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EFFECT OF MOLECULAR ROTATIONS ON ACOUSTIC PROPERTIES OF A TWO-FLUID MEDIUM

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The effect of molecular rotations on the dispersion of the speed of sound and the absorption factor is theoretically analyzed for mixtures of diatomic and monatomic gases with disparate molecular masses. Two types of mixtures are considered: 1) *the molecules of the diatomic component are significantly lighter than the molecules of the monatomic gas, and* 2) *the monatomic molecules have a smaller mass. The calculations show that the effect of rotational relaxation on acoustic characteristics in the range of frequencies close to the critical value can be ignored in the first-type mixtures, whereas the energy exchange between the rotational and translational degrees of freedom of molecules has a considerable effect on the propagation of forced acoustic oscillations in the second case.*

It is shown [1, 2] that the dispersion relationships obtained from linearized equations of two-fluid dynamics [3, 4] offer a rather adequate description of high-frequency (about 100 MHz and higher) dependences of the speed of sound and the absorption factor on frequency for a certain range of concentrations of the components of a mixture of inert gases with disparate masses (helium and xenon). The absence of rotational degrees of freedom of inert-gas molecules simplifies theoretical analysis of the phenomenon and interpretation of experimental data. At the same time, it is of interest to extend the study to a wider class of mixtures, which includes multiatomic molecules. Internal degrees of freedom play a substantial role in molecular energy exchange and can exert a significant influence on the frequency dependences of acoustic parameters.

The objective of the present work is to study theoretically the acoustic properties of gas mixtures consisting of molecules of substantially different mass, in which one of the gases (light or heavy) is diatomic. Two mixtures were studied: hydrogen–xenon and helium–iodine. In the first mixture, light molecules possess rotational degrees of freedom and their relaxation time is quite large (about several hundreds of τ_0, where τ_0 is the mean time between molecular collisions). Heavy molecules possessing rotational degrees of freedom are typical of the second mixture, and the time of rotational relaxation is small (about τ_0). We do not claim that these calculations are extremely accurate because there are no extensive data on rotational relaxation times for the systems examined. The low pressure of iodine vapor at 300 K can become a serious impediment to conducting measurements in iodine mixtures with other gases. Some restrictions of the Euler approximation used here should also be taken into account [2]. Nevertheless, these calculations give some idea about the effect of molecular rotations on acoustic characteristics of mixtures with disparate molecular masses. The results are presented in the form of acoustic characteristics as functions of the parameter $r = \omega/p$ (ω is the angular frequency and p is the pressure).

The equations of two-fluid dynamics in the one-dimensional Euler approximations can be found elsewhere [3, 4]. With account of rotational relaxation of the diatomic component, they have the following form:

$$\frac{\partial n_i}{\partial t} + \frac{\partial n_i v_i}{\partial x} = 0, \qquad m_i n_i\Big(\frac{\partial v_i}{\partial t} + v_i \frac{\partial v_i}{\partial x}\Big) = -\frac{\partial p_i}{\partial x} - K(v_i - v_j); \tag{1}$$

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$$n_i\left(\frac{\partial e_i}{\partial t}+v_i\frac{\partial e_i}{\partial x}\right)=-q(T_i-T_j)+\text{\ae}_{ij}K(v_i-v_j)^2+n_l\theta_i,$$
$$\frac{\partial \varepsilon_l}{\partial t}+v_l\frac{\partial \varepsilon_l}{\partial x}=-(\theta_1+\theta_2). \tag{2}$$

Here n is the number density of the particles, v and $p = nkT$ are the velocity and pressure, respectively, k is the Boltzmann constant, x and t are the coordinate and the time, m is the mass of the molecules, $e = (3/2)kT$ is the mean energy of translational motion of the molecules, T is the temperature, $\varepsilon = kT_r$ is the mean rotational energy of diatomic molecules, and T_r is the rotational temperature. The subscripts i, j, and l take values 1 and 2 and denote the type of the gas (1 for the light gas and 2 for the heavy gas, $l = 1$ if the light gas is diatomic, and $l = 2$ is the heavy gas is diatomic).

