NONEQUILIBRIUM GAS–SURFACE–SOLID IN PROBLEMS OF RELAXATION GASDYNAMICS

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The study of nonequilibrium flows is one of the main problems of physical gasdynamics. As shown by experiment [1-3], most of them can be solved by the theory of multiple temperature equilibrium, when the investigated gas mixture is fully determined by a comparatively small number of macroparameters. The justification of the corresponding models of relaxation hydrodynamics by the apparatus of the kinetic theory of gases was given in [4-5], while the boundary conditions to these models in the whole range of variation of accomodation coefficients were obtained in [6]. In recent years, with developing studies on effects of catalytic properties of surfaces on thermal flows, the improvement of radio-wave propagation through plasma formations, obtaining flows in strongly nonequilibrium populations of quantum levels, the use of multiphase flows for isotope separation, etc. it became necessary to study relaxation effects not only in the gas, but also on the boundary with the surface, as well as inside the solid phase, such as, for example, in aerosol particles. The kinetic theory for this class of problems has not yet been developed, even within the multiple temperature approximation. In the present work this problem has been solved phenomenologically, constructing a hydrodynamic model with the use of balance conditions of energy flows within and on the boundary of interacting phases. We consider specifically the set ofprocesses occurring in a multiple-phase multiple-temperature flow, in which solid particles are found, formed of molecular crystals. At the initial moment of time t = 0 the translational–rotational and vibrational temperatures T_G and T_{iG} of the gas equal the particle temperature T_L ($T_G = T_{iG} = T_L$), inside which the intramolecular vibrational degrees of freedom are excited, $T_{iL} \gg T_L$. This can be done by constructing a source, for example, by an electron beam [7]. For t > 0 the gas excitation starts by heterogeneous mechanisms of energy exchange on the particle surfaces. The energies of vibrational quanta in the gas and of particles are assumed to be near these quantities, for example, in a flow containing the gas and aerosol particles of nitrogen. The latter, thus, emerge in the role of energy carriers [8, 9]. By the estimates obtained in [8], the system with an energy carrier being a complex of a large number of molecules in the solid state can possess a high specific energy capacity $\sim 10^3$ J/g. Therefore, the dynamic problem on the redistribution of intramolecular vibrational energy in the gas–surface–solid system is of much interest. The solution of this problem is the main goal of the present paper. It must be kept in mind that accomodation coefficients of various energy shapes appear in the system of equations describing the relaxation processes. To obtain the structural shape of these coefficients it is necessary to solve the quantum-mechanical problem of interaction of molecules with the surface, particularly the problem of the resonance exchange probability of vibrational energies. Of principal value is obtaining estimates of characteristic time scales of redistribution of intramolecular vibrational energy inside particles of various sizes. The solution of these problems is also included in this work.

Consider the flow of a dispersed medium with closely located intramolecular quanta of magnitude $\hbar\Omega_0$ in the gas and solid aerosol phase, assuming that the particles are spherical, of the same size, and moving together with the gas (Fig. 1). As some cross section 1 the particles are irradiated by an electron beam, and intramolecular oscillations of frequency Ω_0 are excited in them with temperature $T_{iL} \gg T_L$. In this case, as follows from the results of [7], the intramode quanta exchanges in the condensed phase occur very quickly, so that the introduction of a multiple temperature distribution is fully justified. As to translational–vibrational relaxation, in molecular crystals of the N_2 type, where intramolecular quanta are significantly larger than the Debye quanta, it occurs extremely slowly, significantly more slowly than in the gas phase, which is related to the low probability of multiphonon interactions [7]. In what follows we investigate precisely this case. We consider

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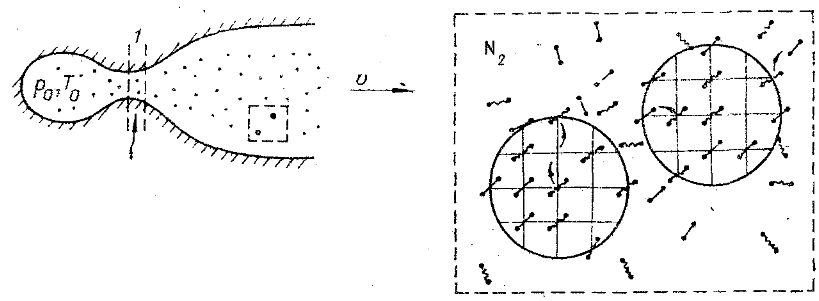

