Gas–Metal Interactions

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Dynamics of gas–surface scattering (interaction and accommodation of translational and vibrational energy) is considered. Evolution of a quasi-particle ensemble is also investigated and the problem of quantum oscillator excitation is solved in the most simple way.

Key words: Gas–surface interaction – Electron and phonon excitations – Exchange interaction – Vibrational relaxation.

1. Introduction

Energy accommodation induced by collisions of gas atoms and molecules with solid surfaces (particularly with metal surfaces) is a fundamental process in chemical physics and was a subject of numerous experimental and theoretical investigations. The main attention has been attached to translational energy accommodation. Survey of the work on this process may be found in review articles [1, 2]. However, a satisfactory understanding of a number of theoretical problems – general expression for the energy transfer probability, normalization of the transition probability distribution density, limiting values of the accommodation coefficient for low and high kinetic energy, multi-phonon excitations, role of electron transitions in metals – is still lacking. In addition experimental data have been recently obtained for the gas molecule vibrational relaxation induced by collisions with a metal surface (see e.g. Ref. [3]). In the present paper we have attempted to take a step toward the solving of this problem.

A lot of different approximations are used in solid-state theory and the theory of interactions and inelastic collisions between gas particles. In the first case it is common practice to use a bulk Debye continuum model for the phonon spectrum and some approximations of electron emission theory [4]. In the second one there

are asymptotic calculations of interaction potentials [5], approximations of vibrational relaxation theory [6], semiclassical approximation in collision theory relative motion of colliding heavy particles is treated classically but transitions between their electronic and vibrational states are described by quantum mechanics), use of model potentials with empirical parameters. The aim of the present investigation is to stay within the framework of these approximations without additional limitations and to obtain analytical solutions of the above-mentioned problems. The simple analytical formulas provide considerable physical insight into the energy relaxation mechanism.

The qualitative picture of the process is as follows. Phonons and electrons of the solid are affected by gas atoms and molecules. This interaction causes creation and/or annihilation of corresponding quasi-particles. Semiclassical approximation gives a possibility to obtain the time-dependent perturbation which results in energy exchange between the gas and the solid.

2. Evolution of the Quasi-Particle Statistical Ensemble

Consider a system of N independent particles where N is equal to the number of vibrational modes or free electrons in the metal target, $N \sim 10^{23}$ (further we suppose that $N \to \infty$). For a finite-time interval this system is affected by the perturbation $V(t)$ which is the sum of the one-particle operators $V_k(t)$. As a result there are transitions of individual particles from one state to another. Our first task is to determine the total energy change probability which contains all multi-particle events.

Let ω_k^1 be the energy change of particle k and $p_k(\omega)_k$ the probability density of this event. Let us then introduce the following quantities:

$$p(\omega) = \sum_k p_k(\omega), \qquad q_k = \int p_k(\omega) \, d\omega, \qquad Q = \sum_k q_k. \tag{1}$$

Let Q have a finite value and $q_k \sim N^{-1}$ (if $V_k \sim N^{-1/2}$ then p_k can be determined by means of the first-order perturbation method; the following orders do not give the finite contribution). q_k is the probability of a single event. Then the total probability of n-particle transition in the system ($n \ll N$, usually $n \sim 1$–10^2) may be expressed as follows:

$$Q_n = \sum_{k_1 < \cdots < k_n} \frac{q_{k_1}}{1 - q_{k_1}} \cdots \frac{q_{k_n}}{1 - q_{k_n}} \prod_{i=1}^{N} (1 - q_i) \xrightarrow[N \to \infty]{} \frac{1}{n!} Q^n \, e^{-Q}. \tag{2}$$

Note that the probability of any transition in the system is $Q' = 1 - W$, $W = \exp(-Q)$, and the most probable number of single transitions is equal to Q (if $Q \gtrsim 1$). If $Q \ll 1$ then only one particle changes its state. So Q is a measure of the interaction $V(t)$ efficiency.

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[1]   Unless otherwise specified, atomic units are used, $\hbar = e = m_e = 1$, and the Boltzmann constant is also put to be equal to unity.

