Archives of Mechanics • Archiwum Mechaniki Stosowanej • 26, 4, pp. 629–636, Warszawa 1974

A semi-continuous model of the scattering of gas atoms by metal surfaces

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THE SCATTERING of gas atoms in the thermal energy range by clean and atomically smooth metal surfaces is considered. The revised version of Landau's theory, based on the continuum model of the solid, is exploited to examine the scattering patterns. The statistical character of the influence of the thermal motion of the metal surface on the gas atom is modelled by means of the two-dimensional normal distribution function. The probability density function of the gas atom scattering in a given direction is obtained (in the analytical form). The approach covers two phenomenological scattering regimes: quasi-elastic and in-elastic.

W pracy rozpatrzono rozpraszanie atomów gazów szlachetnych o energiach termicznych na czystych (tzn. bez zaadsorbowanych gazów) oraz idealnych pod względem struktury krystalograficznej powierzchniach metali. Analizę rozkładów kątowych odbitych atomów gazu oparto na zmodyfikowanym modelu Landaua, w którym ciało stałe jest przedstawione jako ośrodek ciągły. Celem opisu wpływu na atomy gazu ruchu termicznego powierzchni metalu wprowadzono funkcję gęstości prawdopodobieństwa odbicia atomu gazu z prędkością (v_x, v_z) w postaci dwuwymiarowego rozkładu normalnego. Następnie obliczono gęstość prawdopodobieństwa odbicia atomu gazu pod kątem θ_r. Proponowany model dotyczy dwóch wyróżnionych fenomenologicznie rodzajów rozpraszania: quasi-elastycznego i nieelastycznego.

В настоящей работе рассмотрено рассеяние атомов благодарных газов с тепловыми энергиями на чистых (т. е. без адсорбированных газов) и идеальных, по отношению к кристаллической структуре, поверхностях металлов. Анализ угловых распределений отраженных атомов газа опирается на модифицированной модели Ландау, в которой твердое тело представляется как сплошную среду. С целью описания влияния на атомы газа теплового движения поверхности металла введена функция плотности вероятности отражения атома газа со скоростью (v_x, v_z) в виде двумерного нормального распределения. Затем расчитана плотность вероятности отражения атома газа под углом θ_r. Предложенная модель касается двух типов рассеяния различающихся феноменологически: квазиупругого и неупругого.

Notations

a, D the Morse potential parameters,

$f(v_x, v_z)$ the probability density function of the gas atom scattering with the velocity (v_x, v_z),

h Planck constant,

$h(y)$ the probability density function of the gas atom scattering for $y = \mathrm{tg}\theta_r$,

k Boltzmann constant,

m the mass of the gas atom,

m_s the atomic mass of the solid,

m_x, m_z parameters of the $f(v_x, v_z)$ function,

M the coefficient defined by the formula (3.7),

$\overline{M} = M/(4\pi^2)$,

p, q, r the coefficients described respectively by the formulae (3.3), (3.4), (3.5),

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T_s surface temperature,
T_g the kinetic temperature of the gas atom,
$\mathbf{V}_i(V_x, V_z)$ the velocity of the incident gas atom,
$\mathbf{v}_r(v_x, v_z)$ the velocity of the reflected gas atom in the stochastic approach,
$\mathbf{U}_k(U_x, U_z)$ the velocity of the reflected gas atom in the deterministic approach,
$\langle w^2 \rangle$ the mean square displacements of a surface point,
y the quantity defined by the formula (3.8),
$\tilde{\varepsilon}_1$ the average energy transferred by the incident gas atom to the bulk solid modes,
$\tilde{\varepsilon}_2$ the average energy transferred by the incident gas atom to the surface solid modes,
θ_i the angle of incidence of the gas atom,
θ_f the angular position of the peak of the density pattern,
$\Delta\theta$ $= \theta_i - \theta_f$,
θ_r the angle of reflection of the gas atom in the stochastic approach,
θ_D the Debye temperature,
λ the full width of the density pattern measured at half-maximum,
σ_x, σ_z parameters of the $f(v_x, v_z)$ function,
$\Phi(x)$ the function defined by the formula (3.1),
ω frequency of a normal mode,
ω_c the cut-off frequency.

1. Introduction

THE DISCRETE, lattice models of the solid are the main object in the study of gas-solid surface interactions [1]. These theories usually start with an oversimplified description of crystal lattices and even in the advanced stage in the three-dimensional theories rough assumptions concerning the bonds between atoms are used. Further, for discrete models principal use can be made of the statistics of numerical results. However, it is known that for thermal energies of the incident atoms the solid acts as a whole, and for this reason the use of continuum description of the solid seems to be preferable. The continuum models of the solid have not been extensively studied in the context considered and there are only a few papers [2], starting with Landau's [3], in which this approach is used.