Fig. 1

the basic mechanisms affecting the redistribution of vibrational energy in the investigated dispersed medium. Firstly, the collisional deactivation due to the shock mechanism is quite effective at the particle surfaces. If the particles are not excited, the inverse process has very small likelihood due to the low surface temperature $T_W = T_L$ [8] $(\hbar\Omega_0 \gg kT_L)$. If also $T_{iL} \gg T_{iG}$, following some characteristic time τ_i^s one must expect an effective quantum transfer in the gas phase during adsorption of molecules on the surface of aerosol particles [8, 9]. It is, thus, important to select the flow regime in such a manner that this process become dominant. If the molecule acquired a quantum of vibrational energy, then, desorbing, it can transport it into the depth of the gas phase during collisions. To establish the uniform distribution, the diffusion mixing time τ_D at distances equal in order of magnitude to the interparticle distance must be shorter than the time τ_{iG} of vibrational deactivation of molecules in the gas phase, and the condition $\tau_i^s \ll \tau_{iG}$ must also be satisfied. It must be taken into account that even though inside the particle the probability Q_L of vibrational deactivation is low [7], on its surface it can become substantial, with probability $Q_L^s \approx Q_L m^{1/3}$, where m is the number of molecules in an aerosol particle [8]. Hence arises a restriction on particle sizes, which must be chosen in such a manner that the time τ_i^s be shorter than the surface relaxation time of an isolated particle τ_{iL}^s. The fastest process, however, must be the quantum transfer process from inside the particle to the surface τ_i, which after a time $\sim\tau_i^s$ is combined under the action of the heterogeneous mechanism of gaspumping. Therefore the following condition must be satisfied $\tau_i \ll \tau_i^s$, τ_{iL}^s, as in the opposite case the margin of vibrational energy will be used ineffectively and will be gradually deactivated inside the solid phase.

Thus, if the characteristic gasdynamic time of the problem is $t \sim \tau_{iL}$, the basic asymptotic inequality which must be satisfied is

$$\tau_i \lesssim \tau_i^s \leqslant \tau_D \ll \tau_{iL}^s \lesssim \tau_{iG}^s \lesssim \tau_{iL} \sim t. \qquad (1.1)$$

Inequality (1.1) guarantees, in principle, conditions under which the vibrational energy can be transferred to the gas with nonequilibrium of the populated levels of the solid phase. The extent of gas pumping, however, characterized by the ratio $T_{iG}^{max}/T_{iL}^{(0)}$, will depend on the amount of gas mass "smeared" by the energy of internal vibrations, thus reaching the surface of the aerosol particles.

To estimate the time scale τ_i of transport of intramolecular vibrational quanta into the crystal one can use the diffusion approximation [10]. Formally this process can be treated as a thermal conductivity $\lambda_{iL} \sim c_{iL}\gamma_L \langle\hat{v}\rangle d$ with a structure similar to the coefficient $\lambda_{iG} \sim c_{iG}\gamma_G \langle v\rangle l$ of the gas phase for vibrational degrees of freedom [11]. In the expression for λ_{iL} the free mean path is the lattice constant d, and the heat capacity of intramolecular vibrations c_{iL} is similar to the heat capacity c_{iG} in the gas phase. More delicate is the choice of the velocity $\langle\hat{v}\rangle$. In the ordinaty coefficient of thermal conductivity, characterizing heating of a solid body $\lambda_L \sim c_L\gamma_L \langle v\rangle l_f$, $\langle v\rangle$ is the speed of sound, l_f is the mean free path of phonons, and the chaotization mechanism is guaranteed by transfer processes in the first Brillouin zone [12]. However, unlike intraintermode exchanges by quanta [7], the transfer of internal energy from molecule to molecule is not realized by phonons, therefore the quantity $\langle\hat{v}\rangle$ must be determined by different considerations.

Consider initially the following model. Let a molecule be displaced in the lattice to a free site (Schottky defect) or to an intersite position (Frenkel defect), transporting with it internal energy quanta. For such a diffusion displacement the molecule must overcome the potential barrier Q formed by its neighbors. In molecular crystals this potential is insignificant (0.1–0.01 eV), since it is formed by Van der Waals interaction forces. The diffusion coefficient is $\nu \sim \langle \hat{v} \rangle d$, where, according to Frenkel [12], $\langle \hat{v} \rangle \sim d/\tau$, and $\tau = \tau_q \exp(Q/kT_L)$, and τ_q^{-1} is the eigenfrequency of molecular vibration (usually $\tau_q \sim 10^{13}$ Hz). Therefore $\nu \sim \tau_q^{-1} d^2 \exp(-Q/kT_L)$, with the time $\tau_i \sim R^2/\nu$, where R is the particle radius. For the quadrupole interaction of two nitrogen molecules, according to [13], $Q/k \sim 20°$. Taking into account the collective potential of nearest neighbors of the cubic system of the N_2 crystal, for a particle of radius $R \sim 0.1$ μm we obtain $\tau_i \sim 10^{-6}$ sec for $T_L \approx 50$°K.