For the model where molecules are hard spheres, the quantities K, q, and $\text{\ae}_{ij}$, which characterize the exchange rates for momentum and energy of the components of the mixture, are determined by the following formulas [4, 5]:

$$K=\frac{p_1p_2T^*}{(p_1T_2+p_2T_2)D_{12}},\qquad T^*=\frac{m_1T_1+m_2T_2}{m_1+m_2},\qquad q=\frac{3k}{m_1+m_2}K,$$
$$\text{\ae}_{ij}=\frac{T_i/m_i}{T_1/m_1+T_2/m_2},\qquad m_{12}=\frac{m_1m_2}{m_1+m_2},\qquad p=p_1+p_2,\qquad \sigma_{ij}=0.5(\sigma_i+\sigma_j),$$

where σ is the molecule diameter and D_{12} is the binary diffusion coefficient. For $T = 300$ K and $p = 10^5$ Pa, the experimental value $D_{12} = 6.233 \cdot 10^{-5}$ m^2/sec [6] was used for the H_2–Xe system; for the He–I_2 system, this quantity was calculated using the formula for the model with molecules as hard spheres [4]. The relaxation rates of rotational energy in collisions of the molecules of two gases with different temperatures are denoted by θ_1 and θ_2. Using the concept of relaxation of the mean energy of molecular rotations in a gas under the condition of the Boltzmann distribution over the energy levels [7, 8] and taking into account the modifications of formulas for relaxation times in a two-velocity two-temperature mixture [5, 8], we can write

$$\theta_1=\frac{\varepsilon_l-\varepsilon_l^0(T_1)}{\tau_{11}(n_1,T_1)},\quad \theta_2=\frac{\varepsilon_l-\varepsilon_l^0(T^*)}{\tau_{12}(n_2,T^*,T_e)}\quad \text{for}\quad l=1,$$
$$\theta_1=\frac{\varepsilon_l-\varepsilon_l^0(T^*)}{\tau_{21}(n_1,T^*,T_e)},\quad \theta_2=\frac{\varepsilon_l-\varepsilon_l^0(T_2)}{\tau_{22}(n_2,T_2)}\quad \text{for}\quad l=2.$$

Here T_e, the effective temperature, which ensures the fulfillment of the principle of detailed balance for the rates of excitation and deactivation of rotational degrees of freedom in collisions with the molecules of a two-temperature two-velocity medium, is determined by Chidiac et al. [8] and coincides with T^* within the framework of the acoustic approximation, $\varepsilon_l^0 = kT$ is the equilibrium rotational energy, $\tau_{ij} = z_{ij}\tau_{ij}^0$ is the time of rotational relaxation of the diatomic gas of the kind i in collisions with the molecules of the jth gas, τ_{ij}^0 is the mean time between the collisions of a molecule of the ith gas with the molecules of the jth gas, and z_{ij} is the number of collisions of a diatomic molecule of the ith kind with the jth molecules, which is necessary to establish rotational equilibrium. We used the following values of z_{ij} and σ_i: $\sigma_1 = 2.2 \cdot 10^{-10}$ m, $\sigma_2 = 4.94 \cdot 10^{-10}$ m, $z_{11} \approx 325$ [9], and $z_{12} \approx 350$ (approximation of data [7]) for the H_2–Xe system, and $\sigma_1 = 1.96 \cdot 10^{-10}$ m, $\sigma_2 = 4.45 \cdot 10^{-10}$ m, $z_{21} \approx 1.5$ [7, 10], and $z_{22} \approx 1$ (estimation based on formulas [11]) for the He–I_2 system. The time between molecular collisions was calculated using the formula for hard spheres $\tau_{ij}^0 = \pi m_{ij}/(4n_j\sigma_{ij}kT)$ [12], and the molecular constants were takes from [12].

As in [2], Eqs. (1) and (2) were nondimensionalized and linearized. The presence of the source terms related to rotational relaxation of diatomic molecules in Eq. (2) does not allow one to simplify the derivation of the dispersion relation and obtain compact formulas for the roots of this relation by introducing linear combinations of the parameters of a two-component mixture, as was done by Fernandez and Puri [2]. Instead of that, based on the compatibility condition of a system of acoustics equations in its original form (equality to zero of the determinant of the seventh-order matrix), we obtained a dispersion relation, which is a biquadratic equation for the dimensionless wavenumber s. The coefficients of this equation depend on the dimensionless frequency Ω and the parameters of the mixture: $s = k\lambda_{12}$ (k is the wavenumber), $\lambda_{12} = 1/(2^{1/2}\pi n\sigma_{12}^2)$ is the effective mean free path of the molecules (n is the concentration of molecules at $T = 300$ K and $p = 10^5$ Pa), $\Omega = \omega t_0$, $t_0 = \lambda_{12}/u_{01}$ is the characteristic time, which is used for nondimensionalizing of Eqs. (1) and (2), and $u_0 = (kT/m_1)^{1/2}$. The dimensionless values of the absorption factor β and the speed of sound $\bar{u} = u/u_{01}$ [u is the speed of sound in the mixture and $u_{01} = ((5/3)kT/m_1)^{1/2}$ is the Laplace speed of sound in a pure light gas] are determined by the real (Re) and imaginary (Im) parts of the root s_a of the dispersion relation, which describes the propagation of acoustic disturbances: $\beta = (5/3)^{1/2}\mathrm{Im}(s_a)/\Omega$ and $\bar{u} = (5/3)^{-1/2}\Omega/\mathrm{Re}(s_a)$. The characteristics of the process of propagation of small dissipative perturbations are not considered here (they are determined by another root s_d of the dispersion relation). The typical features of these processes are a monotonic increase in the propagation velocity from zero at $\Omega = 0$ to some asymptotic value at high Ω and a decrease (of the exponential type) in the absorption factor from high values at $\Omega = 0$ to zero as $\Omega \to \infty$. In contrast to [2], the calculation of the roots of the dispersion relation and the identification of their real and imaginary parts was performed on a computer.

