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QUASISTATIONARY RELAXATION AND GAS-DYNAMIC PHENOMENA IN A ONE-COMPONENT SYSTEM OF EXCITED ANHARMONIC OSCILLATORS

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UDC 531

At the present time the kinetic theory of vibrational relaxation of molecular gases is the most developed branch of physical kinetics. Among important achievements in this field one has to include the development of general methods of description of systems far from equilibrium [1, 2]. In such cases the anharmonicity of the molecular vibration shows a substantial influence on the behavior of the medium. Until now theoretical analysis of vibrational relaxation of systems of anharmonic oscillators was carried out basically for gases at rest.

In addition, due to advances in the physics of nonequilibrium discharge phenomena it became clear that the correct description of the behavior of strongly excited gases should take into account their relaxational motion. Indeed, as an example, such motion can markedly influence the conditions of vibrational relaxation of gases after the discharge [3], and in fast-flow discharge arrangements it can lead to the breakdown of the pumping regime of the vibrational degrees of freedom of the gaseous mixtures [4]. For a theoretical consideration of a selected class of problems one has to complete a substantial amount of computational

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tasks, related to solving a large number of equations of vibrational kinetics. In order to lower the level of difficulty it is necessary to choose a simple and sufficiently reliable model of the process.

The most economical model describing the vibrational relaxation of molecular gases in a wide range of measurement of their parameters is the quasistationary model of vibrational relaxation of anharmonic oscillators, proposed in [5] (a subsequent account of the foundations of the method is given in [1]). An important merit of the model is the fact that starting with relatively simple equations for macroscopic quantities it permits one to obtain sufficiently detailed information about the state of the gas during the whole process of relaxation. However, in [6], where one studies heating of vibrationally excited nitrogen, it is stated that the results of the calculations performed within the framework of the quasistationary model should differ sharply from the corresponding results of the nonstationary kinetic theory. The possibility of such a discrepancy in case of states of the gas far from equilibrium is related in [6] to the large contribution to the heating of the nonresonant V−V transfer processes between the anharmonic oscillators in the initial stage of relaxation when the distribution function of the molecules on the vibrational levels is formed. Our preliminary results showed a certain inaccuracy of this statement. Moreover, in [7], the application of the quasistationary theory and the recent data on the frequencies of the V−V and V−T transfer processes (see [8]) assured a satisfactory description of the behavior of nitrogen off the vibrational equilibrium after discharge. Therefore it is necessary to directly compare the quasistationary and the nonstationary kinetic models of relaxation of the system of excited anharmonic oscillators.

In the following we consider the possibility of application of the quasistationary model of vibrational relaxation to the description of the dynamic relaxation of nonequilibrium gases of diatomic molecules. An analysis and correction of the analytical relations of the macroscopic form of this model are given. A comparison of results obtained within the framework of the quasistationary and nonstationary kinetic models is carried out. To demonstrate the applicability of the quasistationary model to the calculations of dynamics of the motion of nonequilibrium gases the problem of amplification of weak shock wave in vibrationally excited nitrogen is considered.

Further, the correctness of the description of the relaxation processes is controlled by calculations performed within the sufficiently accurate nonstationary level kinetics model (NLKM). In the case of the isochoric or isobaric relaxation of a one-component system the equations of NLKM, taking into account the most important single-quantum transitions, have the form [1, 6]:

$$df_i/dt = \pi_{i+1} - \pi_i, \quad i = 0, 1, \ldots, i_*. \tag{1}$$

Here $f_i = N_i/N$; N_i is the number of molecules per unit volume on the i-th vibrational level; N is the total number of molecules per unit volume; $\pi_{i+1} = Z\left[P_{i+1,i}f_{i+1} - P_{i,i+1}f_i + \sum_{k=0}^{i_*}\left(Q_{i+1,i}^{k,k+1}f_{i+1}f_k - Q_{i,i+1}^{k+1,k}f_if_{k+1}\right)\right]$; Z is the frequency of collisions of a molecule; $P_{i,i+1}$ and $P_{i+1,i}$ are the transition probabilities of a molecule for the transitions (i → i + 1) and (i + 1 → i) in collision with another molecule; $Q_{i+1,i}^{k,k+1}$ and $Q_{i,i+1}^{k+1,k}$ are the probabilities of the V−V transfer $\begin{pmatrix} k \to k+1 \\ i+1 \to i \end{pmatrix}$ and $\begin{pmatrix} k+1 \to k \\ i \to i+1 \end{pmatrix}$ in collision of two molecules; i_* is the number of the last vibrational level considered (determined from the condition of deliberate neglect of the excitations with $i > i_*$).