Consider now a different model, when the molecule is at rest, but the quantum of internal energy $\hbar\Omega_0$ diffuses around the crystal. This process can be represented as an interaction of anharmonic oscillators, one of them excited, the other not. As is well known from nonlinear mechanics, the energy is then transferred from one oscillator to the other. This fact was used in [14] to explain the effect of filling highly excited vibrational states in molecular crystals. The transition time to the n-th excited level is $\tau_n = (2\mu\omega_e n^2/\beta n! x_e^{n-1})$ [14], where β is the coupling parameter of the two oscillators, $x_e = \hbar\omega_e/4D_e$ is the anharmonicity constant, μ is the reduced mass of the oscillators, D_e is the dissociation energy, and $\hbar\omega_e = (2D_e\beta^2\hbar^2/\mu)^{1/2}$. For nitrogen $x_e \approx 6 \cdot 10^3$, and in the case n = 1 we obtain for the diffusion coefficient in N_2 $\nu \sim d^2/\tau_1 \sim 2 \cdot 10^{-4}$ cm²/sec (for CO $\nu \sim 3 \cdot 10^{-5}$ cm²/sec [10]).

Hence we have the following estimate for $\tau_1 \sim R^2/\nu \sim 6 \cdot 10^{-7}$ with R = 0.1 μm, i.e., a value close to that obtained in the first model. It follows from these estimates that an increase in the particle radius leads to a significant increase in τ_i and a breakdown of inequality (1.1). Thus, the diffusion process, which under normal conditions occurs most slowly in the solid phase, can sometimes be accelerated. This is explained by the weakness of the Van der Waals interaction, as well as by the fact that the aggregate state of molecular crystals is near the melting limit (evaporation) even at low temperatures $T_L \sim 10$–100°K. The result obtained for τ_i is the starting point for the choice of the remaining scales in inequality (1.1), and also serves as a criterion of determining the particle size R. It is seen, for example, that the use of an aerosol energy carrier in systems with mixing [15, 16] will become difficult, since to obtain larger activation volumes of the medium the penetration depth of particles must be significant. According to [17] the last condition of satisfied only by comparatively large particles with R > 1 μm.

We turn now to determination of the characteristic time of "heterogeneous pumping" τ_i^s, related to accomodation processes of vibrational energy at the surface. We note that the study of heterogeneous-catalytic reactions during adsorption at a surface is one of the major directions of contemporary chemical kinetics [18]. The methods used to solve quantum-mechanical problems of V–T relaxation [18] are also suitable in studying exchange resonance at the surface (V–V exchange).*

Consider this problem, assuming that the interaction of a molecule with the surface is determined by the Morse potential (Fig. 2)

$$U = D\left\{\exp\left[-\frac{2\left(r_2 - r_1 - \frac{z_1}{2} - \frac{z_2}{2}\right)}{\lambda}\right] - 2\exp\left[-\frac{\left(r_2 - r_1 - \frac{z_1}{2} - \frac{z_2}{2}\right)}{\lambda}\right]\right\}, \quad (1.2)$$

whose characteristics are found by taking into account the effect of all surface atoms or

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*The splitting in the exciton band in molecular crystals can be neglected within the first approximation, since $\Delta\Omega \sim 5$–20 cm⁻¹ [7].

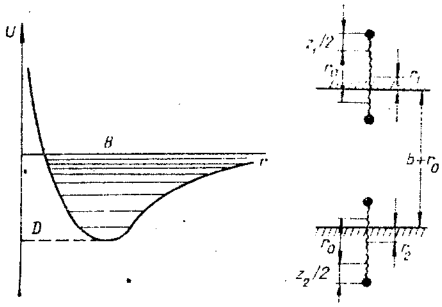

Fig. 2

molecules [19]. In expression (1.2) r_1, r_2 are the deviations of the centers of mass of the gas and crystal molecules from the neutral positions, z_1 and z_2 are the vibrational coordinates of these molecules, D is the depth of the potential well, and λ is its width. To solve the problem one can use perturbation theory, since usually the following conditions hold: r_2/λ, z_1/λ, $z_2/\lambda \ll 1$. Expanding the function (1.2) in these parameters, we obtain $U = U(r_1) + V(r_1, r_2, z_1, z_2)$, where

$$U(r_1) = D\left[\exp\left(-\frac{2r_1}{\lambda}\right) - 2\exp\left(-\frac{r_1}{\lambda}\right)\right], \tag{1.3}$$

$$V(r_1, r_2, z_1, z_2) = \frac{2D}{\lambda}\left[\exp\left(-\frac{2r_1}{\lambda}\right) - \exp\left(-\frac{r_1}{\lambda}\right)\right]\left(r_2 - \frac{z_1}{2} - \frac{z_2}{2}\right) +$$

$$+ \frac{D}{\lambda^2}\left[2\exp\left(-\frac{2r_1}{\lambda}\right) - \exp\left(-\frac{r_1}{\lambda}\right)\right]\left(r_2^2 + \frac{z_1^2}{4} + \frac{z_2^2}{4} - r_1 z_1 - r_2 z_2 + \frac{z_1 z_2}{2}\right) + \ldots$$