In order to determine the total probability density $P(\omega)$ let us introduce the characteristic functions for $p_k(\omega)$ and $p(\omega)$,

$$f_k(\tau) = \int_{-\infty}^{\infty} e^{i\omega\tau} p_k(\omega)\, d\omega, \qquad f = \sum_k f_k, \qquad f(0) = Q, \tag{3}$$

and consider ω as a sum of independent random quantities ω_k. Then the spectral density of the n-particle transition is

$$P_n(\omega) = \frac{W}{n!} \sum_{k_1,\cdots,k_n} p_{k_1}(\omega_1)_* \cdots {}_* p_{k_n}(\omega_n)$$

$$\equiv \frac{W}{n!} \int \cdots \int p(\omega_1) \cdots p(\omega_n)\, \delta\!\left(\sum_i \omega_i - \omega\right) d\omega_1 \cdots d\omega_n \tag{4}$$

and the corresponding characteristic function is given by

$$F_n(\tau) = \frac{W}{n!} \sum_{k_1,\cdots,k_n} f_{k_1}(\tau) \cdots f_{k_n}(\tau) = \frac{W}{n!} f^n(\tau). \tag{5}$$

Summing over $n \geqslant 1$ we obtain

$$F(\tau) = \sum_{n=1} F_n(\tau) = W\{\exp[f(\tau)] - 1\}, \tag{6}$$

$$P(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega\tau} F(\tau)\, d\tau. \tag{7}$$

Let the moments of the distributions $P(\omega)$ and $p(\omega)$ be denoted accordingly by $\langle \omega^k \rangle$ and $\overline{\omega^k}$. Then one can obtain the following relations

$$\langle \omega \rangle = \bar{\omega}, \tag{8}$$

$$\langle \omega^k \rangle = (-i)^k W \frac{d^k}{d\tau^k} [e^{f(\tau)} - 1]_{\tau=0}, \tag{9}$$

$$\langle (\omega - \bar{\omega})^k \rangle = (-i)^k W \frac{d^k}{d\tau^k} \{e^{-i\bar{\omega}\tau}[e^{f(\tau)} - 1]\}_{\tau=0}, \tag{10}$$

$$\langle (\omega - \bar{\omega})^k \rangle = \overline{\omega^k} + (-1)^k \bar{\omega}^k W, \quad k = 2, 3. \tag{11}$$

So the total probability including all many-particle transitions is determined by first-order "probability" $p(\omega)$. In real physical processes the range of the variable ω is usually limited and the expressions (8)–(11) are correct if $p(\omega)$ is localized in this range.

In the case $Q \gg 1$ it can be shown[2] that the spectral distribution $P(\omega)$ can be described by the Gaussian curve

$$P(\omega) = \frac{1}{\sigma(2\pi)^{1/2}} \exp\left[-\frac{1}{2}\left(\frac{\omega - \xi}{\sigma}\right)\right], \quad \xi = \bar{\omega}, \sigma^2 = \overline{\omega^2}. \tag{12}$$

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[2] Let the strong interaction V be proportional to a large parameter a. Then Q, $p(\omega)$ and $f(\tau)$ are proportional to a^2 and when calculating (7) the function $f(\tau)$ may be expanded in the vicinity of $\tau = 0$.

Note that the conditions of the validity of this result may be considered as those for the central limit theorem.

In Sect. 5 we consider the vibrational relaxation process. Let $p(\omega) = p_t(\omega) + p_v(\omega - \Omega)$ where Ω is a vibrational quantum. The width of p_t and p_v is of the order of τ_c^{-1} (τ_c is the collision time, $\Omega\tau_c \gg 1$). The vibrational energy transfer probability Q_v can be obtained by integrating of the corresponding distribution $P(\omega)$ in the vicinity of $\omega \approx \Omega$. Let us introduce the quantity

$$q_v = \int_{\omega \approx \Omega} p_v(\omega - \Omega)\, d\omega. \tag{13}$$

If $q_v \ll 1$ then it follows from (6) and (7) that $Q_v = q_v$. Thus Q_v may be calculated by means of first-order perturbation theory.

In conclusion let us consider the situation when all the quasi-particles are equivalent. In this case one should use transition amplitudes instead of probabilities. For instance the model of a solid adopted by Einstein consisted of atoms each of which vibrates with the same frequency. Then in the semiclassical approximation the problem of gas–solid interaction is analogous to another well-known quantum-mechanical problem, i.e. excitation of a quantum oscillator by an external force. The solution of this problem has already been obtained [7] in a rather complicated way. The many-particle formalism gives the solution with the aid of simple algebraic transformations (see Appendix).

