COLLISION KINETICS OF SLOW ATOMS WITH A HEATED SURFACE

A. S. Dolgov

UDC 533-583.2; 533.6

Interest in the interaction of low-energy (on the order of an electron volt) atomic particles has been determined by a need to predict the changes in the properties of surfaces subjected to bombardment by relatively slow atoms and ions. The demands of practical and experimental work give rise to the theoretical problem of evaluating the probabilities of sticking or reflection of an atom as it collides with a surface and the sputtering coefficients for the surface atoms. Extensive studies have been made of the response of a crystalline surface to the initial impulse transmitted by an incident atom [1-4]. The bombardment of a heated surface is of particular interest. Various features of the interaction of atomic particles with thermally excited surfaces have been treated from one or another standpoint in the literature [5-8]. Some approximate considerations of relevance to this problem are given here. They are based on a comparison between the contributions of the lattice response to the initial impulse and the thermal motion of its atoms, and are not associated with a particular crystalline structure. The specific properties of the bombarded sample appear as parameters of relationships which are calculated independently.

The physical essence of a collision between a slow atom and a heated surface lies in a superposition of a nominally determinate process, stimulated by the impact of the incident atom, and the statistically determined vibrations of the (lattice) atoms. At high temperatures several general considerations may be introduced, which describe the motion of the atoms and asymptotically approach the exact relationships as the temperature increases.

As a rule, the layer of a crystal immediately adjacent to the surface has the most defects. Because of this, a large number of strictly local vibrational states develop, each of which belongs mainly to the defect atom itself. The square of the amplitude of the vibrations of such an atom in the α direction is determined by the quantity $\gamma_\alpha \hbar \omega_\alpha n_\alpha$, where the dependence on the quantum number n_α follows from the correspondence principle at high temperatures, the value of γ_α for each of these atoms depends on the specific conditions under which the atom is found, and ω_α is the frequency of the local vibration. The distribution function of the displacements and velocities of such an atom is given approximately by

$$f(\ldots x_\alpha, v_\alpha \ldots) = \prod_\alpha \frac{1 - e^{-\frac{\hbar\omega_\alpha}{T}}}{\pi} \sum_{n_\alpha} \frac{\exp\left(-\frac{\hbar\omega_\alpha n_\alpha}{T}\right)}{\sqrt{\gamma_\alpha \hbar \omega_\alpha n_\alpha - x_\alpha^2}}\, \delta\left\{v_\alpha - \omega_\alpha \sqrt{\gamma_\alpha \omega_\alpha \hbar n_\alpha - x_\alpha^2}\right\}, \quad n_\alpha > \frac{x_\alpha^2}{\gamma_\alpha \hbar \omega_\alpha}. \tag{1}$$

Replacing the summation in this equation by an integral gives

$$f(\ldots x_\alpha, v_\alpha \ldots) = \frac{\exp\left\{-\sum_\alpha \frac{1}{\gamma_\alpha T}\left(x_\alpha^2 + \frac{v_\alpha^2}{\omega_\alpha^2}\right)\right\}}{\pi^3 T^3 \prod_\alpha \gamma_\alpha \omega_\alpha}, \tag{2}$$

i.e., a Gaussian distribution of displacements and velocities where $f(x_\alpha, v_\alpha) = f_1(x_\alpha) f_2(v_\alpha)$, which corresponds "on the average" to the absence of correlations between the displacements and velocities.

In a similar way, or by calculating the appropriate correlation functions, it can be established that the coordinate-velocity distribution function may be factored for zone vibrations as well; that is, this factorization is a general property of high-temperature atomic vibrations.

These considerations can be used to introduce a simple distribution function for the displacements of the incident atom relative to its position determined by the evolution of

---

Khar'kov. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 1, pp. 27-31, January-February, 1982. Original article submitted November 11, 1980.

0021-8944/82/2301-0022$07.50

the process following the beginning of the interaction of this atom with the surface. This function is a superposition of the distributions defined by the dynamic effect of all the atoms in the crystal and has the form

$$f(x) = \exp\left(-\frac{x^2}{2\langle x^2\rangle}\right)\Big/\sqrt{2\pi\langle x^2\rangle}. \tag{3}$$

The mean square $\langle x^2\rangle$ depends on the time and is calculated as follows:

$$\langle x^2(t)\rangle = \sum_{\mathbf{p},\alpha}\{\langle x^2_{\mathbf{p}\alpha}\rangle\dot{\varphi}^2_{\mathbf{p}\alpha} + \langle v^2_{\mathbf{p}\alpha}\rangle\varphi^2_{\mathbf{p}\alpha}\}. \tag{4}$$

Here the summation over $\mathbf{p}$ corresponds to an enumeration of the the atoms in the crystal; $\langle x^2_{\mathbf{p}\alpha}\rangle$ and $\langle v^2_{\mathbf{p}\alpha}\rangle$ are the mean squares of the displacements and velocities of atom $\mathbf{p}$ and are calculated by standard methods [9]; the functions $\dot{\varphi}_{\mathbf{p}\alpha}$ and $\varphi_{\mathbf{p}\alpha}$ describe the dynamic effect of the initial displacement and of the initial velocity, respectively, on the motion of the incident atom along the normal to the surface, that is, they are the laws of motion of the atom of interest for unit displacements and velocities and have been sought in a number of previously published papers ([1-4], etc.).