If the contribution of the nonresonant V−V processes to the relaxation is insignificant then in the quasistationary approximation the solution of Eq. (1) is given by the dependence [1]

$$f_i \approx \begin{cases} f_i^{(1)}, & i < n_0, \\ f_i^{(2)}, & n_0 \leqslant i \leqslant n_1, \\ 0, & i > n_1, \end{cases} \tag{2}$$

where $f_i^{(1)} = f_0 \exp\left[-i\left(\frac{E_1}{kT_1} - (i-1)\frac{\Delta E}{kT}\right)\right]$ is the lower branch of the Treanor distribution [9]; $f_i^{(2)} = C\ \{1 - B\ [\exp\ (i\delta_{VT}) - \exp\ (n_0\delta_{VT})]/C\}/(i+1)$; $n_0 = \frac{E_1}{2\Delta E}\frac{T}{T_1} + 0.5$ is the vibrational quantum number corresponding to the minimum of the Treanor distribution; $n_1 = n_0 + \delta_{VT}^{-1} \ln\left[1 + (n_0 + 1) \frac{F_\text{T}}{B} \times \exp(-n_0\delta_{VT} - 0.5)\right]$; $F_\text{T} = f_0 \exp\left(-n_0^2 \frac{\Delta E}{kT}\right)$ is the value of the Treanor distribution function for $i = n_0$; f_0 is a norming factor; $B = \frac{P_{10}}{Q_{10}} \frac{kT\delta_{VV}^3}{12\Delta E\delta_{VT}}$; $C = \exp(-0.5)(n_0 + 1)F_\text{T}$; $Q_{10} \equiv Q_{10}^{01}$; E_1 is the excitation energy of the first vibrational level; ΔE is the anharmonic constant; δ_{VT} and δ_{VV} are parameters determining the frequencies of V−T and V−V processes; T_1 is the vibrational temperature of the first vibrational level; T is the gas temperature.

The average number of vibrational quanta, incident on one molecule, and the velocity of change of this number are found from the relations

$$S^{(f)} = \frac{1}{\hbar\omega_0} \sum_i E_i f_i; \tag{3}$$

$$\left(\frac{dS}{dt}\right)^{(f)} = \frac{1}{\hbar\omega_0} \sum_i E_i (\Pi_{i+1} - \Pi_i). \tag{4}$$

Here index f means that the quantities are computed using the explicit distribution function; $\hbar\omega_0$ is the energy of the vibrational quantum; E_i is the excitation energy of the i-th vibrational level of the oscillator; $\Pi_i = Z(P_{i,i-1}f_i - P_{i-1,i}f_{i-1})$ is the flux of molecules from the i-th level to the (i − 1)-th one due to the V−T processes. The distribution function (2) and the relations (3), (4) are the basis of the quasistationary model of relaxation (QMR).

An approximate summation in (3) and (4) with the function (2) yields the result (see [1], Chap. 4, Sec. 5):

$$S^{(f)} \approx S_\text{m} \text{ and } \left(\frac{dS}{dt}\right)^{(f)} \approx \left(\frac{dS}{dt}\right)_\text{m},$$

where

$$S_\text{m} = S_\text{m1} + S_\text{m2}; \tag{5}$$

$$S_\text{m1} = \left[\exp\left(\frac{E_1}{kT_1}\right) - 1\right]^{-1}; \tag{5a}$$

$$S_{\text{m}_2} = \exp(-0{,}5)(n_0 + 1)(n_1 - n_0)F_\text{T}; \tag{5b}$$

$$\left(\frac{dS}{dt}\right)_\text{m} = \left(\frac{dS}{dt}\right)_\text{m1} + \left(\frac{dS}{dt}\right)_\text{m2}; \tag{6}$$

$$\left(\frac{dS}{dt}\right)_\text{m1} = -ZP_{10} \frac{[1 - \exp(-E_1/kT_1)]\,[\exp(-E_1/kT_1) - \exp(-E_1/kT)]}{[1 - \exp(-E_1/kT_1 + \delta_{VT})]^2}; \tag{6a}$$

$$\left(\frac{dS}{dt}\right)_\text{m2} = -ZQ_{10}\left(\frac{6}{e}\right) \frac{\Delta E}{kT\delta_{VV}^3} [(n_0 + 1) F_\text{T}]^2. \tag{6b}$$