3. Interaction of Gas Particles with Electrons and Phonons of a Solid

The most reliable experimental data available are those for the translational accommodation of inert atoms and vibrational accommodation of simple molecules (N_2) by metal surfaces. Ionization potentials of the above gas particles are much greater than the metal work function Φ. For these systems the interaction potential is only approximately subdivided into short-range (exchange) and long-range parts [8]. Nevertheless it is common practice to use model potentials, e.g. the Morse potential

$$U(Z) = D[e^{-2\alpha(Z - Z_e)} - 2\,e^{-\alpha(Z - Z_e)}] \tag{14}$$

with empirical parameters (D is the adsorption heat, Z is the normal distance of the gas particle from the surface, Z_e is the equilibrium distance). The exchange interaction (U_{ex} is the first term in (14)) is determined [5] by the value of the metal electron wave function at the position $\mathbf{R}$ of the gas particle and can be introduced phenomenologically. The form of the corresponding electron operator is $V = \kappa\delta(\mathbf{r} - \mathbf{R})$ where $\mathbf{r}$ is electron coordinate and $\kappa > 0$. Suppose that $\alpha Z \ll 1$. Then $\alpha = (2\Phi)^{1/2}$. Far from the surface the electron wave function can be expressed by a double Fourier series [4]

$$\Psi(r) = \sum_q c_q \exp\{ir(\mathbf{p}_\parallel + 2\pi q) - z[2(\Phi - \mathscr{E}) + (2\pi q + \mathbf{p}_\parallel)^2]^{1/2}\} \tag{15}$$

where q is an inverse lattice vector. Then

$$U_{ex} = \iint \kappa^2 |\Psi(\mathbf{R})|^2 F(\mathscr{E}, T_s)\rho(\mathscr{E}, \mathbf{p}_\parallel)\, d\mathscr{E}\, d\mathbf{p}_\parallel, \tag{16}$$

where $F = [\exp(\mathscr{E}/T_s) + 1]^{-1}$ is the Fermi distribution function of electrons in the metal, T_s is the metal temperature, ρ is the distribution density, $\boldsymbol{p}_{\|}$ is the electron momentum parallel to the surface and the origin of the electron energy $\mathscr{E}$ is the Fermi level. Usually $2\Phi < 4\pi^2 q^2_{\min}$ (for example $\Phi = 0.169$ [9] and $q_{\min} = 0.17$ [10] for tungsten) the exponential dependence of U_{ex} on Z is determined by the term (U_{ex}) with $q = 0$. An important consequence follows from this fact: the possibility of one-dimensional description of the gas–surface interaction. Exponential decrease of the integrand is ensured by the factor F in the range $\mathscr{E} > 0$ (if T_s is not very high, see below) and by the factor $|\Psi|^2$ in the range $\mathscr{E} < 0$. One can consider the function ρ to be constant in the integration region (this question is discussed in Ref. [4]), $\rho = \rho_0 \equiv \rho(0, 0)$. The exponent in $|\Psi|^2$ should be expanded in powers of $\mathscr{E}/\Phi$ and $\mathscr{E}_{xy}/\Phi$, $\mathscr{E}_{xy} = p^2_{\|}/2$. Then one obtains[3]

$$U^0_{ex} = 2\pi\kappa^2|c_0|^2\rho_0 \frac{\alpha}{2Z} \frac{\pi T_s}{\text{sh}(2\pi Z T_s/\alpha)} e^{-2\alpha Z}. \tag{17}$$

If $Z \approx Z_e$, and T_s is not very high ($T_s < 3000 \,^\circ K$), then $2\pi Z T_s/\alpha < 1$ and

$$U^0_{ex} = A \, e^{-2\alpha Z}, \tag{18}$$

where A is defined by (17) and (14), $A = D \exp(2\alpha Z_e)$.

From the qualitative point of view U_{ex} should be characterized by its influence upon the electron spectrum in the metal. Let us determine the ratio γ of the interaction between two neighbouring energy states to the mean energy interval between them (this interval is equal to the reciprocal of the energy state density). Similarly to previous calculations one can obtain

$$\gamma = \frac{2Z}{\alpha} U_{ex}(Z). \tag{19}$$

U_{ex} is essentially near the turning point Z_t, $U_t \equiv U_{ex}(Z_t) = 2D + E + 2[D(E + D)]^{1/2}$. Here and hereafter E means the normal motion kinetic energy (for the adsorbed gas particle $E \simeq -D$). Note that $\gamma = 1$ if $\alpha = 0.6$, $Z = 2$ Å, $U_{ex} = 2.16$ eV. If the corresponding value $\gamma_t \ll 1$ then the electron spectrum is not changed as in the case of physical adsorption. When $\gamma_t \sim 1$ there is rearrangement of electron distribution and chemosorption takes place. The obtained results depend only on parameters of the static electron distribution and consequently are valid not only for metals.