In the present paper, we intend to describe the use of the continuous model for the analysis of rare gas atoms scattering in the thermal energy range by clean and atomically smooth metal surfaces. Only those processes will be regarded in which the de Broglie wavelength of the gas atom is small compared with the characteristic interaction length.

This requirement validates the assumption that the model obeys the laws of classical mechanics.

2. The gas-metal surface energy exchange

We started with the revised version of Landau model [4] in which the solid was regarded as a semi-infinite, isotropic, elastic continuum. The modified Debye model was employed to represent the frequencies ω of the solid modes. These frequencies are limited by the cut-off frequency ω_c [5].

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The average energy, transferred by the incident gas atom to the bulk ($\tilde{\varepsilon}_1$) and surface ($\tilde{\varepsilon}_2$) solid modes, was calculated using the following assumptions:

the Morse potential represents the interaction of the gas atom with the solid as a whole; this potential depends on the distance of the gas atom from the equilibrium position of the solid surface;

the gas-solid coupling is described by a linear function of the displacement of a point on the solid surface.

The values of $\tilde{\varepsilon}_1$ and $\tilde{\varepsilon}_2$ depend on the mass and the incident velocity of the gas atom, on the values of the interaction potential parameters, and the physical properties of the solid (its density and elasticity). The exact forms of $\tilde{\varepsilon}_1$ and $\tilde{\varepsilon}_2$ are given in [4].

The model described above enables us to calculate the velocity components (U_x, U_z) of the gas atom leaving the surface:

$$U_x = V_x$$
$$U_z = \sqrt{V_z^2 - \frac{2}{m}(\tilde{\varepsilon}_1 + \tilde{\varepsilon}_2)(1 - T_s/T_g)}, \tag{2.1}$$

if V_x, V_z are the velocity components of the gas atom with the mass m, impinging on a solid surface at the angle θ_i; T_s and T_g are the temperature of the surface and the kinetic temperature of the gas atom, respectively.

Hitherto, the original Landau's theory has been modified only by taking into account the more realistic solid model—i.e., the elastic continuum instead of a fluid type continuum—and by using the Morse potential instead of the simplified, pure repulsive potential originally used in the Landau paper.

3. The scattering pattern

For the description of the scattering pattern we have introduced to our previous pure deterministic model certain stochastic concepts. Bearing in mind that the normal and tangential (to the solid surface) components of the velocity of the incident gas atom can be treated independently, we have chosen a two-dimensional normal distribution function $f(v_x, v_z)$, giving the probability density of the gas atom scattering with the velocity (v_x, v_z). This function has been represented as a product of two normal distributions:

$$f(v_x, v_z) = \frac{2}{2\pi\sigma_x\sigma_z[\Phi(m_z/(\sqrt{2}\sigma_z))+1]} \exp\left[-\frac{(v_x-m_x)^2}{2\sigma_x^2} - \frac{(v_z-m_z)^2}{2\sigma_z^2}\right]$$
$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt. \tag{3.1}$$

Now, as the mean values of the distribution function we take the velocity components of the reflected gas atom, obtained previously from the deterministic model—i.e., we assume:

$$m_x = U_x, \quad m_z = U_z. \tag{3.2}$$

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The expressions for the dispersions σ_x and σ_z we choose on the basis of pure phenomenological considerations, founded on the analysis of available experimental data. These data [1] show that the following factors are decisive for the type of gas-metal scattering considered: p is the distance of closest approach of the gas atom to the surface during the collision, q the average number of vibrations of a point on the metal surface within the characteristic interaction time—i.e., the time during which the incident gas atom covers the distance equal to the characteristic interaction length a, r the average characteristic velocity of points of the solid surface.

The significance of the first factor has been discussed, for example, by MILLER, SUBBARAO [6]. In the same paper is given the approximate formula, describing this quantity.

Following their arguments we assume that the coefficient p can safely be taken in the form:

$$p = 1 + \frac{2kT_g}{D}\cos^4\theta_i, \tag{3.3}$$

where D is the well depth of the Morse potential.

The quantity q can be expressed as the ratio of the characteristic interaction time $\tau_g = a/V_z$ and the characteristic time of vibrations $\tau_c = 2\pi/\omega_c$—i.e.,

$$q = \frac{\tau_g}{\tau_c} = \frac{a\omega_c}{2\pi V_z}. \tag{3.4}$$

Note that in the gas-solid scattering processes considered $q \geqslant 1$.