The quantity $V(r_1, r_2, z_1, z_2)$ is the perturbation potential, determining the probabilities of the various transitions. In studying V—T relaxation one usually uses the condition $D \gg \hbar\Omega_0$ [18], under which the number of levels in the potential well is quite large ($n \gg 1$). The calculation of the transition probabilities is facilitated in this case, since the motion of an adsorbed particle can be treated quasiclassically. In the case of molecular crystals of type N_2, CO_2, etc., the condition $D \lessgtr \hbar\Omega_0$ holds, and in this case the approximation $n \gg 1$ also holds (thus, for N_2 in the case of the Morse potential the number of levels is $n \approx (\lambda\sqrt{2mD}/\hbar) \sim 20$). The terms in the perturbation potential which are dependent on r_1 and r_2 determine the transition probabilities τ_0^{-1} for the transitions during which the translational energy of the gas molecules changes, while the crystal emits or absorbs phonons. This problem was solved within first-order perturbation theory in the displacement coordinate of the surface atom around the equilibrium position (see Fig. 2), when the perturbation is proportional to a linear combination of the normal lattice coordinates [20]. Therefore, only a single phonon can be excited (or absorbed) in a single perturbation act.

In principle, the multiphonon interaction can also be included within first-order perturbation theory [21], using the condition of independence of a sequence of several phonons following the staying time of a molecule in the adsorption well. In the problem under consideration, exchange of internal vibrational energies between gas and crystal molecules occurs through V—V processes, and these transitions in expressions (1.3) correspond to the terms depending on z_1, z_2, r_1. The excitation of vibrational energy in the V—T channel is negligibly small [21]. Therefore, the transitions between the levels of the adsorption well and between intramolecular levels can be considered as independent of each other. If the adsorbed molecule has j vibrational quanta, and the crystal molecule has m, then by perturbation theory the probability of single-quantum V—V exchange per unit time equals

$$\left(\frac{1}{\tau}\right)_{m,m-1}^{j,j+1} = \frac{2\pi}{\hbar}\left|\left\langle\frac{D}{2\lambda^2}\left[2\exp\left(-\frac{2r_1}{\lambda}\right) - \exp\left(-\frac{r_1}{\lambda}\right)\right]\right\rangle\right|^2 z_{1j,j+1}^2 z_{2m,m-1}^2 \rho(E_e),$$

where $\rho(E_e) \approx (\hbar\omega_D)^{-1}$, $z_{1j,j+1}$, and $z_{2m,m-1}$ are harmonic oscillator matrix elements. Calculating $\left\langle\frac{D}{2\lambda^2}\left[2\exp\left(-\frac{2r_1}{\lambda}\right) - \exp\left(-\frac{r_1}{\lambda}\right)\right]\right\rangle$ by the wave functions of the discrete spectrum of the Morse potential, we obtain

$$\left(\frac{1}{\tau}\right)_{m,m-1}^{j,j+1} = (j+1)\, m\tau_0^{-1}, \quad \left(\frac{1}{\tau}\right)_{m,m+1}^{j,j-1} = j\,(m+1)\,\tau_0^{-1},$$

where $\tau_0^{-1} = \pi\frac{\omega_0^2}{\Omega_0^2}\frac{v^2}{\omega_D}$; Ω_0 is the frequency of intramolecular vibrations of gas and solid phase molecules, $\omega_0 = \sqrt{\frac{2D}{m}}\frac{1}{\lambda}$ is the oscillation frequency of an adsorbed particle near the bottom of the well, and $v = \sqrt{\frac{2E}{m}}\frac{1}{\lambda}$ is the oscillation frequency at the level with energy E.

In what follows it is required to average over the energy E the expression for the transition probability, having the form $\bar{\tau}_0^{-1} = \frac{\pi}{2}\frac{\omega_0^4}{\Omega_0^2}\frac{1}{\omega_D}$.

To solve problems of resonance exchange between the gas and the crystal, it is necessary to write down the kinetic equation for the population of levels in the adsorption well with account of V—V processes and the boundary conditions required to solve these equations. Similarly to the case of V—T relaxation [18], we write these equations in the Fokker—Planck

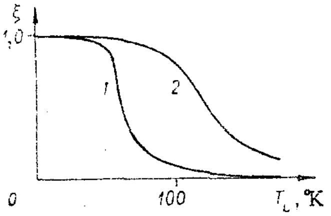

Fig. 3

approximation, assuming that during capture molecules are adsorbed at the top level of the well with a probability equal to unity [18, 21]. We then obtain

$$\Delta E^2\frac{d}{dE}\frac{1}{\tau_\Sigma}\frac{d}{dE}A(E)+\frac{\Delta E^2}{kT_L}\frac{d}{dE}\frac{A(E)}{\tau_\Sigma}+\frac{p\tau\ \exp\left(-\frac{\Delta\varepsilon}{kT_L}\right)\Delta\varepsilon\exp\left(\frac{D-E}{kT_L}\right)}{\tau_0\left[1-\exp\left(-\frac{\Delta\varepsilon}{kT_{iL}}\right)\right]}-\frac{A(E)}{\tau_0}=0. \qquad (1.4)$$