Index m means that the considered quantity belongs to a set of quantities determining the macroscopic form of the quasistationary model of relaxation (MQMR). The first pieces in the above expression show the contribution to the sum (3) and (4) of the terms related to levels with quantum numbers from the interval $0 \leqslant i < n_0$, and the second pieces show the contribution of the terms described by the quantum numbers $n_0 \leqslant i \leqslant n_1$.

In this work we will illustrate the possibility of application of the macroscopic form of QMR to the description of vibrational relaxation on the example of the molecular gas N_2. The numerical comparison of the formulas of QMR with the corresponding approximate expressions MQMR shows that they give different results for the same cases. In Fig. 1 (1: T = 300, 2: 500, 3: 900°K) we show the dependence of the ratio $(dS/dt)_\text{m}(dS/dt)_\text{k}^{(f)}$ (dashed lines) on the average number of vibrational quanta S [the index k shows that the calculation of the considered quantity is carried out by using function (2)]. In finding $(dS/dt)_\text{m}$ the vibrational temperature was found from the equation $S_\text{m}(T, T_1) = S$, and in finding $(dS/dt)_\text{k}^{(f)}$ from the equation $S_\text{k}^{(f)}(T, T_1) = S$. It is seen in Fig. 1 that the ratio under consideration is practially equal to unity only in the region of small departure from equilibrium of the gas. In the regions of moderate and large departure from equilibrium the dependences have a nonmonotonic character and markedly differ from unity. As we will see later the lack of monotony in the region of moderate departure from equilibrium is due to the incorrect replacement of the Treanor branch of the distribution function by the Boltzmann distribution in derivation of the formulas (5a) and (6a) and the overestimated result in the region of large departure from equilibrium is due to the loss of the factor in (6b).

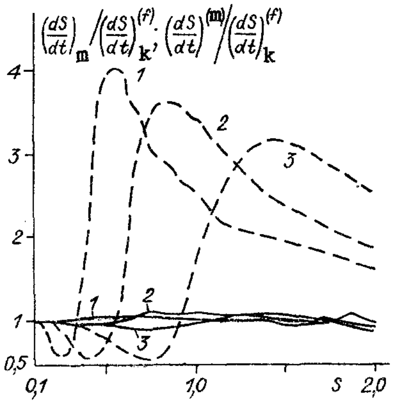

Fig. 1

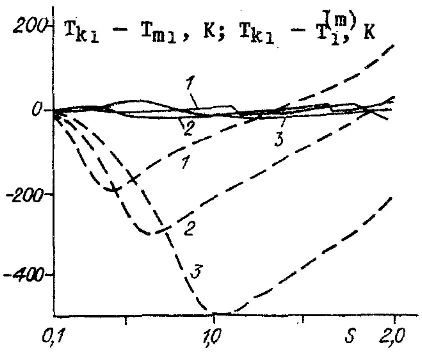

Fig. 2

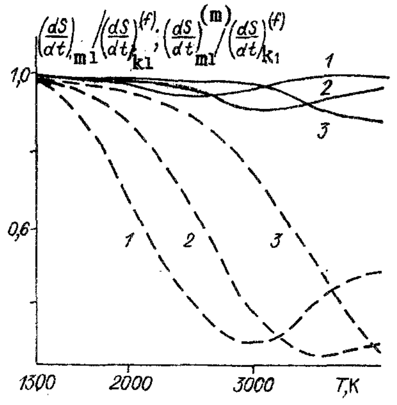

Fig. 3

In deriving the more accurate expressions of QMR one has to take into account the following relations