When considering the perturbation of the electron motion in solids the following fact should be taken into account. Energy transfer occurs if the corresponding electronic energy level exists and is free. As the energy of translational and vibrational transitions investigated below is considerably lower than the forbidden zone

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[3] The next term in the q-expansion of U_{ex} is $U^q_{ex}/U^0_{ex} \sim \exp\{-[\alpha_q - \alpha - 2\pi^2\alpha q^2/\alpha_q(\alpha + \alpha_q)]Z\}$ $\cos(2\pi q R_{\|})$, $\alpha_q = (\alpha_2 + 4\pi^2 q^2)^{1/2}$. Note that there exist the phenomena which depend on tangential variations of the potential, e.g. rainbow scattering.

width in semiconductors these transitions may occur in metals. The density $p_e(\omega)$ of the transition $\mathscr{E} \to \mathscr{E}' = \mathscr{E} + \omega$ is given by

$$p_e(\omega)\, d\omega = \iiint \left| \int_{-\infty}^{\infty} e^{i\omega t} \langle \mathscr{E}', \boldsymbol{p}'_{\|} | V_{tf} | \mathscr{E}, \boldsymbol{p}_{\|} \rangle\, dt \right|^2 F(\mathscr{E})[1 - F(\mathscr{E}')]$$

$$\cdot \rho_0\, d\boldsymbol{p}_{\|}\, d\mathscr{E}\, \rho_0\, d\boldsymbol{p}'_{\|}\, d\omega. \tag{20}$$

The indices i and f take account of the internal state change of the gas particle. When calculating (20) the value of the factor $Z = Z_t$ is taken out of the integral (as the behaviour of the integrand is determined by the exponential term). As a result one obtains

$$p_e(\omega) = \zeta_e J, \qquad J = \left| \int_{-\infty}^{\infty} A\, e^{i\omega t - 2\alpha Z(t)}\, dt \right|^2, \tag{21}$$

where

$$\zeta_e = C_e \rho(\omega), \qquad C_e = (2Z_t/\alpha)^2, \qquad (\omega) = \frac{\omega \exp{(\omega/2T_s)}}{2 \operatorname{sh}{(\omega/2T_s)}}. \tag{22}$$

Note that the deduction of the expressions for the exchange interaction is based only on the exponential decreasing of the electron wave function far from the surface. There were no assumptions about electron behaviour inside the solid.

Consider now the translational accommodation as a result of the phonon transitions in the solid. If surface vibration is described by the usual Debye model (see for instance Ref. [1]) with the modal frequency distribution $L_D(\omega)\, d\omega = 3\omega^2/\omega_D^3\, d\omega$ ($\omega < \omega_D$, ω_D is the Debye frequency) then the corresponding density $p_{ph}(\omega)$ has a form

$$p_{ph}(\omega) = \zeta_{ph} J, \qquad |\omega| < \omega_D; \qquad p_{ph}(\omega) = 0, \qquad |\omega| > \omega_D, \tag{23}$$

$$\zeta_{ph} = C_{ph} \varphi(\omega), \qquad C_{ph} = 6\alpha^2/M\omega_D^3. \tag{24}$$

where M is the crystal atom mass. It is interesting that the dependences of p_e and p_{ph} on ω (if $|\omega| < \omega_D$) are similar.

4. Translational Energy Accommodation

Using the above results we consider the translational accommodation process. The expression for J in (21), (23) has the form [11]

$$J = \left| \frac{2\pi E}{\alpha v \operatorname{sh}{(\pi\lambda)}} \{\lambda \operatorname{ch}{[(\pi - \tilde{\varphi})\lambda]} + y^{-1} \operatorname{sh}{[(\pi - \tilde{\varphi})\lambda]}\} \right|^2, \tag{25}$$

where v is the velocity of the gas atom with the mass m, $\lambda = |\omega|/\alpha v$, $y = \operatorname{tg}\tilde{\varphi} = (E/D)^{1/2}$. The width of the distribution $p(\omega)$ is seen to be of order αv (the width of the normalized distribution $P(\omega)$ may be much greater provided that Q is large).