The boundary conditions at the bottom of the adsorption well E = 0 and its peak E = D are

$$\text{for}\quad E=0\quad \frac{\Delta E}{\tau'_\Sigma}\frac{dA(0)}{dE}+\frac{\Delta E}{kT_L}\frac{A(0)}{\tau'_\Sigma}+\frac{p\tau_D\Delta\varepsilon\exp\left(-\frac{D}{kT_L}\right)}{\tau_0\left[\exp\left(\frac{\Delta\varepsilon}{kT_{iL}}\right)-1\right]}-\frac{A(0)}{\tau_0}=0, \qquad (1.5)$$

$$\text{for}\quad E=D\quad \frac{p\Delta\varepsilon}{\exp\left(\frac{\Delta\varepsilon}{kT_{iG}}\right)-1}-\frac{A(D)}{\tau_D}-\frac{\Delta E\,dA(D)}{\tau'_\Sigma DE}-\frac{\Delta E A(D)}{kT_L\tau_\Sigma}+\frac{p\tau_D\exp\left(-\frac{\Delta\varepsilon}{kT_{iL}}\right)\Delta\varepsilon}{\tau_0\left[1-\exp\left(-\frac{\Delta\varepsilon}{kT_{iL}}\right)\right]}-\frac{A(D)}{\tau_0}=0.$$

Equations (1.4), (1.5) were obtained by summation over all vibrational levels i of the corresponding equations for the populations n_i, multiplying by the quantity $i\Delta\varepsilon$, where $\Delta\varepsilon = \hbar\Omega_0$ and $A(E) = \sum_{i=1}^{\infty} in_i(E)\Delta\varepsilon$.

We note that in calculating the transition probabilities the energy reading was taken in reverse order, i.e., the top of the well corresponded to the value E = 0, and the bottom to E = –D. In expressions (1.4), (1.5) $\tau_D = 2\pi\hbar/kT_L$ is the desorption probability per unit time, $p=\frac{n\langle v\rangle}{4}\left[1+\frac{n\langle v\rangle\tau'_q\exp\left(\frac{D}{kT_L}\right)}{4\sigma_0}\right]^{-1}$ is the flow of molecules adsorbed at the upper level in the case of the Langmuir model, $\tau'_q \sim 10^{-13}$ is the period of a single oscillation of a gas molecule at the surface, $\sigma_0 \sim 10^{15}$ cm^{-2} is the number of molecules covering a monomolecular layer of area 1 cm^2 of aerosol surface, and

$$\Delta E=\hbar v(E);\ \tau_\Sigma^{-1}=\sum_{l=1}^{\infty}\frac{l^2}{\tau(i,l)}.$$

As in the case of studying V–T relaxation [18], an analytic solution can be obtained if it is assumed that ΔE, τ_Σ^{-1}, τ_0^{-1} are independent of E, and the average values of these quantities appear in Eqs. (1.4), (1.5). This solution is

$$A(E)=p\tau_De_{iL}-\frac{p\tau_D(e_{iG}-e_{iL})}{\varepsilon+\exp\left(-\frac{D}{kT_L}\right)+\frac{\Delta E}{kT_L}\varepsilon\frac{\tau_D}{\tau'_\Sigma}}\left[\varepsilon\left(1+\frac{\Delta E}{kT_L}\right)\left(1+\varepsilon\frac{\Delta E}{kT_L}\right)+\left(1-\varepsilon\frac{\Delta E}{kT_L}\right)\exp\left(-\frac{E}{kT_L}\right)\right],$$

where $\varepsilon=\frac{\tau'_\Sigma}{\tau_0}\left(\frac{kT_L}{\hbar\omega_0}\right)^2=\frac{kT_L\omega_D}{20n\hbar\Omega_0^2};\ (\tau'_\Sigma)^{-1}=\sum_n n\tau^{-1}(l,n)\approx 10\pi n\left(\frac{\omega_0}{\omega_D}\right)^2\frac{kT_L}{\hbar};$

$$e_{iL}=\frac{\Delta\varepsilon}{\exp\left(\frac{\Delta\varepsilon}{kT_{iL}}\right)-1};\quad e_{iG}=\frac{\Delta\varepsilon}{\exp\left(\frac{\Delta\varepsilon}{kT_{iG}}\right)-1}.$$

The energy flow from a particle to the gas is

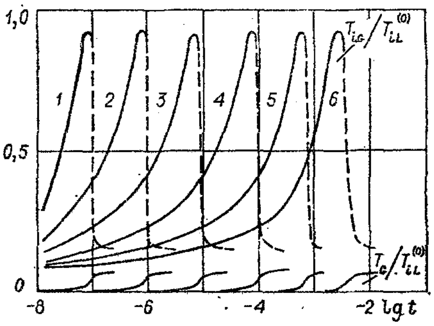

Fig. 4

$$Q=\frac{A(D)}{\tau_D}-pe_{iG}=\frac{p\,\frac{\Delta E}{kT_L}\,\varepsilon\,\frac{\tau_D}{\tau_\Sigma'}\left[1-\exp\left(-\frac{D}{kT_L}\right)\right]}{\varepsilon+\exp\left(-\frac{D}{kT_L}\right)+\frac{\Delta E}{kT_L}\,\varepsilon\,\frac{\tau_D}{\tau_\Sigma'}}(e_{iL}-e_{iG}).$$