$$\left(\frac{dS}{dt}\right)_k^{(f)} = \left(\frac{dS}{dt}\right)_{k1}^{(f)} + \left(\frac{dS}{dt}\right)_{k2}^{(f)}; \tag{7}$$

$$\left(\frac{dS}{dt}\right)_{k1}^{(f)} \approx -Z \sum_{i=1}^{n_0-1} \left(P_{i,i-1}f_i^{(1)} - P_{i-1,i}f_{i-1}^{(1)}\right); \tag{7a}$$

$$\left(\frac{dS}{dt}\right)_{k2}^{(f)} \approx -Z \sum_{i=n_0}^{n_1} P_{i,i-1}f_i^{(2)}. \tag{7b}$$

In the case $n_0 \gg 1$ the formula (7b) becomes

$$\left(\frac{dS}{dt}\right)_{k2} \approx -\frac{2\delta_{VT}}{\mathrm{e\,xp}\,(2\delta_{VT}) - 1}\left(\frac{6}{e}\right) ZQ_{10}\frac{\Delta E}{kT\delta_{VV}^3}[(n_0+1)F_T]^2 - ZP_{10}(n_0+1)F_T\frac{\exp[(n_0-1)\delta_{VT} - 0,5]}{\exp(\delta_{VT}) + 1} \equiv \left(\frac{dS}{dt}\right)_2^{(m)}. \tag{8}$$

Equating (8) and (6b) for large departure from equilibrium state of the gas (i.e., under conditions where the second term in (8) can be neglected) we see that $\left(\frac{dS}{dt}\right)_{m2} \Big/ \left(\frac{dS}{dt}\right)_2^{(m)} \approx \frac{\exp(2\delta_{VT}) - 1}{2\delta_{VT}}$. For nitrogen at low temperatures (comparable with room temperature) this ratio is close to 2.

We will analyze the possible effect of the replacement of the Treanor branch of the distribution function by the Boltzmann distribution function, as done in deriving (5a). If we take into account the relation $F_T \sim \exp\left[-\left(\frac{E_1}{2kT_1}\right)^2 \frac{kT}{\Delta E}\right]$, then according to (8), the velocity of change of the vibrational energy of the system should strongly depend on T_1. At a fixed gas temperature the dependence of the vibrational temperature on the variable S is determined from the equation

$$S_1(T,\ T_1) + S_2(T,\ T_1) = S. \tag{9}$$

In this manner we can see that even a small inaccuracy in the form of Eq. (9) can lead to a visible error in the determination of $(dS/dt)^m$. In Fig. 2 for various gas temperatures (values are the same as in Fig. 1) are given the dependences of the difference $T_{1k} - T_{1m}$ (dashed lines) on S, where T_{1k} and T_{1m} are the values of T_1 found by means of QMR and MQMR, respectively. The plot shows that the error in finding the vibrational temperature of the first level is the largest in the range of S corresponding to the cases of moderate departure of the state of the system from equilibrium (i.e., when $S_{m1} \gg S_{m2}$, but $\left|\left(\frac{dS}{dt}\right)_{m2}\right| > \left|\left(\frac{dS}{dt}\right)_{m1}\right|$). Moreover, the peaks of the dependences depicted in Fig. 1 for $\left(\frac{dS}{dt}\right)_m \Big/ \left(\frac{dS}{dt}\right)_k^{(f)}$ fall precisely in the region of the largest errors in T_1. In conditions of a large departure from equilibrium this effect is less apparent. From what has been said it follows that using the expressions for S_{m1} can bring about a substantial inaccuracy in the description of the process of vibrational relaxation.

The replacement of the Treanor branch of the distribution function by the Boltzmann distribution made in the derivation of the analytic expression (6a) largely underestimates the values of $(dS/dt)_{k1}^{(f)}$. It is illustrated in Fig. 3, where for various gas temperatures (values are same as in Fig. 1) the dependence of the ratio $\left(\frac{dS}{dt}\right)_{m1}\Big/\left(\frac{dS}{dt}\right)_{k1}^{(f)}$ on T_1 is depicted by dashed lines. It is seen that in determining the velocity of vibrational relaxation of a system only slightly off equilibrium [when $\left|\left(\frac{dS}{dt}\right)_{m2}\right| \leqslant \left|\left(\frac{dS}{dt}\right)_{m1}\right|$] it is necessary to take into account the Treanor character of the population of the lower vibrational levels.