The coefficient r is described as the ratio of the square root of the mean square displacement of a point on the solid surface $\langle w^2\rangle$ and the characteristic time of vibrations τ_c:

$$r = \sqrt{\langle w^2\rangle}\,\omega_c/(2\pi). \tag{3.5}$$

For the quantity $\langle w^2\rangle$ we have adopted the well known formula, which follows from the Debye theory of vibrations of the elastic solid [7], namely:

$$\langle w^2\rangle = \frac{3h^2T_s}{m_s\theta_D^2 k}. \tag{3.6}$$

Here m_s is the atomic mass of the solid, θ_D—the bulk Debye temperature, h—the Planck constant.

Now, it seems plausible to assume that the three factors referred to above are independent and hence, for an isotropic surface ($\sigma_x = \sigma_z$), we write:

$$\sigma_x = \sigma_z = Mpqr. \tag{3.7}$$

The proportionality coefficient M is regarded as a semi-universal constant (i.e., the same for all thermal energy rare gas atoms, scattered by clean and atomically smooth metal surfaces). The resulting formula for the probability density function $h(y)$ of the gas atom scattering in a given direction has the form:

$$h(y) = \frac{1}{\pi(y^2+1)[\Phi(m_z/(\sqrt{2}\sigma_z))+1]}\exp\left[-\frac{(U_x-yU_z)^2}{2\sigma_x^2(y^2+1)}\right]\times$$
$$\times\left\{\exp\left[-\left(\frac{yU_x+U_z}{\sigma_x\sqrt{2y^2+2}}\right)^2\right]+\frac{\sqrt{\pi}(yU_x+U_z)}{\sigma_x\sqrt{2y^2+2}}\left(1+\Phi\left(\frac{yU_x+U_z}{\sigma_x\sqrt{2y^2+2}}\right)\right)\right\}, \tag{3.8}$$
$$y = \operatorname{tg}\theta_r.$$

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4. Results

We shall use the familiar parameters $\Delta\theta$ and λ to characterise the scattering patterns (Fig. 1).

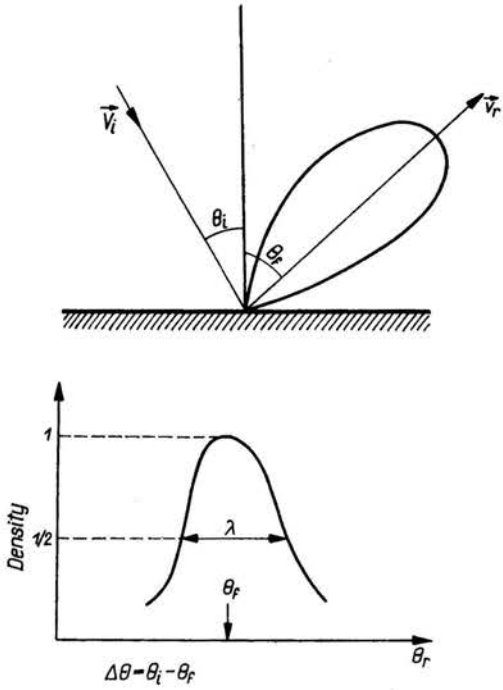

FIG. 1. The density pattern.

Figures 2, 3 and 4 illustrate the typical calculated density patterns for $\theta_i = 0°$ and $\theta_i = 60°$, respectively.

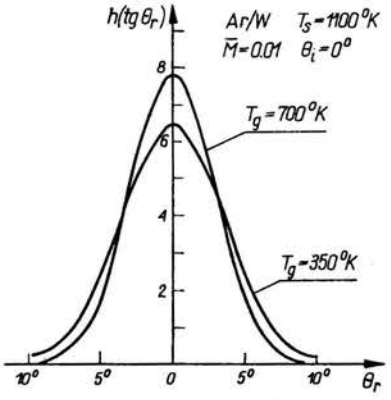

FIG. 2. The dependence of the density pattern on the gas temperature T_g. Ar/W, $\theta_i = 0°$, $T_s = 1100°K$, $\overline{M} = 0.01$.

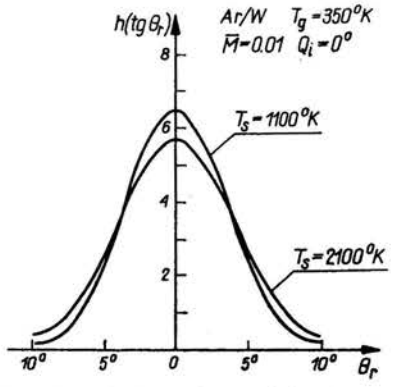

FIG. 3. The dependence of the density pattern on the surface temperature T_s. Ar/W, $\theta_i = 0°$, $T_g = 350°K$, $\overline{M} = 0.01$.

