface, when the effective value of the perturbation potential $V^{(2)}$ increases appreciably with the particle energy E_z. As a consequence, the frequency of emission (absorption) of phonons by the particle should indeed increase (and τ should decrease) as a function of E_z.

6. DISTRIBUTION OF MOLECULES UNDERGOING DESORPTION

We turn to the analysis of phenomena that occur in the scattering of molecular beams by a surface. In the general case the reflected beam includes both rapidly (elastically) scattered molecules and molecules that have undergone trapping by the surface—in particular, particles that have had time to reach complete equilibrium with the wall. The distribution of the molecules undergoing desorption has been investigated in Refs. 4 and 28, whose authors succeeded in distinguishing the molecules that had been delayed a fairly long time at the surface (after the incident beam was switched off) for the shape of their distribution to be unchanging in time. It was discovered that the distribution of particles undergoing desorption from the surface after complete relaxation is not of the equilibrium (Maxwellian) form either with respect to the magnitude of their velocity or with respect to the directions of departure. The results obtained are extremely important from two points of view. They imply that a large number of other well known theoretical and experimental results should be reexamined in cases when the *a priori* argument that molecules undergoing desorption have an equilibrium distribution has been built into the foundations of the method of investigation from the outset (see, e.g., the literature surveyed in Ref. 21). In addition (and we shall be interested specifically in this aspect here), the sensitive "non-Maxwellian effect" that has been discovered can serve as a good basis for checking the microscopic theory of the interaction of molecules with a surface.

In principle, the possibility of a nonequilibrium distribution of the molecules being desorbed from a surface already becomes understandable in the framework of a boundary condition of the type (15) with (16) taken into account. In equilibrium the distribution f^+ of all the particles moving away from the surface turns out to be Maxwellian, as it should be, but the distribution of those of the particles which are flying away from the surface after complete relaxation [the second term in (15)] has a nonequilibrium form, since the function α depends on E_z. Strictly speaking, however, a direct interpretation of the individual terms in (15) is not legitimate, since this equation was obtained for stationary conditions and does not make it possible to detail the lifetime of particles on the surface. For a systematic description of the phenomenon under consideration it is necessary to examine the time-dependent solution of the kinetic equation (8).

Integrating (8) over time, we go over to the integral form of the kinetic equation of the particles in the region within the range of the surface forces:

$$\begin{aligned}\rho(t)=&\int_0^t dt'\exp\left\{-\left[\tau^{-1}+\theta(E_z)\frac{\zeta}{L}\right](t-t')\right\}\\ &\times\left[\tau^{-1}\rho_0(t')+\theta(E_z)\frac{\zeta}{L}f^-(t')\right]\\ &+\exp\left\{-\left[\tau^{-1}+\theta(E_z)\frac{\zeta}{L}\right]t\right\}\rho(0). \qquad (22)\end{aligned}$$

The equilibrium function ρ_0 in (22) is normalized to the unknown density of surface particles, which, in the general case, satisfies Eqs. (11) and (12). We shall consider the solution of Eq. (22) for the case[4,28] when the flux incident on the surface is switched off at time $t = 0$; we also assume that there is no transport of particles parallel to the surface. Over times $t \gg \tau$, $t \gg t_{\text{fl}} \sim L/\bar{v}$, although there is a decrease in the number of particles on the surface, the form of the distribution function ρ, as follows from (22), does not change. In this case the lifetime (13) does not depend on t, and the number of particles, as follows from (11), decreases exponentially. Taking this into account, we obtain from (22)

$$\rho(t)\big|_{t\gg\tau,t_{\text{fl}}}=\exp\left(-\frac{t}{t_a}\right)\left[1+\theta(E_z)\tau\frac{\zeta}{L}\right]^{-1}\rho_0(0). \qquad (23)$$

Substituting (23) into (13), for the average time of adsorption in the nonequilibrium conditions under consideration we obtain

$$\begin{aligned}t_a^{-1}=&\left\{\int d\gamma\,\rho_0\theta(E_z)\frac{\zeta}{L}\left[1+\tau\frac{\zeta}{L}\right]^{-1}\right\}\Big/\\ &\left\{\int d\gamma\,\rho_0\left[1+\tau\frac{\zeta}{L}\theta(E_z)\right]^{-1}\right\}. \qquad (24)\end{aligned}$$

We note that in the limiting case when the characteristic time of flight $t_{\text{fl}} \sim L/\bar{v}$ is significantly greater than τ (heavy particles or low temperatures) the expression (24) reduces to the expression for $t_a^{(0)}$ in equilibrium.