A more correct description in the framework of MQMR can be achieved by way of approximating the function f_i on the segment $2 \leqslant i \leqslant n_0 - 1$. The character of the approximation is easy to understand by considering the explicit form of the expressions for $S_{k1}^{(f)}$ and $(dS/dt)_{k1}^{(f)}$:

$$S_{k1}^{(f)} \approx f_0 D(a, q),$$

$$\left(\frac{dS}{dt}\right)_{k1}^{(f)} \approx -ZP_{10}\exp(-\delta_{VT})\left\{1 - \exp\left[-\frac{a}{T}(T_1 - T)\right]\right\} f_0 D(a - \delta_{VT}, q),$$

where

$$D(a, q) = \sum_{i=1}^{n_0-1} i\exp(i^2 q)\exp[-i(a+q)]; \quad a = \frac{E_1}{kT_1}; \quad q = \frac{\Delta E}{kT}.$$

In writing the last equation the relation of the detailed balance was used $P_{i-1,i} = P_{i,i-1}\exp \times [-a + 2q(i-1)]$.

In order to compute the sum D we suggest replacing the function $\Phi(i) = \exp(i^2 q)$ by the function

$$\varphi(i) = \begin{cases} \exp(\beta i - \alpha), & 2 \leqslant i \leqslant i_0, \\ \exp(\varkappa i - \gamma), & i_0 < i \leqslant n_0 - 1. \end{cases} \tag{10}$$

Here $i_0 = (\gamma - \alpha)/(\varkappa - \beta)$; $\alpha = 2(2 + \Delta_1)q$; $\beta = (4 + \Delta_1)q$; $\gamma = (n_0 - 1)(n_0 - \Delta_2 - 1)q$; $\varkappa = [2(n_0 - 1) - \Delta_2]q$. The points of intersection of the functions $\Phi(i)$ and $\varphi(i)$ correspond to the following values of the variable i: $i_{(1)} = 2$, $i_{(2)} = 2 + \Delta_1$ and $i_{(3)} = n_0 - \Delta_2 - 1$, $i_{(4)} = n_0 - 1$. In result we obtain

$$\begin{aligned} D(a, q) \approx e^{-a}\Big\{1 + \frac{e^{-\eta}}{(1 - e^{-\rho})^2}\big[e^{-\rho}(2 - e^{-\rho} - e^{-\rho i_0}) - \\ - (1 + i_0)(1 - e^{-\rho})e^{-\rho i_0}\big] + \frac{e^{-\xi}}{(1 - e^{-\mu})^2}\big[i_0(1 - e^{-\mu})(e^{-\mu} - e^{-(n_0 - i_0)\mu}) + \\ + e^{-\mu}(1 - e^{-(n_0 - i_0)\mu}) - (n_0 - i_0)(1 - e^{-\mu})e^{-(n_0 - i_0)\mu}\big]\Big\} \equiv D^{(m)}(a, q), \end{aligned} \tag{11}$$

where $\eta = (1 + \Delta_1)q$; $\rho = a - (3 + \Delta_1)q$; $\mu = a - (2n_0 - \Delta_2 - 3)q$; $\xi = (i_0 - 1)a - [i_0(2n_0 - \Delta_2 - 3) - (n_0 - 1)(n_0 - \Delta_2 - 1)]q$. In determining the norming factor f_0 it is sufficient on the interval $2 \leqslant i \leqslant n_0 - 1$ to use instead of the function $\Phi(i)$ an approximation of the form $\exp(\beta i - \alpha)$ and on the interval $n_0 \leqslant i \leqslant n_1$ to replace the distribution $f_i^{(2)}$ by the distribution $C/(i + 1)$. In this case

$$f_0 \approx \frac{1 - e^{-\rho}}{e^{-\alpha}\left(e^{-2\rho} - e^{-n_0\rho}\right) + (1 - e^{-\rho})\left[1 + e^{-\rho} + (n_0 + 1)e^{-\varepsilon}\ln\left(\frac{n_1 + 1}{n_0 + 1}\right)\right]} \equiv f_0^{(m)} \tag{12}$$