The accomodation coefficient of vibrational energy is then

$$\xi=\frac{\pi^2\left(\frac{\omega_0}{\omega_D}\right)^2\left(\frac{\omega_0}{\Omega_0}\right)^2}{\frac{kT_L}{20n\hbar}\,\frac{\omega_D}{\Omega_0^2}+\exp\left(-\frac{D}{kT_L}\right)+\pi^2\left(\frac{\omega_0}{\omega_D}\right)^2\left(\frac{\omega_0}{\Omega_0}\right)^2}. \tag{1.6}$$

The quantity ξ can also be considered as a probability of resonance exchange of vibrational energy at the surface during adsorption.

The dependence $\xi(T_L)$ is shown in Fig. 4 for the case $T_D = \hbar\omega_D/k = 50°$ and two values of the potential depth $d/k = 400$ and $800°$ (curves 1, 2, respectively). It is seen that for increasing T_L the coefficient ξ changes from unity to small values in a quite narrow temperature interval. This is explained by the decreasing role of the adsorption mechanism of energy transfer due to the increase in the term $\exp(-D/kT_L)$ in expression (1.6). The main mechanism of resonance exchange in this case can be the shock mechanism, if the corresponding value of T_L is admissible from the point of view of existence of a solid phase. This mechanism was not taken into account in obtaining expression (1.6), since if adsorption exists it is negligibly small. It follows from the data shown in Fig. 3 that for specific materials (molecular crystals) an exact determination of quantities as D, ω_D, ω_0, etc. is important, which is not always possible at the present time. The fact that ξ depends only on the temperature T_L is related to the assumption of an infinite number of levels of the intramolecular oscillator. A similar calculation, performed in the case of a two-level intramolecular oscillator, shows that ξ also depends on the internal temperature T_{iL}.

We provide without derivation the function $\xi = \zeta_1 + \zeta_2$ for n = 1, modeling a well with a small number of levels. In this case

$$\zeta_1=\frac{\pi^{3/2}e}{12}\,\frac{\hbar}{kT_L}\,\frac{\omega_D^3}{\Omega_0^2}F_1(T_L),\quad F_1(T_L)=\left\{\int\limits_{\left(\frac{D}{\hbar\omega_0}-\frac{1}{2}\right)}^{\infty}\frac{\exp(-2y)\,y\,dy}{\exp\left(\frac{\hbar\omega_0}{kT_L}y\right)-1}\right\}^{-1},$$

$$\zeta_2=\left[1-\frac{24\pi^{1/2}}{e}\,\frac{\hbar}{kT_L}\,\frac{\omega_0^4}{\omega_D^3}F_1(T_L)^{-1}\right]\frac{\omega_0^2}{\Omega_0^2}F_2(T_L),$$

$$F_2(T_L)=\frac{1}{kT_L}\int\limits_0^{\infty}\left[\frac{2E^{3/2}}{D^{1/2}(D-E)}\left(1-\frac{D}{E}\right)+\frac{\pi}{2}+\operatorname{arctg}\sqrt{\frac{D}{E}}\right]^2\exp\left(-\frac{E}{kT_L}\right)dE.$$

Here the coefficient ζ_1 is related to V–V processes in the adsorption well, and the coefficient ζ_2 to V–V exchange of gas molecules, occurring in the continuous spectrum. The last mechanism was not taken into account in the problem of a many-level adsorption well. Estimates show that for a deep well the fraction of the energy carried by nonadsorbed molecules is negligibly small. It follows from the expressions for ζ_1, ζ_2 that $\xi \ll 1$, i.e., the mechanism of resonance exchange is less effective in a well with a small number of levels.

We turn now to constructing a hydrodynamic model of a nonequilibrium gas–surface–solid

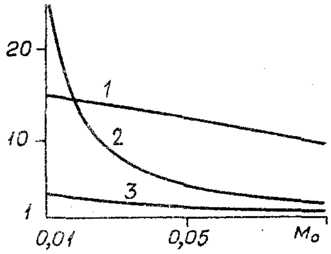

Fig. 5

system, in which the corresponding variables are denoted by the subscripts G, s, L. Equations for the changes of various energy shapes and boundary conditions characterizing the continuity of flows on the phase separation boundary can be obtained by using balance conditions of the flow energies [22].

