

INFLUENCE OF THE INITIAL SPATIALLY INHOMOGENEOUS TEMPERATURE PERTURBATIONS
ON VIBRATIONAL RELAXATION DYNAMICS

I. A. Kirillov, B. V. Potapkin, V. D. Rusanov,
M. I. Strelkova, and A. A. Fridman

UDC 533.9

The vibrational relaxation of a nonequilibrium molecular gas ($T_V > T$) plays an important role in the physics of gas lasers, laser chemistry [1], and plasma chemistry [2]. This paper is devoted to an analysis of the dynamics of V-T relaxation with spatially inhomogeneous perturbations of the translational temperature taken into account.

We assume that the translational T and vibrational T_V temperature distributions

$$T(t=0, x) = T_0 + g(x), T_V(t=0, x) = T_{V0} + h(x) \quad (1)$$

at the initial time fluctuate weakly in the space ($|g(x)| \ll T_0$, $|h(x)| \ll T_{V0}$) and the V-T relaxation rate depends on the space coordinate. If the vibrationally excited molecule density is relatively large and their heterogeneous deactivation can be neglected (i.e., the inequality $\tau_{VT} \ll L^2/\chi_V$ is satisfied, where τ_{VT} is the V-T relaxation time, χ_V is the vibrational thermal diffusivity factor, and L is the characteristic dimension of the system), then, in the case of a sharp temperature dependence of the V-T relaxation time $\tau_{VT} = \tau_{VT}^0 \exp(B/T^{1/3})$ [1], the heat conductivity and convective heat transfer cannot restore the spatial homogeneity of the gas temperature distribution. Under these conditions, the relaxation to equilibrium will be inhomogeneous in nature.

The effect mentioned can be described by the following system of equations:

$$nc_V \frac{\partial T}{\partial t} = n \frac{\varepsilon_V(T_V) - \varepsilon_V(T)}{\tau_{VT}} + \lambda_T^T \nabla^2 T; \quad (2)$$

$$nc_V^V \frac{\partial T_V}{\partial t} = -n \frac{\varepsilon_V(T_V) - \varepsilon_V(T)}{\tau_{VT}} + \lambda_V^V \nabla^2 T_V, \quad (3)$$

where n is the gas density, T and T_V its translational and vibrational temperatures, $\varepsilon_V(T_V) = \varepsilon[\exp(\varepsilon/kT_V) - 1]^{-1}$ is the mean vibrational energy per molecule, ε is the quantum of vibrational energy; λ_T^T , λ_V^V are translational and vibrational heat conduction factors [3]. Let us note that in the case of a strong distinction between the vibrational and Boltzmann distribution functions, the influence of the vibrational-translational conductivity λ_V^T must be taken into account [4].

It was assumed in writing (1) and (2) that the convective heat transfer can be neglected as compared with the heat conduction. This is valid if the inequality $(1/T)(d\delta T/dt) \ll \chi_T/a^2$ is satisfied that corresponds to small Peclet numbers $Pe = va/\chi_T$, where $\chi_T = \lambda_T^T/nc_V$ is the translational thermal diffusivity factor, v is the scale of the mean mass flow rate, a is the characteristic dimension of the temperature inhomogeneity, and $d\delta T/dt$ is its rate of change with time.

In order to follow the evolution of small perturbations $T_1(x, t)$, $T_{V1}(x, t)$ of the translational and vibrational temperatures at times when the main background (T_0 , T_{V0}) can still be considered invariant, we linearize the system (1)

$$\frac{\partial T_1}{\partial t} = \omega_{TT} T_1 + \omega_{TV} T_{V1} + \chi_T \frac{\partial^2 T_1}{\partial x^2}; \quad (4)$$

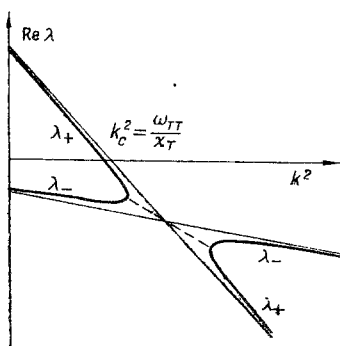


Fig. 1

$$\frac{\partial T_{V1}}{\partial t} = \omega_{VT} T_1 + \omega_{VV} T_{V1} + \chi_V \frac{\partial^2 T_{V1}}{\partial x^2}, \quad (5)$$

where

$$\begin{aligned} \hat{\tau}_{VT} &= \frac{\partial \ln \tau_{VT}}{\partial \ln T}; \quad \omega_{TT} = \tau_{VT}^{-1} \left[-\hat{\tau}_{VT} \frac{\varepsilon_V(T_V) - \varepsilon_V(T)}{c_V T} - \frac{c_V^V(T_0)}{\hat{c}_V} \right]; \\ \omega_{VV} &= -\tau_{VT}^{-1}; \quad \omega_{TV} = \tau_{VT}^{-1} \frac{c_V^V(T_V)}{c_V}; \quad \omega_{VT} = -\omega_{TT} \frac{c_V}{c_V^V(T_V)}. \end{aligned}$$