First let $D \gg E, T$ (T is the translational temperature). Then

$$J = \left(\frac{2\pi D}{\omega_0} \right)^2 (1 + x)^2 \exp{\left[-2x \left(1 - \frac{E}{3D} + \cdots \right) \right]}, \tag{26}$$

where $x = |\omega|/\omega_0$, $\omega_0 = \alpha(2D/m)^{1/2}$ is the basic frequency of the potential (14).

From a simple numerical estimate of C_s and C_{ph} one can draw the conclusion that translational accommodation is a result of the phonon transitions. The basic parameters of the distribution $P(\omega)$ are

$$Q = \tfrac{9}{8}B\omega_0^2, \qquad \beta \ll 1; \qquad Q = \tfrac{5}{2}BT_s\omega_0, \qquad \beta \gg 1, \tag{27}$$

$$\bar\omega = \tfrac{7}{4}B\omega_0^3, \tag{28}$$

$$\overline{\omega^2} = \tfrac{15}{4}\beta\omega_0^4, \qquad \beta \ll 1; \qquad \overline{\omega^2} = \tfrac{7}{2}BT_s\omega_0^3, \qquad \beta \gg 1, \tag{29}$$

where $\beta = 2T_s/\omega_0$, $B = (C_{ph} + C_e)(2\pi D/\omega_0)^2$.

If $E < \bar\omega$ and $W \ll 1$ then mainly adsorption occurs and the adsorption probability is

$$\alpha_{ads} = 1 - \exp(-\bar\omega/T). \tag{30}$$

In the region of low temperatures classical calculation of the accommodation coefficient $\tilde\alpha$ ($T \to T_s \to 0$, $\tilde\alpha \to \tilde\alpha_0$, $W \to W_0$) has given $\tilde\alpha_0 = 1$, that is the colliding particles are all adsorbed, and the so-called "quantum" theory has given $\tilde\alpha_0 = 0$ [1, 2] (physically meaningless result). Our consideration results in $\tilde\alpha_0 = 1 - W_0$. So it is just the gas particle which causes crystal excitation and loses its kinetic energy that is adsorbed. This expression for $\tilde\alpha_0$ explains the results (see Ref. [2]) of experimental investigations of the inert gas translational accommodation on a tungsten surface. In the series of inset gases He–Xe the values of D and (consequently) Q increase ($Q \ll 1$ for He, $Q \gg 1$ for Ar, $Q \gg 1$ for Xe, $T \to T_s \to 0$).

Let now $E \gg D$. Then the expression for J can be written as (result of Ref. [12])

$$J = \left[\frac{\pi\omega m}{2\alpha^2 \operatorname{sh}(\pi\omega/2\alpha v)}\right]^2. \tag{31}$$

The mean value of the energy loss is

$$\bar\omega = C_{ph}\int_0^{\omega_D} \omega^2 J\, d\omega. \tag{32}$$

If $v \gg \omega_D/\alpha$ one obtains $\bar\omega/E = 4\, m/M$, i.e. is the classical result ($m \ll M$). If $v \ll \omega_D/\alpha$ then the upper limit in (32) can be put equal to infinity as in the case of metal electron excitation

$$\bar\omega = C_{e,ph}\frac{16\pi}{15}\alpha(2E^5/m)^{1/2}. \tag{33}$$

Substituting C_e from (22) into (33) and making corresponding estimations one can find that even in the case of small m and large M (for instance $m = 4$, $M = 184$ for He–W) phonon transitions (as compared with electron transitions) contribute significantly to translational accommodation (up to $E \simeq 0.5\,\text{eV}$ for the He–W system).

The dependence of the accommodation coefficient upon gas particle mass may be seen from Eqs. (28), (29), (33). As $E \to \infty$ the classical result is approached, and $\tilde\alpha \sim m$; at lower E, $\tilde\alpha \sim m^{-1/2}$. But the experimental He–W data indicate that at temperatures $T = 100\text{–}400\,°\text{K}$ $\tilde\alpha(\text{He}^4) > \tilde\alpha(\text{He}^3)$. It should be noted that using the