The effect of rotational relaxation on the functions $\bar{u}(r)$ and $\beta(r)$ was studied by comparing the theoretical curves with and without account of this process. The main features of these curves are determined by the existence of some specific characteristics such as the critical composition and frequency (or the critical value of the parameter r^*) in systems consisting of molecules with disparate molecular mass. For concentrations of the light component close to the critical value c_1^*, these specific features are as follows:

1) for $c_1 = c_1^*$ and $r = r^*$, the propagation velocities of small perturbations according to the acoustic and dissipative mechanisms and the corresponding absorption factors coincide, and the degeneration of the roots of the dispersion relation $s_a = s_d$ is observed [1, 2];

2) the concentration c_1^* determines the boundary between two types of the dispersion curves $\bar{u}(r)$: there is negative dispersion ($\partial\bar{u}/\partial r < 0$) near r^* for $c_1 < c_1^*$ and positive dispersion ($\partial\bar{u}/\partial r > 0$) near r^* for $c_1 > c_1^*$ [1, 2];

3) for $c_1 = c_1^*$, the sound absorption factor has a sharp maximum at $r = r^*$.

For both increasing and decreasing c_1 relative to c_1^*, the peak value of β decreases and the dependence $\beta(r)$ becomes less steep. It should be noted that these properties of the acoustic characteristics were derived theoretically, the experimental verification has not been obtained for all concentrations c_1, and there are significant difficulties in interpretation of the measurement results for the speed of sound and the absorption factor within the range $0.45 \leqslant c_1 \leqslant 0.6$ [1, 2]. This is possibly connected with the fact that, for the above compositions of the mixture, the dissipative mechanism of transfer of small perturbations can transform to the acoustic mechanism at $r \approx r^*$; thus, a high-frequency degeneration and interaction of two acoustic-type modes occurs [1]. The range of concentrations mentioned by Bowler and Johnson [1] is called critical, and the theoretical and experimental results [1, 2] outside this range are in good agreement for the He–Xe mixtures.

A comparison of numerical results in the present work shows that the general shape of the curves $\bar{u}(r)$ and $\beta(r)$ plotted [1, 2] for mixtures of monatomic gases (He–Xe) is also typical of mixtures with a diatomic component. However, the difference in two systems considered is manifested in a different form.

The presence of molecular rotations has a slight effect on the critical parameters of the H_2–Xe mixture: $c_1^* = 0.481$ and $r^* = 4.08 \cdot 10^7$ MHz/Pa without regard for rotations of the H_2 molecules and $c_1^* = 0.474$ and $r^* = 4.08 \cdot 10^7$ MHz/Pa with account of them. Because of coincidence of the corresponding curves $\beta(r)$ and $\bar{u}(r)$ near $r = r^*$, their plots are not given here. As for other compositions of this mixture, the presence of molecular rotations is noticeable in the region $r \sim 5 \cdot 10^6$ MHz/Pa, where dispersion of the speed of sound caused by rotational relaxation occurs [7].