As a result we obtain the following system of equations in dimensionless variables:

$$Ku\frac{d}{dt}(e_L+e_{iL}) = -\frac{K\xi\rho_L^{(G)}}{(\xi+4K+\xi_1)}\left[e_{iL}^{(s)}-\left(1+\frac{\xi_1}{\xi}\right)e_{iG}\right]-\frac{3\alpha K\rho_L^{(G)}}{(4K+3\alpha)}[e_G(T_L)-e_G(T_G)], \tag{1.7}$$

$$Ku\frac{de_{iG}}{dt} = \frac{K\xi}{\xi+4K+\xi_1}\left[e_{iL}^{(s)}-\left(1+\frac{\xi_1}{\xi}\right)e_{iG}\right]+\frac{K\xi Q_{iG}^*}{\xi+4K+\xi_1}[e_{iG}(T_G)-e_{iG}(T_{iG})],$$

$$Ku\frac{de_G}{dt} = \frac{3\alpha K}{(\alpha+4K)}[e_G(T_L)-e_G(T_G)]-\frac{K\xi Q_{iG}^*}{\xi+4K+\xi_1}[e_{iG}(T_G)-e_{iG}(T_{iG})],$$

$$\rho_L^{(G)}(e_{iG}+e_G)+e_{iL}+e_L=1,$$

where e_G, e_{iG} are the translational—rotational and vibrational energies, referred to the energy of a unit mass of gas and particles e_0 at moment of time t = 0, e_L, e_{iL}, respectively, are the energies of thermal motion of phonons and intramolecular vibrations of the solid phase, excited by an electron beam [7], $\rho_L^{(G)} = \varepsilon_L\gamma_L/\gamma_G$; γ_L is the density of the solid phase, $\varepsilon_L = (4\pi/3)\cdot R^3N_L$ is the Van der Waals number for a continuum of particles N_L, $Ku = [\tau\langle v\rangle 4\pi R^2N_L]^{-1} = R/\tau\langle v\rangle\varepsilon_L$ is a parameter determining the ratio of the mean time between collisions of molecules with aerosol particles to the characteristic process time τ, $\xi_1 \leqslant 1-\xi$ is the deactivation coefficient of vibrational energy at the surface, $Q_{iG}^* = \tau/\tau_{iG}$ is a dimensionless quantity related to the vibrational relaxation time τ_{iG} in the gas, and α is the thermal accomodation coefficient. In deriving the system of equations (1.7) it was assumed that relaxation processes are represented in the Landau—Teller form. The dimensionless coefficients in front of the square brackets were calculated as in [17, 23], using the method of the boundary sphere, so that Eqs. (1.7) were valid for an arbitrary value of the number K and normalized by the value $\Phi_{iG}^{(0)} = (K\langle v\rangle/3R)[\xi/(4K+\xi+\xi_1)]$ [22]. In the calculations we used the expression for the accomodation coefficient (1.6) with account of the isothermal Langmuir adsorption, i.e., in these equations and in the coefficients appearing in them the quantity ξ was multiplied by the factor:

$$M = [1+n\langle v\rangle\tau_q'\exp(D/kT_L)/4\sigma_0]^{-1}.$$

Since establishing the exact relation between values of the internal energy $e_{iL}^{(s)}$ at the surface and e_{iL} inside the particles is difficult, in the calculations we took $e_{iL}^{(s)} = e_{iL}$.

In system (1.7) there are no terms related to vibrational relaxation inside the particles, since the corresponding time, according to [7], is short for N_2 ($\tau_{iL} \sim 1$ sec).

Figure 4 shows results of calculating changes in time of the temperatures T_{iG}, T_G for different regimes and particle sizes indicated in Table 1 for $\rho_L^{(G)} = 0.1$; $T_{iL}^{(0)} = 3000°$; $T_G^{(0)} = T_L^{(0)} = T_{iG}^{(0)} = 20°$.

This numerical solution verifies the analytic results obtained earlier [22], according to which a significant excess of the mass of the condensed phase over the mass of the gas $\rho_L^{(G)} \ll 1$ is required for effective transfer of vibrational energy into the gas. The analytic solution of system (1.7) for a first "fast" stage of gas excitation is [22]

$$\frac{T_{iG}}{T_{iL}^{(0)}} = (1+\rho_L^{(G)})^{-1}[1-\exp(-q_1t), \text{ where } q_1 = 3\varepsilon_L\Phi_{iG}^{(0)}(1+\rho_L^{(G)}),$$

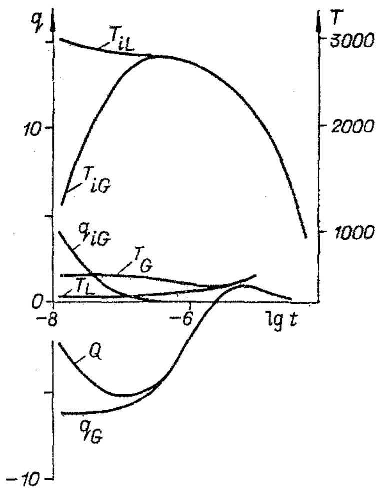

Fig. 6

whence it follows that to obtain a ratio $T_{iG'}/T_{iL}^{(o)} \approx 1$ a necessary condition is $\rho_L^{(G)'} \ll 1$. Thus, it has been shown that the required property of maximum gas excitation by an aerosol energy carrier is determined by the collective effect of particles, i.e., by the parameters ε_L, Ku, $\rho_L^{(G)}$, and cannot be obtained by analyzing the motion in a gas of separated aerosol particles. Particle evaporation, however, was not included in the model considered. Due to energy expenditure upon evaporation the temperature T_G must not grow, as was shown in Fig. 4. Therefore, the descending parts on the curves are denoted by points. They do not correspond to a real process, for example, for a dispersed medium with N_2 particles, since in this region one can no longer neglect evaporation in the general energy balance. Estimates show that for the initial values of $T_{iL}^{(o)}$, $T_L^{(o)}$, $T_G^{(o)}$, $T_{iG}^{(o)}$, $\rho_L^{(G)}$ considered the stored vibrational energy suffices for total particle evaporation. Therefore, the question of flow uniformity arises again.