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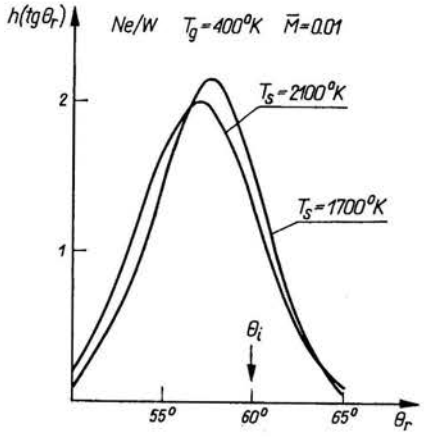

FIG. 4. The lobular scattering pattern. Ne/W, $\theta_i = 60°$, $T_g = 400°K$, $\overline{M} = 0.01$.

It is seen that the lobular scattering, known from experimental data, is obtained. The plot of the function $h(\mathrm{tg}\theta_r)$ vs. θ_r is symmetrical for $\theta_i = 0°$ and not symmetrical for $\theta_i \neq 0°$.

Figures 5 and 6 represent the features of the theoretical intensity distributions as functions of the surface and gas temperature. The width λ of the density patterns increases with T_s, but diminishes with T_g. Similarly, the values of the parameter $\Delta\theta$ increase with T_s and decrease with T_g.

An interesting point is that the case $\Delta\theta = 0°$ occurs as a rule for $T_s \neq T_g$. Further, it is important to note that, generally speaking, we have obtained:

$$\begin{aligned} \Delta\theta_{\mathrm{Ar}} &> \Delta\theta_{\mathrm{Ne}} > \Delta\theta_{\mathrm{He}}, \\ \lambda_{\mathrm{Ar}} &> \lambda_{\mathrm{Ne}} > \lambda_{\mathrm{He}}. \end{aligned} \tag{4.1}$$

The results shown in Figs. 7, 8 illustrate the dependence of the density patterns on the incidence angle θ_i.

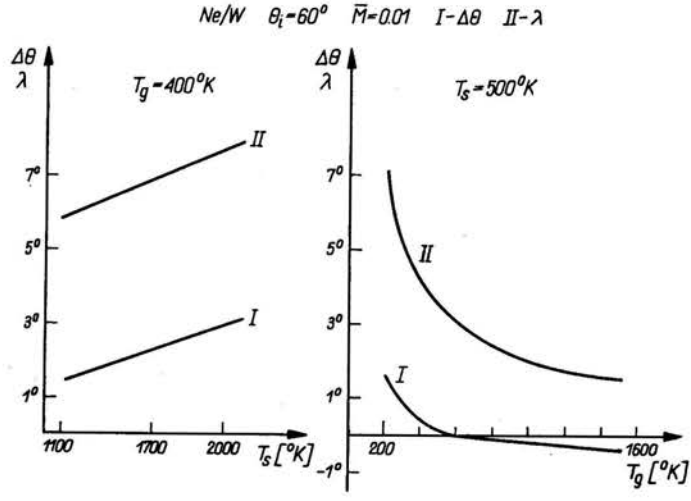

FIG. 5. The dependence of $\Delta\theta$ and λ parameters on T_g and T_s. Ne/W, $\theta_i = 60°$, $\overline{M} = 0.01$, I—$\Delta\theta$, II—λ.

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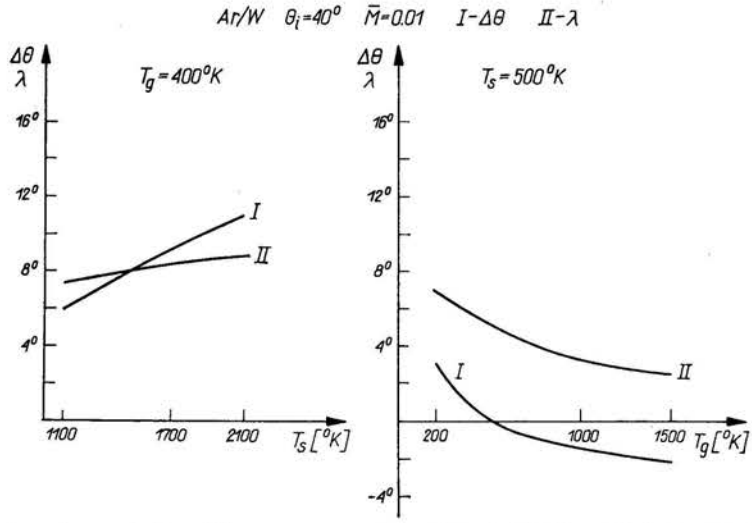

FIG. 6. The dependence of $\Delta\theta$ and λ parameters on T_g and T_s. Ar/W, $\theta_i = 40°$, $\bar{M} = 0.01$, I—$\Delta\theta$, II—λ.