As t increases, the quadratic dispersion increases from zero at t = 0 to some limiting value corresponding to "thermalization" of the incident atom. The duration of the thermalization stage is on the order of a single cycle for condensation of the inherent lattice and can be fairly long if the condensing atom is much different from the atoms of the crystal. The quantity $\langle x^2(t)\rangle$ plays the role of a temperature (with the appropriate scale).

Equations (3) and (4) can be used to find several properties of collisions between slow atoms and surfaces which are generally valid for different crystalline structures. If the energy of the thermal vibrations is much less than the energy of an incident atom and the cutoff energy for the interaction, then separation of an atom will occur within some time interval of the moment t_i when the displacement for separation of the given atom, calculated neglecting the thermal motion, is maximal (several maxima may contribute). Near this maximum the atom's motion relative to its nominal position is similar to harmonic motion at a frequency ω which is less than, but of the same order as, the limiting frequency of vibration of an atom (this behavior is found by analyzing a number of nonstationary problems). This harmonic law can be arbitrarily extended to times far from t_i, that is, to times which do not contribute significantly to the probability of separation. The component of the total motion determined by the thermal motion of the crystal is also vibrational in nature and can be approximated by a sinusoidal dependence at roughly the same frequency with a random amplitude a and random phase shift β relative to the function given above. Separation of an atom occurs when the amplitude of the resultant vibration exceeds some value b corresponding to the potential cutoff or, in other words, reaches an arbitrary boundary of the region of interaction between the incident atom and the crystal surface. In view of the above remarks, the phase shift of the resultant vibration relative to the initial forced impulse need not be large. Elementary calculations yield

$$x^2_m + 2x_m a\cos\beta + a^2 > b^2. \tag{5}$$

This inequality is generally satisfied for a limited range of variation in β. The ratio of this interval to 2π is indeed, the probability of separation for given values of x_m, a, and b. Thus, we have

$$\begin{aligned} &W = 0, \quad a < b - x_m,\\ &W(a) = \frac{1}{\pi}\arccos\frac{b^2 - a^2 - x^2_m}{2x_m a}, \quad b + x_m > a > b - x_m,\\ &W(a) = 1, \quad a > b + x_m \end{aligned} \tag{6}$$

(the last of these three cases does not fully meet the above assumptions; however, under the conditions being examined here, the extremely large values of a hardly contribute).

The conditional probability of separation near the i-th "danger point" is found by averaging the function W(a) of Eq. (6); i.e.,

$$W_i = \sqrt{\frac{K\pi}{2\langle E_i\rangle}}\int_0^\infty W(a)\exp\left(-\frac{Ka^2}{2\langle E_i\rangle}\right)da, \tag{7}$$

where K is the effective rigidity such that $\langle E_i \rangle = K\langle x^2(t_i)\rangle$.

A calculation using Eq. (7) in the approximation

$$\langle E_i \rangle \ll \frac{K}{2}(b - x_{mi})^2, \ \frac{K}{2}x_{mi}^2,$$

yields

$$W_i = \frac{1}{\pi K}\left(\frac{b}{x_{mi}}\right)^{\frac{1}{2}} \frac{\langle E_i \rangle}{(b - x_{mi})^2} e^{-\frac{K(b-x_{mi})^2}{2\langle E_i \rangle}}. \qquad (8)$$

Similarly, for $x_{mi} > b$ we obtain

$$W_i = 1 - \frac{1}{\pi K}\left(\frac{b}{x_{mi}}\right)^{\frac{1}{2}} \frac{\langle E_i \rangle}{(x_{mi} - b)^2} e^{-\frac{K(x_{mi}-b)^2}{2\langle E_i \rangle}}. \qquad (9)$$

If, however, $x_{mi} \simeq b$, then

$$1 > W_i \geqslant 1/2. \qquad (10)$$

Equations (7)—(10) can be used to determine the conditional probabilities for all the extremal distances between the atom and the nominal crystal surface. If the dominant contribution is associated with one such maximum, then the separation probability for the given impact parameter W is equal to the corresponding value of W_i. If, however, several maxima make significant contributions, then

$$W = \sum_{i=1}^{\infty} W_i \prod_{j=1}^{i-1} (1 - W_j). \qquad (11)$$

Equations (7)—(11) determine the continuous variation in the probability W with changes in the incident particle velocity and temperature. It is also evident that for relatively low incident velocities ($x_m < b$), the probability of separation is increased by heating the surface, while for relatively large velocities ($x_m > b$) the probability is decreased, and that the role of the temperature is greatest when the condensing atom is identical to the crystal atoms. The observed separation probability is an average of Eq. (11) over the distribution of collision parameters.