and $(\varepsilon = qn_0^2 + 0.5)$. We note that the application of the relation (11) and (12) assures such a selection of the parameters of approximation Δ_1 and Δ_2, which in wide ranges of variation of T_1 and T for a given gas allows one to attain the best agreement of the results for S_1 and $(dS/dt)_1$ according to the formulas

$$S_1^{(m)} = f_0^{(m)} D^{(m)}(a, q); \tag{13}$$

$$\left(\frac{dS}{dt}\right)_1^{(m)} = -ZP_{10}\exp(-\delta_{VT})\left\{1 - \exp\left[-\frac{a}{T}(T_1 - T)\right]\right\} f_0^{(m)} D^{(m)}(a - \delta_{VT}, q) \tag{14}$$

with the analogous results of calculations performed by means of QMR.

For the parameter $S_{k2}^{(f)} = \frac{1}{\hbar\omega_0} \sum_{i=n_0}^{n_1} E_i f_i^{(2)}$, one can obtain an approximate expression

$$S_{k2}^{(f)} \approx \exp(-0.5)(n_0+1) F_T \left\{ n_1 - n_0 + \frac{n_1 - n_0}{\exp[\delta_{VT}(n_1 - n_0)] - 1} - \frac{1}{\exp(\delta_{VT}) - 1} \right\} \equiv S_2^{(m)}. \tag{15}$$

In case of nitrogen the numerical comparison of the characteristic quantities for the parameters Δ_1 and Δ_2 gives the values: $\Delta_1 = 1.514 + 2.79 \cdot 10^{-3}T$, $\Delta_2 = 1$. In Figs. 1-3 (solid lines) one can see a pronounced improvement of accuracy of the description of vibrational relaxation in the framework of the macroscopic form of QMR in passage from the formulas (5a), (5b), (6a), (6b) to the formulas (8), (11)-(15). Below by MQMR we understand the model based on application of the indicated more accurate relationships.

We apply MQMR to the calculation of the isobaric relaxation of vibrationally excited nitrogen and compare our results with analogous results obtained by means of NLKM. In solving the problem by the methods of NLKM Eq. (1) are supplemented by the relation $\sum_i E_i f_i = \hbar\omega_0 S$ and the equation of energy balance

$$3.5kT + \hbar\omega_0 S = 3.5kT_0 + \hbar\omega_0 S_0 \tag{16}$$

where S_0 and T_0 are the initial values of the parameters S and T. The described system of equations was integrated numerically (for $i_* = 50$) with the aid of the algorithm of solution of stable systems of ordinary differential equations given in [10]. The investigation of vibrational relaxation within the MQMR approach was carried out on the basis of the equations $\frac{dS}{dt} = \left(\frac{dS}{dt}\right)_1^{(m)} + \left(\frac{dS}{dt}\right)_2^{(m)}$, (16) and $S_1^{(m)}(T, T_1) + S_2^{(m)}(T, T_1) = S$. In both models the following temperature dependences were used $Q_{10}(T) = 3 \cdot 10^{-7}T$ [8] and $P_{10}(T) = A \exp(-bT^{-1/3}) + GT^g$ [7], where $A = 2.24 \cdot 10^4$, $b = 308.5$, $G = 4.02 \cdot 10^{-15}$, $g = 2.474$ (the dependence $P_{10}(T)$ is given for the temperature interval 300°K $\le T \le$ 4000°K), and δ_{VT}, δ_{VV} were given by expressions from [1].

The solution of the equations of NLKM was obtained for various initial distribution functions. Only those functions were used which assured a diffusion of the vibrational energy on lower levels. Calculations performed for conditions 300°K $\le T \le$ 2000°K and $S_0 \le 2.0$ showed that the form of the initial distribution practically does not affect the character of the dependences S(t) and T(t). This fact is clarified by the course of the V−V transfer processes, which assures the reconstruction of the initial distribution and within the characteristic time τ_{VV} brings the gas to the state with a quasistationary distribution function. In the process of reconstruction the upper vibrational levels are populated (this leads to formation of a plateau of the function f_i). Thereafter, through the upper levels the transmission of energy from the vibrational to the translational degrees of freedom takes place. Heating of the gas due to the nonresonant V−V transfer of molecules during the formation of the distribution function is negligibly small as compared to the general heating due to the V−T transfers. Therefore, if initially the vibrational energy is concentrated in the lower levels (i.e., the energy losses due to the V−T collisions are small), then independently of the character of its distribution during the time $\tau_{VV} \ll \tau_{VT}$ (τ_{VT} is the characteristic time of the V−T heating of the gas) the gas should pass into a state with a quasistationary distribution function determined by the values of the parameters $S \approx S_0$ and $T \approx T_0$.