It follows from (4) and (5) that the rate of change of the perturbation amplitude of the form $e^{\lambda t} \cos kx$ is determined by the expression

$$\lambda_{\pm} = \frac{(-\chi_T k^2 + \omega_{TT} - \chi_V k^2 + \omega_{VV})}{2} \pm \sqrt{\frac{(-\chi_T k^2 + \omega_{TT} + \chi_V k^2 - \omega_{VV})^2}{4} + \omega_{TV} \omega_{VT}}. \quad (6)$$

For the relaxation of a strongly excited gas ($\varepsilon_V(T_V) - \varepsilon_V(T) \gg c_V T$) proceeding from the lower vibrational level ($\hat{\tau}_{VT} < 0$, $\chi_T > \chi_V$ [4]) we obtain $\omega_{TT} > 0$, $\omega_{VV} < 0$, $\omega_{VT} \omega_{TV} < 0$ from (6). The dependence of $\text{Re } \lambda$ on k^2 is represented in Fig. 1 for these conditions, whence it is seen that the fine-scale perturbations damp out in the initial stage of the relaxation because of heat conduction while the "longwave" fluctuations grow. The characteristic spatial scale

$$l_c = 2\pi \sqrt{\frac{\chi_T}{\omega_{TT}}} = 2\pi \sqrt{\frac{c_V T}{\chi_T \tau_{VT} \varepsilon_V(T_V) - \varepsilon_V(T)} \left| \frac{1}{\hat{\tau}_{VT}} \right|}, \quad (7)$$

which corresponds to the mean length of the heat conduction, can be extracted in the system.

To study the nature of V-T relaxation in times when the translational temperature starts to grow explosively, the mixed boundary value problem (2), (3) with initial (1) and boundary conditions

$$\left. \frac{dT}{dx} \right|_{x=0,L} = \left. \frac{dT_V}{dx} \right|_{x=0,L} = 0 \quad (8)$$

was solved numerically. The initial perturbation $g(x)$ was given in the form of "white noise" with $\langle \delta T^2 \rangle = 0.8 \cdot 10^{-4} \text{ deg}^2$. Four vibrational degrees of freedom of the CO_2 molecule and its dissociation because of stored vibrational energy [2] were taken into account in the computation whose results are represented in Fig. 2. The following values of the parameters were used: $n = 3 \cdot 10^{18} \text{ cm}^{-3}$, $T_0 = 100^\circ\text{K}$, $T_{V0} = 3500^\circ\text{K}$, $\varepsilon_1 = 2396 \text{ cm}^{-1}$, $\varepsilon_2 = 1351 \text{ cm}^{-1}$, $\varepsilon_3 = 672 \text{ cm}^{-1}$, $\chi_T = 3\chi_V = 1.4 \text{ cm}^2/\text{sec}$, $B = 72 \text{ deg}^{1/3}$, $c_V = (5/2)k$, $\tau_{VT}^0 = 10^{-3} \text{ sec}$. The nature of the solution does not change qualitatively when the thermal diffusivity factor $\chi_T(T)$, dependent on the translational temperature, is used.

The substantially inhomogeneous nature of the relaxation during which three stages can provisionally be separated out should be noted. Initially intensive damping of the fine-scale perturbations occurs, then a quite definite spatially inhomogeneous temperature distribution is formed that is smoothed out as thermodynamic equilibrium is approached. This qualitative description is illustrated graphically in Fig. 3 where the time dependence of the r.m.s. deviation of the solution of the problem (1)-(3), (8) from the spatially homogeneous solution of (2) and (3) is displayed.

The presence of temperature gradients in the relaxing system results in a change in the mean relaxation time. In fact, we write $T = \langle T \rangle + \delta T(x)$, where $\langle T \rangle$ is the value of the tem-