It is worth emphasizing that the preceding approach by no means ignores the collective excitations in the crystal. The functions φ and $\dot{\varphi}$ in Eq. (4) are sums along the normal of both short- and long-wave vibrations. However, explicit representations of φ and $\dot{\varphi}$ as expansions over vibrations with fixed frequencies are not needed here. These dependences can be found independently (see, for example, [1-4]).

The breaking away (separation) of an atom from the surfance leads to distortions in the velocity and displacement distribution of the atoms near the separation point. Because of this fact, the above equations are valid only over the time interval in which the incoming atom interacts with the surface. Thus, the possibility of repeated capture of an atom that has broken away is assumed to be negligible. In a three-dimensional medium, where the atoms are held on the surface by both longitudinal and transverse forces, repeated capture is unlikely.

Here it is also assumed that no other atom comes into contact with a particular part of the surface before a thermodynamic equilibrium distribution is reestablished. Given that the relaxation time is on the order of the vibrational period of the atoms (about 10^{-13} sec), it may be concluded that the system will be able to relax to an equilibrium state for any reasonable intensity of bombardment. The conditions for applicability of Eq. (11) are also independent of the way the atoms move after breaking off in some cycle of the vibrations.

It should also be pointed out that Eqs. (8) and (9), which were written under the assumption that the thermal displacements are small compared to the maximum displacement produced by the impact of an incident atom, have a wider range of applicability than permitted by the harmonic approximation. The motion of an incident atom along the normal to the surface is given in general by some function

$$x(t) = F\{t, x_0(0), \ldots x_{p\alpha}(0), v_{p\alpha}(0)\ldots\}, \qquad (12)$$

where $x_0(0)$ is a set of initial data determining the motion $x_0(t)$ of a particular atom assuming that the thermal vibrations can be neglected. Including the relative smallness of the contribution of the initial thermal displacements of the atoms in the crystal for times near the "danger point," Eq, (12) can be rewritten in the form

$$x(t) = x_0(t) + \sum_{p,\alpha} \left\{ \frac{\partial F(t, x_0(0), \ldots 0, 0 \ldots)}{\partial x_{p\alpha}(0)} x_{p\alpha}(0) + \frac{\partial F \quad (t, x_0(0), \ldots 0, 0 \ldots)}{\partial v_{p\alpha}(0)} v_{p\alpha}(0) \right\}. \tag{13}$$

Comparing Eq. (13) with the corresponding exact harmonic expression

$$x(t) = x_0(t) + \sum_{p,\alpha} \{\dot{\varphi}_{p\alpha} x_{p\alpha}(0) + \varphi_{p\alpha} v_{p\alpha}(0)\} \tag{14}$$

shows that Eqs. (13) and (14) differ only by some independently determined functions. Thus, in this situation, anharmonocity leads only to a renormalization of the functions φ and $\dot{\varphi}$, that is, ultimately to a change in the scales for the quantitites $\langle x^2(t_i)\rangle$ and $\langle E_i\rangle$ used above, with retention of all the equations containing these quantities. Note that here it is assumed that the anharmonic effects are assumed small only for the equilibrium thermal vibrations. The motion of the atoms may be highly anharmonic following the impact of a fast incident atom.

These results are applicable both to condensation and to sputtering of atoms by relatively slow atomic particles. In the latter case $\langle E_i\rangle$ must be replaced by a constant that coincides with T in the harmonic limit. Equations (8) and (9) determine the role of the energy of the incident particles x_m, the characteristics of the bombarded surface K and b, and the temperature $\langle E_i\rangle$, and can be used in a wide variety of real physical situations.

LITERATURE CITED

1. R. W. Zwanzig, "Collision of a gas atom with a solid surface," J. Chem. Phys., 32, No. 4 (1960)
2. A. A. Pyarnpuu, The Interaction of Gas Molecules with Surfaces [in Russian], Nauka, moscow (1974).
3. R. G. Barantsev, The Interaction of Rarefied Gases with Streamlined Surfaces [in Russian], Nauka, Moscow (1975).
4. F. Goodman and H. Wachman, The Dynamics of Gas Scattering by Surfaces [Russian translation], Mir. Moscow (1980).
5. D. S. Strijenov, "Influence of thermal motion in a solid on the interaction of an atom colliding with the solid surface, "Fluid Dynam. Trans., 5, Pt. II (1971).
6. Yu. P. Tambovtsev, "Nonequilibrium classical theory of the interaction of gas atoms with a solid surface "Manuscript deposited at VINITI No. 7189-73 Dep.; No. 7319-73 Dep. (1973).
7. A. E. Galanov, "Model for the inelastic scattering of atoms on a crystalline surface in the impulse approximation, "Prikl. Mekh. Tekh. Fiz., No. 6 (1976).
8. V. I. Zhuk, "On the capture of gas atoms at a solid surface," Prikl. Mekh. Tekh. Fiz., No. 1 (1979).
9. A. Maradudin, E. Montroll, and G. Weiss, Theory of Lattice Dynamics in the Harmonic Approximation, Academic Press, New York (1971).