SCATTERING KERNEL OF GAS PARTICLES ON THE SURFACE OF A NONEQUILIBRIUM SOLID

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The solution of the kinetic equation for the distribution function of adsorbed gas atoms is used to construct the scattering kernel for a nonequilibrium state of the surface.

Existing models of the scattering kernel of a dilute gas on a surface are limited by the assumption that the solid is in equilibrium [1, 2]. This assumption does not allow one to describe correctly transport processes in the gas due to temperature and pressure gradients near the nonequilibrium surface, since the lack of thermodynamic equilibrium in the plane of the surface causes an additional flux of gas along the surface (the entrainment effect) which can become significant under certain conditions [3, 4].

Depending on the energy, the gas atoms [1] can either scatter and remain free, or suffer transitions into bound states and then escape from the surface after a certain time interval. If the mean collision time of the free gas atoms with the surface is much smaller than the relaxation time of the atoms due to phonons of the solid, and the lifetime of atoms in the adsorbed state, on the other hand, is much larger than this time, then the adsorbed particles can better adjust to the nonequilibrium state of the boundary and give a dominant contribution to the entrainment, acquiring a mass velocity due to the temperature gradient on the surface. In this case which is characteritic for the scattering of gases that are not too light by monocrystals, the distribution function of the desorbed gas atoms will depend on this mass velocity and the entrainment effect can be included in a fairly simple way in the Nochilla model of the scattering kernel [5].

We consider the region of space $z > 0$ near a plane crystal surface $z = 0$ with a small temperature gradient ∇T_s along the x axis. The space is occupied by a gas of noninteracting adsorbed particles with a small temperature gradient ∇T_g, which in general is not equal to ∇T_s.

Since it is assumed that the state of the adsorbed gas—solid system is close to equilibrium, the steady-state distribution function of adsorbed atoms with respect to the velocity **v** can be represented in the form

$$f(\mathbf{v}, x, z) = f^0(\mathbf{v}, x, z)(1 + \varphi(\mathbf{v}, x, z)), \tag{1}$$

where f^0 is a local-equilibrium Maxwell—Boltzmann distribution function in the field of the surface potential $U(z)$, and $\varphi = \varphi_g k^{-1} T_g^{-2} \nabla T_g + \varphi_s k^{-1} T_s^{-2} \nabla T_s$ is a perturbation.

The nonequilibrium correction φ_s can be found from the solution of a linearized kinetic equation for f, describing the interaction of gas atoms with the collective thermal fluctuations of the lattice atoms of the solid. Unlike the alternative approach of [4], this method is based on the formal theory of scattering and allows one to take into account multiple gas—phonon interactions. It leads to a different result for the entrainment effect than that of [4]. Our approach is based on the kinetic description of the motion of gas atoms in the field of the fluctuating surface potential; a phenomenological variation of this method was used in [2, 6]. The quantum kinetic equation introduced in [3] transforms into the quasiclassical Fokker—Planck equation when the surface potential is smoothly varying ($\lambda d^{-1} << 1$):

$$v_x \frac{\partial f}{\partial x} + v_z \frac{\partial f}{\partial z} - \frac{1}{m} \frac{\partial U}{\partial z} \frac{\partial f}{\partial v_z} = \frac{\partial}{\partial v_i} \left(A_i f + B_{ij} \frac{\partial f}{\partial v_j} \right), \tag{2}$$

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where i, j = x, y, z. Single scattering of particles on the boundaries of the potential well will be assumed to be elastic. An inelastic boundary condition for (2) can easily be constructed with the help of scattering theory [1, 4].

The coefficients B_{ij} and A_i depend on v and z and go to zero when $z \to \infty$ and are nonzero in a narrow surface layer of width of order d. $B_{ij}(N)$ is a functional of the nonequilibrium distribution function of phonons $N = N^0 + \Delta N$, where N^0 is the local-equilibrium Planck function, and $\Delta N = N^0(1 + N^0)(n_g k^{-1} T_g^{-2} \nabla T_g + n_s k^{-1} T_s^{-2} \nabla T_s)$ is the perturbation. In the relaxation time approximation [7]

$$n_s = -\tau\hbar\omega \frac{\partial\omega}{\partial Q_x}.$$

Neglecting the dependence of f, U, A_i, and B_{ij} on z in the adsorbed layer, after linearizing (2) and equating terms containing ∇T_s, we obtain an equation for φ_s for temperatures $kT_s \gg \hbar v_z d^{-1}$, where $T_s = T_g = T$:

$$\frac{\partial}{\partial v_i}\left(B_{ij}(N^0)\frac{kT}{m} f^0 \frac{\partial\varphi_s}{\partial v_j}\right) = \frac{\partial}{\partial v_i}\left(B_{ij}(N^0(1 + N^0)n_s)\frac{\partial f^0}{\partial v_j}\right). \tag{3}$$

Equation (3) indicates a diffiusion process in the velocity space of the adsorbed particles on account of multiple interactions of the particles with nonequilibrium phonons of the solid and will be valid in the case of a smooth surface potential well with specularly reflecting sides.