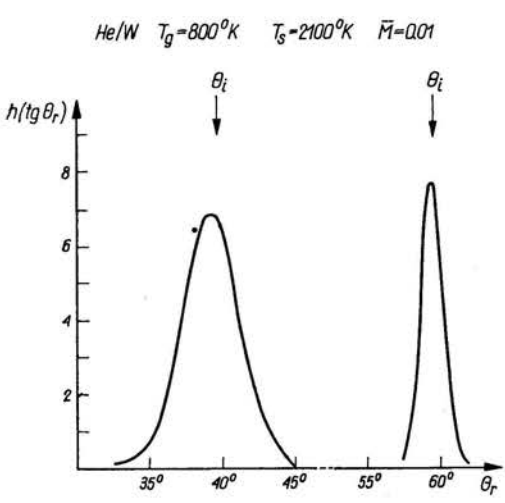

FIG. 7. An example of the quasi-elastic scattering pattern. He/W, $T_g = 800°K$, $T_s = 2100°K$, $\bar{M} = 0.01$.

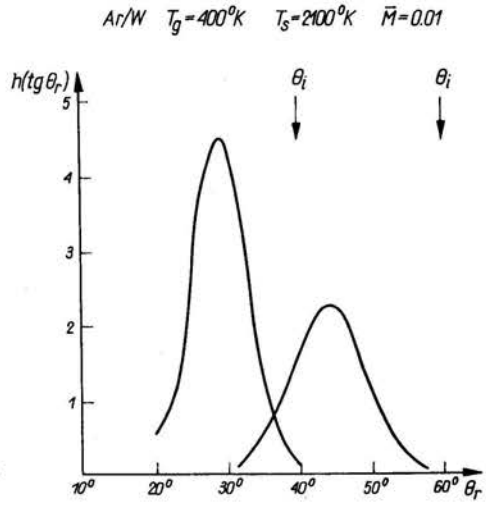

FIG. 8. An example of the inelastic scattering pattern. Ar/W, $T_g = 400°K$, $T_s = 2100°K$, $\bar{M} = 0.01$.

In the case of He, the deviation $\Delta\theta$ is almost equal to zero and the width λ diminishes with θ_i. Such behaviour is characteristic for the quasi-elastic regime of rare gases thermal scattering [8].

By contrast, for Ar, the deviation $\Delta\theta$ may differ substantially from zero and the width λ increases with θ . These features characterise the inelastic regime of thermal scattering [8]. The occurrence of the two regimes appears to be an asset of this approach.

The dependence of the density pattern on θ_i is rather complex, as may be seen in Fig. 9; this is due to the competitive influence of different factors, discussed previously. Behaviour

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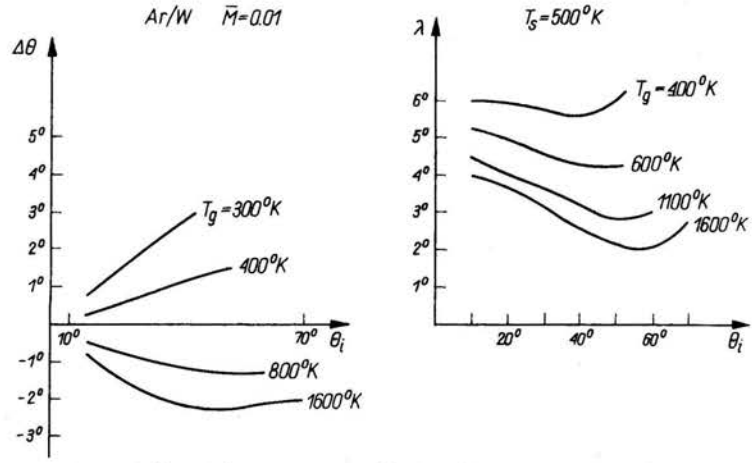

FIG. 9. The dependence of $\Delta\theta$ and λ parameters on θ_i, for different gas and surface temperatures. Ar/W, $\overline{M} = 0.01$.

similar to that presented in Fig. 9 has been observed in many rare gases scattering experiments [1].

The above qualitative results satisfactorily reproduce the essential characteristics of the scattering considered of the gas atoms. This fact seems to support the claim that the approach, based on the continuum description of the solid, can at least be as useful as the results of discrete theories.

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Received September 3, 1973.

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