Substituting the expression (23) into (9), for the distribution of molecules flying away from the surface after complete relaxation we obtain

$$f^+\propto\alpha(E_z)\exp(-E/T_S). \qquad (25)$$

Here we have omitted a factor that is independent of the state of the particle and describes the exponential decrease of the number of such molecules in time, and the function $\alpha(E_z)$ is given by the expression (16). In accordance with (25) the distribution function f^+ does indeed turn out to be a nonequilibrium function and is described by the same function $\alpha(E_z)$ that appears in the time-independent boundary condition (16). As follows from (23), the non-Maxwellian character is a direct consequence of the fact that the ensemble of surface particles is an open system and particles can fly out into the gas. Since the departure frequency ζ/L depends on the particle velocity, the distribution function (23) of the surface particles and, with it, the distribution (25) of the departing particles are found to be nonequilibrium (and remain such as $t\to\infty$). If, however, the departure of particles is forbidden, i.e., if we set $\zeta/L = 0$, the distribution function of the surface particles becomes an equilibrium function.

In the experiments of Refs. 4 and 28 the flux G^+ and mean energy ε^+ of the particles undergoing desorption were measured as functions of the direction of departure. For these quantities it is not difficult to obtain, with the aid of (25) and (16),

$$G^+=\int dv\,v^2v_zf^+\propto\cos\theta[1+\beta(3/2)^{1/2}\cos\theta]^{-1}, \qquad (26)$$

$$\begin{aligned}\varepsilon^+=&\int dv\,v^2v_zEf^+\Big/\int dv\,v^2v_zf^+\\ &\approx2T_S[1+\beta(3/2)^{1/2}\cos\theta]/[1+(5/2)^{1/2}\cos\theta], \qquad (27)\end{aligned}$$

where θ is the angle between the direction of the particle velocity and the normal to the surface. The corresponding equilibrium quantities are $G_0^+\propto\cos\theta$ (the cosine law) and $\varepsilon_0^+=2T_S$. As above, we determine the values of β from experimental data for α_E. Since we do not know the data for α_E on the clean Pt surface that was used in Ref. 4, we have made use of the values of α_E for a W surface, and the corresponding values of β, shown in Fig. 3. (As is well known,[7] the observed values of α_E depend strongly on the kind of gas and on the covering of the surface, but vary little from one pure metal to another.) Figure 5 shows the experimental

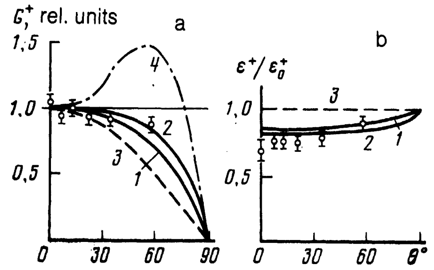

FIG. 5. Dependence of the flux G^+ (a) and mean energy ε^+ (b) of particles undergoing desorption on the direction of departure for the Ar/Pt system. The experimental points are data from Ref. 4 for $T_S = 110$ K; the curves 1 and 2 are calculated using Eqs. (26) and (27) for $T_S = 110$ K and $T_S = 375$ K; curve 3 is the equilibrium distribution of the departing molecules; curve 4 is from the theory of Ref. 17 for $T_S = 250$ K.

data for Ar and the theoretical dependences (the solid curves) corresponding to the expressions (26) and (27). In view of the simplicity of the τ-approximation used for the molecule-phonon collision integral the agreement obtained between the theoretical and experimental dependences must be regarded as highly satisfactory.