We seek φ_s in the form

$$\varphi_s(\mathbf{v}) = \Phi(v) v_x, \quad v = |v_z|. \tag{4}$$

It can be shown that if the average speed $\bar{v}$ of the atoms of the gas is much less than the mean speed of sound c in the solid, then $B_{zz} \gg B_{zx} \sim B_{xz} \gg B_{ij}$, i, j = x, y. Then (3) can be simplified and reduces to the following equation for Φ:

$$\frac{\partial^2\Phi}{\partial v^2} - \frac{mv}{kT}\frac{\partial\Phi}{\partial v} = H(v),$$

$$H(v) = \frac{1}{B_{zz}(N^0)}\left(\frac{m}{kT}\right)^2 \frac{mv}{kT} B_{zx}(N^0(1 + N^0)n_s). \tag{5}$$

Putting $\xi = v(m/2kT)^{1/2}$, we obtain

$$\frac{\partial^2\Phi}{\partial\xi^2} - 2\xi\frac{\partial\Phi}{\partial\xi} = h(\xi), \tag{6}$$

where

$$h(\xi) = \frac{2kT}{m} H\left(\xi\left(\frac{2kT}{m}\right)^{1/2}\right).$$

Equation (6) has the inhomogeneous solution

$$\Phi(\xi) = \Phi_0(\xi)\int_0^{\xi}\frac{d\xi'}{E(\xi')\Phi_0^2(\xi')}\int_0^{\xi'} d\xi'' E(\xi'')\Phi_0(\xi'')h(\xi''),$$

$$\Phi_0(\xi) = \int_0^{\xi} d\xi' \exp\xi'^2 = \mathrm{Erfi}\,\xi, \quad E(\xi) = \exp(-\xi^2). \tag{7}$$

The entrainment velocity of the particles along the surface will be

$$u_x = -\int d\mathbf{v} v_x f^0 \varphi_s \frac{1}{kT^2}\nabla T = -c\tau\left(\frac{2kT}{m}\right)^{1/2} B\frac{\nabla T}{T}, \tag{8}$$

where $B \sim k\Theta/mc^2$.

An analogous formula for u_x was obtained in [4] without taking into account the multiplicity of the gas–phonon interactions, however the resulting value of B is significantly different. In [4]

$$B^* \sim b\frac{\omega_D^3 m}{\rho_s c^3}\frac{\left(\frac{kT}{m}\right)^{1/2}}{c}, \tag{9}$$

where $b \sim 10^{-2}$. For solids having the usual dispersion law, equation (9) can be rewritten in the form $B^* \sim 10^{-2}\, m\bar{v}(Mc)^{-1}$ and hence for temperatures that are not too high $B^* \sim 10^{-3}$ and B^* goes to zero when $T \to 0$.

Under the same conditions B in (8) is at least an order of magnitude larger. In addition, B does not depend on T and M, and unlike B^*, it is inversely proportional to m. Therefore the treatment of diffusion of adsorbed atoms in velocity space using the kinetic equation (2) leads to qualitatively new results for the entrainment effect.

Let β be the adhesion coefficient. That, is, β is the fraction of particles incident on the surface from a steady flux that are adsorbed. Let $R^0(\mathbf{v}' \to \mathbf{v})$ be the scattering kernel for the other particles. Using the fact that the entrainment mass velocity u_x acquired by the particles in the bound state is conserved upon their desorption, the nonequilibrium scattering kernel, in the framework of the model discussed here, can be written in the form

$$R(\mathbf{v}'\to\mathbf{v}) = (1-\beta)R^0(\mathbf{v}'\to\mathbf{v}) + \beta\frac{v_z}{2\pi}\left(\frac{m}{kT}\right)^2 \exp\left[-\frac{m}{2kT}\left((v_x-u_x)^2+v_y^2+v_z^2\right)\right], \tag{10}$$

where u_x is given by (8).

NOTATION

z, coordinate perpendicular to the surface; x, coordinate in the plane of the surface; T_s, local temperature of the solid; T_g, local temperature of the gas; v, velocity of the gas atoms; f, total velocity distribution function of the gas atoms; f^0, local-equilibrium gas distribution function; φ, perturbation of the gas distribution function; k, Boltzmann constant; λ, deBroglie wavelength of a gas atom; U, surface potential; d, characteristic linear scale of the variation of U; A_i and B_{ij}, friction and diffusion coefficients in v-space; N, total phonon distribution function; N^0, local-equilibrium phonon distribution function; ΔN, perturbation of the phonon distribution function; τ, relaxation time in the phonon subsystem; ω, phonon frequency; Q_x, x component of the wave vector of a phonon; $\hbar$, Planck's constant; Φ, auxiliary perturbation function; the solution of the inhomogeneous differential equation (6); Φ_0, solution of the homogeneous differential equation corresponding to (6); $v = |v_z|$, absolute value of the z-component of the velocity of gas atoms; ξ, dimensionless velocity; u_x, mass velocity of particles along the x axis; B, dimensionless coeffcient; M and m, masses of atoms of the solid and gas, respectively; c, speed of sound in the solid; Θ, characteristic vibrational temperature of surface atoms; ω_D, Debye frequency; ρ_s, density of the solid; b, dimensionless coefficient; β, adhesion coefficient; R, total scattering kernel; R^0, scattering kernel of free particles.

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