In Fig. 4 we give times of a fixed energy loss $\tau_{(H)}$ as functions of S_0 in the following conditions $N_0 = 2.67 \cdot 10^{19}$ cm^{-3}, $S_0 = 0.1$-2.0 ($\tau_{(H)}$ is time in which one molecule releases on the average the energy $H \cdot 10^{-2}\, \hbar\omega_0 [S - S_{eq}(T_{eq})]$; S_{eq} and T_{eq} are the values of S and T corresponding to the final equilibrium distribution). The plot shows a good agreement between the results obtained by the MQMR and NLKM methods (lines 1 and 2). The largest discrepancy of the values of $\tau_{(H)}$ takes place in the initial stage of relaxation for $0.6 \le S_0 \le 1.1$, although it does not exceed 30%. In the course of relaxation the discrepancy of values obtained by both methods decreases. For instance, for $50 \le H \le 70$ the discrepancy does not exceed 15%. In the final stage of relaxation (H = 95) the results agree within 7%. In Fig. 4 we also show the dependence of the total contribution of the V−V processes to the heating of the gas on S_0. It shows that with increase of the initial nonequilibrium the contribution of the V−V processes to the total heating increases, but does not exceed 120°K ($S_0 \le 2.0$).

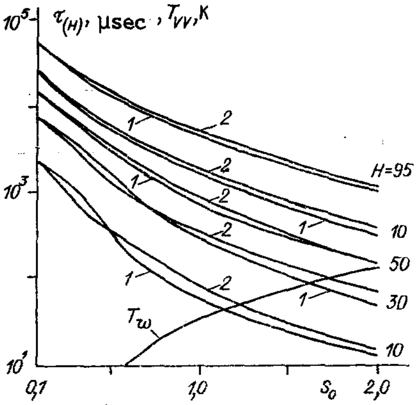

Fig. 4

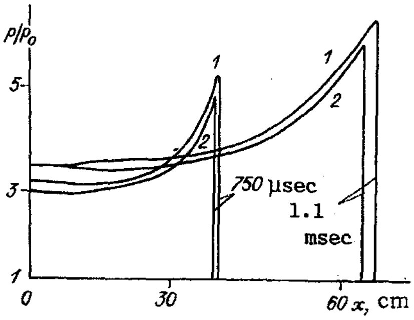

Fig. 5

To demonstrate the capabilities of MQMR in studies of the dynamics of motion of vibrationally off-equilibrium molecular gases we consider the problem of propagation of a weak shock wave in excited nitrogen. It is shown in [11] that such a wave will be amplified and will attain the stationary regime of spontaneous explosion. The accuracy of the calculations will be determined by way of comparing them with the results of calculations based on NLKM.

The wave is generated by a piston beginning at time t = 0 a uniform motion along the x-axis. This motion is such that in case of an equilibrium gas it would correspond to the velocity of the compression jump $v_{shw} = 1.1c_0$ (c_0 is the speed of sound in equilibrium unexcited gas). One assumes that in front of the shock wave the parameters of the excited gas N_0, T_0 and $S_0 > S_{eq}(T_0)$ are constant, and the processes of dissociation and electronic excitation of molecules can be neglected.