Debye spectral density $L_D(\omega)$, which is valid at low ω and depends upon only one parameter ω_D, appears to be incorrect in the case when the whole acoustic branch is important. The Debye model does not take account of the dispersion, and the upper spectral limit ω_D is connected with the behaviour of L_D at low ω: $L_D = 3\omega^2/\omega_D^3$. One can propose the following simple model for $L(\omega)$ which takes account of the above remarks:

$$L = \frac{3\omega^2}{\omega_D^3}, \quad \omega < \omega_c; \qquad L = L_c = \text{const}, \quad \omega_c < \omega < \omega_f;$$

$$L = 0, \quad \omega > \omega_f, \tag{34}$$

$$(\omega_c/\omega_D)^3 + L_c(\omega_f - \omega_c) = 1. \tag{35}$$

Expression (35) is the normalization condition. Isotope effect in the He–W system can be explained if ω_c is twice or three times less than ω_D. The problem of quantitative determination of the model parameters requires special consideration. Note that the dynamics of the surface atoms in the crystal are not identical to the dynamics of the bulk atoms [13], and the empirical parameters of the model should be determined from surface experiments.

In conclusion let us note the following problem. The accommodation coefficient was usually calculated using first-order perturbation theory. But the value of the total "probability" Q has been shown (see Refs. [1, 2]) to be often much larger than unity. There were attempts to "improve" first-order theory by means of division of Q by $(1 + Q/4)^2$ [1] or by Q [14]. The agreement of the first-order result for the accommodation coefficient with the classical limit for large kinetic energy was considered as fortuitous and misleading [1]. The results obtained in Sects. 2, 4 explain this problem.

5. Vibrational Relaxation

Consider now the process of vibrational energy transfer from the gas molecules to the solid. Formerly the adsorption of the gas molecule was usually considered to be the first step in the vibrational deactivation process, and "direct" mechanism was supposed to be unlikely [3]. The approach suggested in Ref. [15] for vibrational deactivation of diatomic molecules (the values $T = 600\ °K$ and $\Omega/T \simeq 3$ were used there for estimations) is incorrect because of the relations $\Omega \gg \alpha v$ (the sudden perturbation theory used in Ref. [15] is valid for the opposite inequality) and $\omega_D < \Omega$ (transfer of the vibration quantum to one phonon of the solid is impossible). In Ref. [16] vibrational relaxation is considered as a result of the energy exchange between the molecular vibrations and conduction electrons induced by the interaction of the molecular "vibrational" dipole moment with the "free" electrons of the metal. An analogous model was also considered in Ref. [17]. This model has been criticized in Refs. [18]. Nevertheless the problem of the vibration–electron energy exchange is of great interest and can be solved without any assumptions about the behaviour of the individual metal electron. This circumstance has been emphasized when obtaining the expression for the exchange interaction.

Consider at first direct vibrational deactivation of the gas molecule induced by a collision with the metal surface[4]; interaction potentials developed as a series in x, the deflection (normal to the surface) of molecular atom from the equilibrium position, as it does in the theory of the gas phase vibrational relaxation (see for example Ref. [6]). The Morse potential is used for the description of the translational motion and the following expression can be obtained for the vibrational transition probability:

$$Q_v^{ex} = \frac{8\pi\alpha}{v} \zeta_e(\Omega)|x_{10}D|^2[(5y + 3y^3)(\pi - \tilde{\varphi}) + 5y^2 + \tfrac{4}{3}y^4], \qquad (36)$$

where x_{10} is the matrix element of the transition $1 \rightarrow 0$. Estimation for N_2 at room temperature and $D \simeq 0.1$ eV gives $Q_v^{ex} \sim 10^{-3}–10^{-2}$ which is in agreement with experiment. So the "direct" mechanism of vibrational relaxation due to exchange interaction can be realized.

In the case when the molecule is adsorbed near the surface the probability of the vibrational transition per unit time is

$$\tilde{Q}_v^{ex} = 2\pi\zeta_e(\Omega)|2\alpha x_{10}D|^2. \qquad (37)$$

Estimation of (37) gives $\tilde{Q}_v^{ex} \sim 10^{10}$ sec^{-1}.