The agreement with experiment can be improved for G^+ (Fig. 5a) and ε^+ (Fig. 5b) as well, if we assume that the values of β for Pt are slightly greater than for *W*. This assumption is natural, since the Debye temperature for platinum is lower than that for tungsten, and the relaxation of the molecules on the less hard surface of Pt should proceed more slowly. This is also indicated by the results of the experiments of Refs. 29 and 30, from which it follows that the probability of surface trapping of Ar atoms is lower for a Pt surface than for a W surface.

In Refs. 4 and 28 it was also reported that a non-Maxwellian effect analogous to that for argon but slightly smaller is observed for CH_4, while for Xe and N_2 a deviation from Maxwellian form of the distribution function of the particles undergoing desorption was not observed, within the limits of the experimental errors. These qualitative results also agree with the formulas (26) and (27) with the appropriate values of β. It should be stressed that these results are in direct correspondence with the results of the study of heat transfer in strongly nonequilibrium conditions (Sec. 5). For the gases Xe and N_2 the experimental data on both the heat transfer and the distribution of the particles undergoing desorption can be described even with $\alpha = \text{const}$ in (15), while for Ar and CH_4 it is necessary in both cases to take into account the dependence (16) of α on E_z. Since the same function α appears in the boundary condition (15), and determines the deviation of the distribution function (25) of the desorbing molecules from the equilibrium form, the results of our paper[27] and Sec. 5 can be regarded as the discovery of the phenomenon of non-Maxwellian desorption at the level of transport processes.

In the general case formula (26) for different values of β describes a family of curves $G^+(\theta)$ lying, like the curves 1 and 2 in Fig. 5a, between the dashed curve (the cosine law) and the horizontal straight line $G^+ = G^+(\theta = 0)$. This means that the angular distribution of the flux of desorbing particles deviates from the equilibrium distribution at larger values of θ, but the maximum number of departing particles are moving, as before, along the normal to the surface ($\theta_m = 0$). A qualitatively new picture can arise in the case when τ in (8) and, as a consequence, the parameter β in (16) are increasing functions of the energy E_z of the molecules. Evidently, this situation should be realized when the surface temperature appreciably exceeds the Debye temperature and the relaxation of the particles becomes many-phonon relaxation. In this case the distribution $G^+(\theta)$ is analogous to the dashed-dotted curve in Fig. 5a and the maximum of the flux of desorbing particles occurs at a certain angle of emergence $\theta_m \neq 0$. The opposite situation occurs if β in (16) is a decreasing function of the energy (for the case of light particles at room temperatures, see Sec. 4). If β decreases faster than $E_z^{-1/2}$, the distribution $G^+(\theta)$ lies below the dashed curve in Fig. 5a, i.e., there exits a sharply pronounced maximum of the flux in the direction of the normal; in addition, $\varepsilon^+ > \varepsilon_0^+$. This behavior was predicted in Ref. 31.

The distribution of molecules undergoing desorption was also investigated theoretically in an earlier paper.[17] The dependence $G^+(\theta)$ obtained in this paper is shown in Fig. 5a by the dashed-dotted curve and does not agree with experiment. In Ref. 17 an extension[14,18] of the theory of random walks to the case of larger jumps was used. Here the usual *a priori* assumption was made that the function α in the boundary condition of the type (15) is the transition probability for the transition of a molecule from $E_z > 0$ into bound states ($E_z < 0$). With this definition α was found to be a decreasing function of E_z (since molecules with larger E_z ($E_z > 0$) have a lower probability of transition to levels with $E_z < 0$), and this led to a qualitative explanation of the non-Maxwellian effect. In fact, as was shown above, the function α in the usual boundary condition (15) has an unusual meaning, and its dependence on the energy is associated mainly with the dependence on E_z of the frequency ζ/L of the emergence of particles with $E_z > 0$ into the gas phase.