Within the framework of MQMR the system of equations describing the nonstationary motion of the gas and accounting for the energy exchange between the vibrational and translational degrees of freedom of the molecules, has the form

$$\frac{\partial N}{\partial t}+\frac{\partial (Nv)}{\partial x}=0,\quad \frac{\partial (Nv)}{\partial t}+\frac{\partial}{\partial x}\left(\frac{p}{m}+Nv^2\right)=0,$$
$$\frac{\partial e}{\partial t}+\frac{\partial}{\partial x}[(e+p)v]=-N\hbar\omega_0\left(\frac{dS}{dt}\right)^{(m)},\quad \frac{\partial S}{\partial t}+v\frac{\partial S}{\partial x}=\left(\frac{dS}{dt}\right)^{(m)}. \tag{17}$$

Here v and p = kNT are the velocity and pressure of the gas; $e=\frac{N}{2}(5kT+mv^2)$; m is the mass of a molecule; $\left(\frac{dS}{dt}\right)^{(m)}=\left(\frac{dS}{dt}\right)_1^{(m)}+\left(\frac{dS}{dt}\right)_2^{(m)}$.

In the framework of NLKM the system of gas-dynamic equations is represented by the relations

$$\frac{\partial N_i}{\partial t}+\frac{\partial (N_i v)}{\partial x}=N(\pi_{i+1}-\pi_i),\quad i=0,1,\ldots,i_*,$$
$$\frac{\partial (Nv)}{\partial t}+\frac{\partial}{\partial x}\left(\frac{p}{m}+Nv^2\right)=0, \tag{18}$$
$$\frac{\partial e}{\partial t}+\frac{\partial}{\partial x}[(e+p)v]=-N\sum_{i=1}^{i_*}E_i(\pi_{i+1}-\pi_i).$$

The notation used here is the same as in (1) and (17).

Equations (17) and (18) were solved numerically with the aid of the methods given in [12, 13]. The propagation of the shock wave created by the piston in the gas with the parameters $S_0 = 1$, $T_0 = 300$°K, $N_0 = 2.67\cdot10^{19}$ cm^{-3} is characterized in Fig. 5 where a plot of pressure as a function of coordinate at the moments of time 750 μsec and 1.1 msec is given (1 – NLKM, 2 – MQMR). It is apparent that the results of the calculations by the MQMR method agree with the results according to NLKM to within 10%. The application of MQMR in the given case assures a good accuracy of description of the process of vibrational relaxation with reasonable computational effort [the ratio of the time of numerical solution of Eqs. (18) and (17) was about 500].

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PHENOMENOLOGICAL MODEL OF FIRST-ORDER PHASE TRANSITIONS IN A DEFORMABLE ELASTIC MEDIUM

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We assume that the continuous medium under consideration can be described with the help of averaged quantities and that these quantities satisfy the laws of conservations of mass, momentum, and energy [1]

$$\partial\rho/\partial t + \operatorname{div}(\rho\mathbf{v}) = 0; \tag{1}$$

$$\partial/\partial t(\rho\mathbf{v}) + \operatorname{div}(\rho\mathbf{v}\otimes\mathbf{v} - \mathbf{P}) = \rho\mathbf{f}; \tag{2}$$

$$\partial/\partial t(\rho(U + (1/2)|\mathbf{v}|^2)) + \operatorname{div}(\rho(U + (1/2)|\mathbf{v}|^2)\mathbf{v} - \varkappa\Delta\Theta - P\langle\mathbf{v}\rangle) = \rho\boldsymbol{f}\cdot\mathbf{v} + \rho g \tag{3}$$

everywhere in the region $\Omega \subset \mathbf{R}^3$ occupied by the medium for all values of the time t in the interval (0, T) for any state of the continuous medium. Here ρ is the density; $\mathbf{v}$ the velocity; P the symmetric stress tensor; U the specific internal energy; Θ the temperature; $\varkappa$ the thermal conductivity; $\mathbf{f}$ the external body force density; g the internal heat source density. Equations (1) through (3) have the form of the abstract conservation law $\partial A/\partial t + \operatorname{div}(A\mathbf{v} - \varphi) = X$, and when the functions A, $\mathbf{v}$, and φ have first-order discontinuities it is necessary to use the integral identity $\iiint_\Gamma (A(\mathbf{l} + \mathbf{v}) - \varphi)\nu d\Gamma = \iiiint_G X dG$ for an arbitrary volume G of the four-dimensional region $\Omega_T = \Omega \times (0, T)$ enclosed by a smooth surface Γ whose outward normal is $\boldsymbol{\nu}$ ($\mathbf{l}$ is a unit vector along the time axis).

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