If the molecule has an electric multipole moment another mechanism of vibration quantum absorption by the metal is also possible. Let us take into account the "image" forces. Charge image corresponds to the real molecular charge distribution. Vibrational motion of the molecule induces periodic change in the metal charge density. Conduction electrons are characterized by the definite inertia. So charge vibrations in the molecule and in the metal are out of phase. This circumstance results in vibrational energy absorption and Joule heat release. We shall consider transitions between low-lying vibrational levels. Then molecular vibrations are small-amplitude and τ-approximation can be used (τ is the relaxation time of electron density in the metal). After simple transformations the following expression for the probability of molecular vibrational deactivation per unit time can be obtained:

$$\tilde{Q}_v^m = \left| \frac{\partial^2 U_m}{\partial q \, \partial q'} q_{10}^2 \right| \frac{\Omega\tau}{1 + (\Omega\tau)^2}, \qquad (38)$$

where U_m is the energy of interaction between the molecular multipole and its electric image, q and q' are vibrational coordinates of the molecule and its "image". For the allowed molecular dipole transitions

$$\tilde{Q}_v^d = \frac{|d_{10}|^2}{16Z^3} (1 + \cos^2 \theta) \frac{\Omega\tau}{1 + (\Omega\tau)^2}, \qquad (39)$$

where d_{10} is the matrix element of the dipole transition $1 \rightarrow 0$, θ is the angle between the molecular dipole and the normal to the surface. The problem of finding the

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[4]   The results (6)–(12), (36), (37) have already been reported at the conference in the Institute of Chemical Physics, Moscow, 1977.

relaxation time τ in the crystal near the surface has not been solved. Using the value of τ from the theory of metal optic properties [19] results in $\tilde{Q}_{\text{v}}^{\text{d}} \sim 10^{10} \sec^{-1}$.

It should be noted that weak dependence of vibrational transition probability on all kinds of parameters (e.g. D, Φ, v, m) agrees with experimental data and is connected with the resonance character of energy transfer when the translational energy of relative motion is slightly changed. Remember that the well-known Landau–Teller model for vibrational-translational transfer in the gas gives $Q_{\text{v}} \sim \exp\left(-\pi\Omega/\alpha v\right)$. The problem of gas–surface vibrational relaxation will be more carefully considered in a special paper.

6. Concluding Remarks

The mechanism of gas–surface energy relaxation has been investigated and a general expression for the energy transfer probability has been obtained using semiclassical approximation. All many-phonon (and many-electron) transitions are taken into account by formula (7). It should be emphasized that "many-phonon" expressions are determined by the function $p(\omega)$, the "one-phonon" transition probability density which can be calculated from first-order perturbation theory.

Exchange interaction is analysed on the basis of the general properties of the electron energy distribution and the exponential behavior of the electron density far from the surface, and three regions for interaction energy ($\gamma \ll 1, \gamma \sim 1, \gamma \gg 1$) are introduced. These regions correspond to the empirical energy classification in the investigations of the interaction of rarefied gases with solid surfaces [10] and to the division of the adsorption processes into physical and chemical ones (depending on the bond energy of the adsorbed particles) [20]. When interaction is very strong, $\gamma \gg 1$, the rearrangement process of metal electron structure is apparently that a number of metal electrons is localized at the atoms near the collision point (where the gas-surface interaction is the strongest). This circumstance justifies application of the pairwise potential method in the numerical investigation of the gas particle trajectory when $E \gtrsim 100$ eV. At low energy this method is incorrect due to the delocalization of the metal valence electrons.

In Sects. 4 and 5 are established the mechanism of inelastic collisions and the role of electrons and phonons in the energy accommodation process. Special consideration is required for the more concrete problems such as the mechanism and kinetics of nonequilibrium adsorption, and the results of the present work can be used for this purpose. At the present time there is poor information about the parameters (for instance D) of the gas–solid interaction and only order-of-magnitude estimations are possible.

It is to be emphasized that the well-known Debye model of the solid cannot give adequate description of phenomena which are described by different ranges of the phonon spectrum. For example the value of ω_{D} determined by heat capacity measuring at low temperature (low-frequency spectral range) is larger than ω_{D} obtained from electron diffraction experiments (see Ref. [21]) where the upper

range of the spectrum is the most important. A new simple model for the acoustic branch of the phonon spectrum is considered in Sect. 4.

Appendix

Quantum harmonic oscillator in the field of the external force

The problem of finding the transition probabilities in the system with the Hamiltonian

$$H = -\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} - \omega^2 x^2\right) - f(t)x \tag{A.1}$$

(here the oscillator mass is taken to be equal to unity and the force $f(t)$ vanishes quickly as time t approaches $\pm\infty$) is equivalent to the following one:

$$H = -\frac{1}{2}\sum_{k=1}^{N}\left(\frac{\partial^2}{\partial x_k^2} - \omega^2 x_k^2\right) - f((t)x_1. \tag{A.2}$$