Figure 5 shows results of calculating changes in the medium parameters as a result of particle evaporation during subsonic flow in a channel of constant cross section, obtained on the basis of conservation laws [17] (curves 1-3 correspond to $T_G/T_G^{(o)}$; $1/\rho_L^{(G)}$, and p/p_0). These data imply a limiting value of $\rho_L^{(G)}$, for which the flow can still be realized. For higher values of $(\rho_L^{(G)})^{-1}$ the pressure varies, which implies a nonuniform character of flow during evaporation. This situation can, obviously, be improved by a change in flow geometry.

We note that the performed study model of a dispersed medium (1.7) with explicit determination of rates of heterogeneous processes (1.6) indicates a method of studying dispersed media with nonequilibrium heterogeneous chemical reactions [24], among which one includes expansion of the solid phase products [25, 26], prospective methods of isotope separation [27], etc. The principal moment in these problems is account of the motion of the collective of particles interacting with the flow, and not that of an isolated particle. An important problem to which the approach discussed above is applicable is that of controlling thermal flows to the surface due to its "chemical" composition [28]. Figure 6 shows the evolution of thermal flows, among them q_{iG}, from the nonequilibrium excited vibrational degrees of freedom to the surface, obtained on the basis of calculations of the gas—surface—solid medium (1.7) with account of the structure of the catalytic coefficient (1.6) (α = 0.01; $\rho_L^{(G)}$ = 0.1; $T_{iG}^{(o)} = T_G^{(o)}$ = 300°; $T_L^{(o)}$ = 50°; $T_{iL}^{(o)}$ = 3000°):

$$q_{iG} = \left(\lambda_{iG} \frac{\partial T_{iG}}{\partial r}\right)_s = \gamma_G R \Phi_{iG}^{(0)} \left[e_{iL}^{(s)} - (1 + \xi_1/\xi)\, e_{iG}\right],$$

$$q_G = \left(\lambda_{aG} \frac{\partial T_G}{\partial r}\right)_s = \gamma_G R \Phi_{aG} (T_L - T_G),\ \Phi_{aG} = \frac{K \langle v \rangle}{R} \frac{\alpha}{4K + 3\alpha},\ Q_G = q_{iG} + q_G.$$

As follows from these calculations, the quantity q_{iG} can be an important part in the general thermal balance only for small thermal accomodation coefficients $\alpha \sim 10^{-2}$. This is explained by the relatively low energy capacity of the vibrational degrees of freedom and the relatively large difference $T_L^{(o)} - T_G^{(o)}$. Besides, to conserve the given quantity q_{iG}/Q_G a constant

TABLE 1

No. of curve, Fig. 4	p, Pa	R, m	K	ε_L	v/R	No. of curve, Fig. 4	p, Pa	R, m	K	ε_L	v/R
1	10^5	10^{-6}	4	10^{-2}	10^{11}	4	10^4	10^{-4}	0,4	10^{-3}	10^9
2	10^5	10^{-5}	0,4	10^{-2}	10^{10}		10^3	10^{-5}	40	10^{-4}	10^{10}
	10^4	10^{-6}	40	10^{-3}	10^{11}		10^2	10^{-6}	4000	10^{-5}	10^{11}
3	10^4	10^{-5}	4	10^{-3}	10^{10}	5	10^3	10^{-4}	4	10^{-4}	10^9
	10^3	10^{-6}	400	10^{-4}	10^{11}		10^2	10^{-5}	400	10^{-5}	10^{10}
						6	10^2	10^{-4}	40	10^{-5}	10^9

energy input to the solid phase is needed. Without an energy input, the condition T_{iL} = const at the boundary of the solid phase is possible when there exists a mechanism of selective adsorption with respect to various vibrational modes [29].

In conclusion, we would like to point out the advantage of the complex approach developed in the present paper for solving actual problems of relaxation gasdynamics. For its realization it is important to construct model hydrodynamic equations with account of nonequilibrium processes in the internal degrees of freedom, simultaneously occurring in the various aggregate states, and perform calculations for these equations by means of quantum-mechanical methods for the various coefficients, taking into account the specifics of the elementary interactions in the gas, the solid (liquid) phase, and on the surfaces separating them.

The results of the investigated simple gas—surface—solid system (1.7) show how to proceed in solving new aerophysical problems. There is no doubt that the development of further work in the direction indicated will lead not only to obtaining new qualitative and quantitative results, but also to corresponding generalizations in the theory of nonequilibrium processes.

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