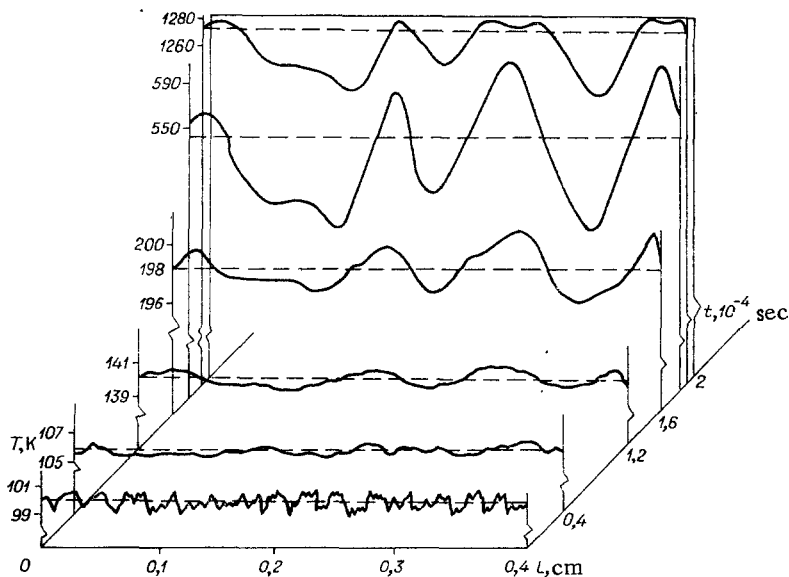


Fig. 2

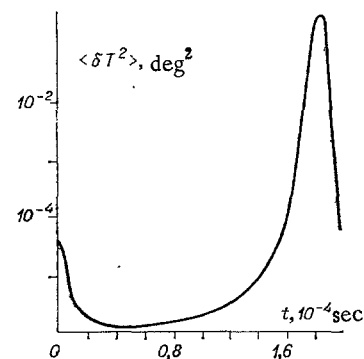


Fig. 3

perature averaged with respect to the space, and $\delta T(x) \ll \langle T \rangle$ is the deviation from the mean background. Let us expand the relaxation velocity in a power series in the inhomogeneity:

$$Q_{VT}(T(x)) = \frac{\varepsilon_V(T_V) - \varepsilon_V(T)}{\tau_{VT}(T)} = Q_{VT}(\langle T \rangle) + \frac{\partial Q_{VT}}{\partial T} \delta T + \frac{\partial^2 Q_{VT}}{\partial T^2} \frac{1}{2} (\delta T)^2 + \dots$$

and let us take the average of this expression with respect to the space

$$\langle Q_{VT} \rangle = Q_{VT}(\langle T \rangle) + \frac{\partial Q_{VT}}{\partial T} \langle \delta T \rangle + \frac{\partial^2 Q_{VT}}{\partial T^2} \langle \delta T^2 \rangle + \dots$$

Considering the fluctuation spectrum Gaussian ($\langle \delta T \rangle = 0$), we obtain that if $\partial^2 Q_{VT} / \partial T^2 > 0$, the the mean relaxation time for an inhomogeneous temperature distribution will be higher than for a homogeneous distribution

$$\langle \tau_{VT} \rangle = \tau_{VT}(\langle T \rangle) \left[1 + \frac{\partial^2 Q_{VT}}{\partial T^2} \frac{1}{2} \langle \delta T^2 \rangle \right].$$

If $Q_{VT}(T)$ is a concave function of the translational temperature ($\partial^2 Q_{VT} / \partial T^2 < 0$), then the spatially inhomogeneous relaxation will be slower than the homogeneous on the average. The first case is realized in the initial stage of the relaxation when a temperature increase results in an acceleration of the V-T exchange, the second is near thermodynamic equilibrium, where a rise in the translational temperature of the gas results in a reduction in relaxation intensity because of depletion of the vibrational reservoir.

Let us note that the spatially inhomogeneous vibrational relaxation mode can be related to the decay of an elevated pressure discharge on separate filaments extended along the gas flow. If the characteristic length (7) is taken as the spacing between the filaments, then we obtain the quantity ~ 0.1 cm for the parameter values mentioned above, which is in agreement with visual observations on a microwave plasmotron in a supersonic gas flow [5].

LITERATURE CITED

1. B. F. Gordiets, A. N. Osipov, and A. A. Shelepin, Kinetic Processes in Gases and Molecular Lasers [in Russian], Nauka, Moscow (1980).
2. V. D. Rusanov, A. A. Fridman, and G. V. Sholin, "Physics of a chemically active plasma with nonequilibrium vibrational excitation of molecules," Usp. Fiz. Nauk, 134, No. 2 (1981).
3. H. Andersen, "Derivation of hydrodynamics equations from the Boltzmann kinetic equations," Kinetic Processes in Gases and Plasma [Russian translation], Atomizdat, Moscow (1972).
4. S. V. Dobkin and É. E. Son, Heat Conduction of a Vibrationally-Excited Molecular Gas, No. 2006, VINITI (1981).
5. R. I. Azizov, et al., "Carbon dioxide dissociation in nonequilibrium plasma," Proc. 5th Intern. Symp. Plasma Chemistry, Vol. 2 (1981).