After orthonormal transformation to the new coordinates

$$q_i = \sum_k e_{ik}x_k, \qquad x_k = \sum_i e_{ik}q_i \tag{A.3}$$

(note that $e_{ik} \sim N^{-1/2}$ [22]) we obtain

$$H = -\frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial^2}{\partial q_i^2} - \omega^2 q_i^2 + f(t)e_{i1}q_i\right). \tag{A.4}$$

Wave functions of the free oscillator

$$\Psi^n(x) = (\omega/\pi)^{1/4}(2^n n!)^{-1/2}\exp\left(-\omega x^2/2\right)H_n(\omega^{1/2}x) \tag{A.5}$$

are transformed by means of the addition theorem for the Hermite polynomial

$$\frac{1}{n!}H_n(\omega^{1/2}x_k) = \sum_{m_1+\cdots+m_N=n}\prod_{i=1}^{N}\frac{(e_{ik})^{m_i}}{m_i!}H_{m_i}(\omega^{1/2}q_i). \tag{A.6}$$

When calculating the transition amplitude S_{nm} (here n and m are finite numbers) it should be taken into account that the total (many-phonon) excitation of the whole vibrational system as $N \to \infty$ is determined by one-phonon processes in a single mode. Consider first transition without excitation. In order to determine S_{00} we expand the wave function of the mode k in functions of ground and first excited states

$$\psi_k = a_0^k(t)\psi_k^0 + a_1^k(t)\psi_k^1, \; a_i^k(-\infty) = \delta_{i0}. \tag{A.7}$$

Simple transformations give, with an accuracy up to the order N^{-1},

$$\operatorname{Re} a_0^k(\infty) = 1 - p_k/2, \, p_k = |e_{k1}q_k^{10}\tilde{f}|^2, \tag{A.8}$$

$$\tilde{f} = \int_{-\infty}^{\infty} f(t)\, e^{i\omega t}\, dt, \tag{A.9}$$

$$S_{00} = \langle\Psi^0(-\infty)\mid\Psi(\infty)\rangle = \prod_{k=1}^{N}(1 - p_k/2 + iv_k) = \exp\left(-p/2 + iv\right), \tag{A.10}$$

where $v_k = \operatorname{Im} a_0^k(\infty)$, $v = \sum v_k$ (v is not needed for calculation of the transition probability which is equal to $|S_{00}|^2$) and

$$p = \sum_{k=1}^{N} p_k = |x^{10}\tilde{f}|^2. \tag{A.11}$$

Here the equality $|q_i^{10}|^2 = |x_k^{10}|^2$ is also used. Note that the value of p is not changed (with accuracy to N^{-1}) if a finite number of members is dropped from the sum (A.10). For a_1^k in (A.7) we have (with an accuracy up to the order of $N^{-1/2}$)

$$a_1^k(\infty) = -i\, e_{k1} q_k^{10}\tilde{f}. \tag{A.12}$$

If the considered mode has an initial excitation that is $a_i^k(-\infty) = \delta_{i1}$ the expressions analogous to (A.3) and (A.12) can be obtained.

Wave function of the initial state consists of the sum of products $\prod_{l \neq k_i}\psi_1^0 \prod_{i=1}^{n}\psi_i^1$ From Eq. (A.4) one can see that transitions in different modes are taking place independently. So $\Psi'^{(n)}(\infty)$ results from Ψ'^n by substitution ψ_1^0 in Ψ'^n for $a_0^1(\infty)\psi_1^0 + a_1^1(\infty)\psi_1^1$ (this circumstance has been used in calculating S_{00}) and by analogous replacement of ψ_k^1. Simple algebraic transformations give the following expression:

$$S_{nm} = \langle \Psi'^m \mid \Psi'^{(n)}(\infty)\rangle = S_{00}(n!\,m!)^{1/2} \sum_{k=0}^{\min(n,m)} \frac{A^{n-k}(-A^*)^{m-k}}{(m-k)!\,(n-k)!\,k!}, \tag{A.13}$$

where $A = -ix^{10}\tilde{f}$. Transition probability can be obtained from Eq. (A.13),

$$P_{nm} = |S_{nm}|^2 = n!\,m!\,e^{-p}p^{n+m}\left[\sum_{k=0}^{\min(n,m)} \frac{(-1)^k p^{-k}}{(m-k)!\,(n-k)!\,k!}\right]^2, \tag{A.14}$$

that is the result of Ref. [7]. However the present approach is much simpler. It is also clear why P_{nm} depends only on p that is formally first-order calculated "probability" of the transition $0 \to 1$.

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