7. OTHER KINETIC PHENOMENA: CONCLUDING REMARKS

We shall cite a number of other results that demonstrate the possibilities of the theory developed above. Even with the aid of the relations (15)–(17), obtained in the relaxation-time approximation for the molecule-phonon collision integral, it is possible to give a qualitative explanation of the basic laws of the scattering of beams by a surface in the thermal regime[1)]—in particular, the dependence of the angular distribution of the reflected particles on the surface temperature, average incident-particle energy, and angle of incidence. The somewhat limited nature of the τ-approximation is manifested, as we should expect, in a quantitative analysis. For example, when the fraction α_t of the beam particles that become thermalized on the surface is calculated with the use in (15) and (16) of values of the parameter β that have been determined, as above, from experimental data for the energy-accomodation coefficient, the result in a number of cases in an appreciable underestimate in comparison with the experimental[29,30] value of α_t. At the same time, a good quantitative description of α_t, and even of the angular distribution of the scattered particles, for all three gases mentioned can be achieved in the case when the parameter β and also the angular distribution (17) of the elastically scattered particles are determined from experimental data for the same surface temperature, and one can predict, in accordance with

(15), (16), and (17), the angular distribution of the reflected beam at another surface temperature.

Generalization of the proposed method to the case of polyatomic gases makes it possible to construct a microscopic theory of the phenomenon of the nonequilibrium polarization (with respect to the directions of the angular momentum) of molecules interacting with a surface.[1,2,32] In this case it is possible to describe by unified arguments the molecular polarizations that arise in a low-density gas in the presence of a temperature difference between the gas and the surface[32] and a flow of the gas over the surface.[2] In such a theory it is possible, in particular, to describe the recently observed[33] strong decrease of the thermal polarization (by a factor of 25 for N_2/Pt) when the surface temperature changes from 300 to 100 K. This decrease of the polarization (like the temperature dependence of α_E) turns out to be related to the growth of the effective region of interaction of the molecules with phonons, and is predicted by the theory automatically if the values of that part of the function α in the formula of the type (15) that does not depend on the orientation of the angular momentum are determined from an independent experiment to measure α_E.

In the framework of the present approach it is possible to predict a fundamentally new effect in a gas-solid system—namely, nonlocalization of the flow of a gas over a surface, manifested as the mutual entrainment of volume and surface gas flows. There is a contribution to the volume flow of gas in a channel, proportional to the gradient ∇n_S of the density of surface particles, and a contribution to the surface current, proportional to the gradient ∇n_V of the volume density. The possibility of such an effect follows directly from the form of the system of kinetic equations (4), (8), (9), which predetermines the mutual dependence of the distribution function ρ of the surface particles and the distribution function f of the gas in the volume of the channel even for small occupation of the surface, when collisions of adsorbed and gas particles can be neglected. It has been found that the entrainment effect is important in, e.g., the isothermal flow of a gas in thin channels of diameter 20–100 Å; here it fundamentally changes the dependences of the gas flow on the physical parameters of the system (the temperature and channel diameter). Allowance for this effect makes it possible to describe known, but previously unexplained experimental data on the flow of gases in nuclear[34] and fine-pore filters—in particular, the dependence of the flow of CH_4 on the temperature and average pore diameter[35] and the anomalous temperature dependence of a helium flow.[36]

To conclude the paper we note the following. It is evident that the most surprising result of the theory constructed is the fact that a single (not only qualitative, but also, in most cases, quantitative) description of the phenomena considered and mentioned above can be achieved even in the simplest, relaxation-time approximation for the molecule-phonon collision integral. To a certain degree the reasons for this become clear if we take into account that for strong interaction with phonons (Fig. 2b) the frequency of emission (absorption) of phonons by a molecule with $E_z > 0$ should depend weakly on the state (E_z) of the molecules. To a certain extent the feasibility of the simple τ-approximation is also determined by the fact that the interaction of the molecules with phonons is not the only physical process in the evolution of molecules in the region within the range of the surface forces. As shown above, the arrival of particles and their departure into the gas phase turn out to play a key role in the description of the phenomena considered. We note that it is precisely the systematic inclusion of the processes of incidence and departure of particles in the kinetic equation of the surface particles [on the basis of a correct description of the particles above the potential well ($E_z > 0$)] that distinguishes our theory from all other previous attempts[14–18] to construct a kinetic theory of the interaction of gas molecules with a surface.

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[1] At not-too-high energies, when appreciable thermalization of the particles on the surface is observed.

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