A significant effect of rotational degrees of freedom of molecules on the values of c_1^* and r^* is observed for the He–I_2 mixture: $c_1^* = 0.481$ and $r^* = 2.42 \cdot 10^7$ MHz/Pa without account of rotations of the I_2 molecules and $c_1^* = 0.504$ and $r^* = 2.28 \cdot 10^7$ MHz/Pa with account of them. The curves $\bar{u}(r)$ determined by two roots of the dispersion equation for the critical composition of the He–I_2 mixture are shown in Fig. 1. The calculations with account of molecular rotations (solid curves) and without it (dashed curves) are plotted; the curves corresponding to the acoustic and dissipative roots are marked by 1 and 2, respectively. Because of the small time of rotational relaxation of iodine, this process has a significant effect on the speed of sound within the

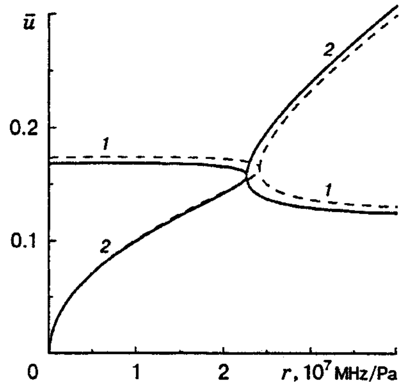

Fig. 1

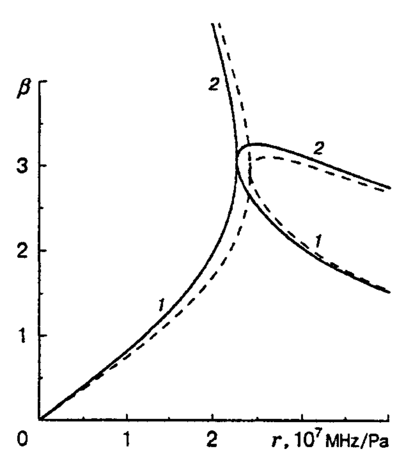

Fig. 2

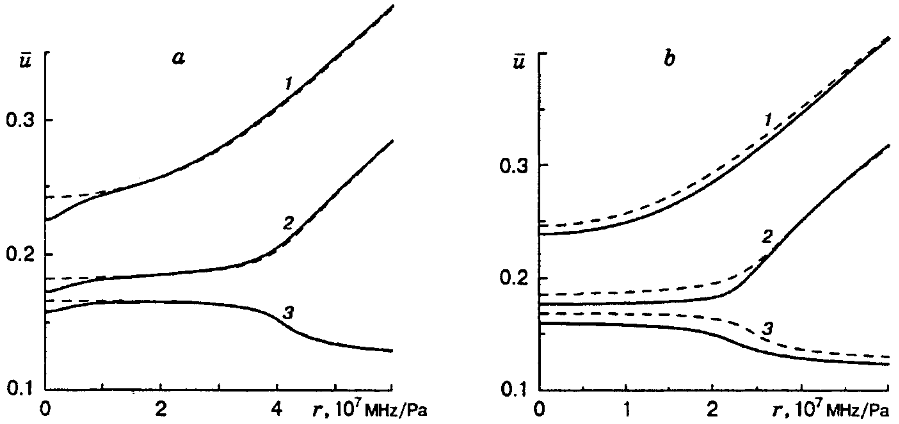

Fig. 3

entire range of r examined and significantly decreases this quantity as compared with its values for a mixture of monatomic gases. A shift of the critical frequency toward lower values is clearly seen in the figure.

The dependence $\beta(r)$ for the critical composition of the He–I_2 mixture is shown in Fig. 2. The effect of rotation of the I_2 molecules increases with increasing r and has a maximum at $r \approx r^*$ (the notation is the same as in Fig. 1).

Figure 3a shows the dispersion dependences for H_2–Xe mixtures of different compositions, the same for He–I_2 mixtures is plotted in Fig. 3b; curves 1–3 refer to the light-component concentrations of 0.75, 0.55, and 0.45 ($c_{01} = 0.45$ and 0.55 correspond to near-critical compositions, for which dramatic changes in the parameters should be observed in passing through the critical frequency); the calculation results with account of molecular rotations (solid curves) and without it (dashed curves) are plotted. Because of limited applicability of the Euler approximation at small values of c_1 (when the ignored contribution of thermal conductivity in energy equations becomes commensurable with the remaining terms [2]), the calculation data for $c_1 < 0.45$ are not presented here.

The effect of rotation of hydrogen molecules in H_2–Xe mixtures on the acoustic characteristics is manifested in the region of comparatively low frequencies ($r < 5 \cdot 10^6$ MHz/Pa, i.e., for frequencies close to the inverse time of rotational relaxation of hydrogen molecules in the mixture), where the transition from rotationally equilibrium to frozen speed of sound occurs, after which the curves with and without account of molecular rotations almost coincide. As the concentration of H_2 increases, the effects of low-frequency dispersion due to rotational relaxation become more and more noticeable in the graphs. In the range of values

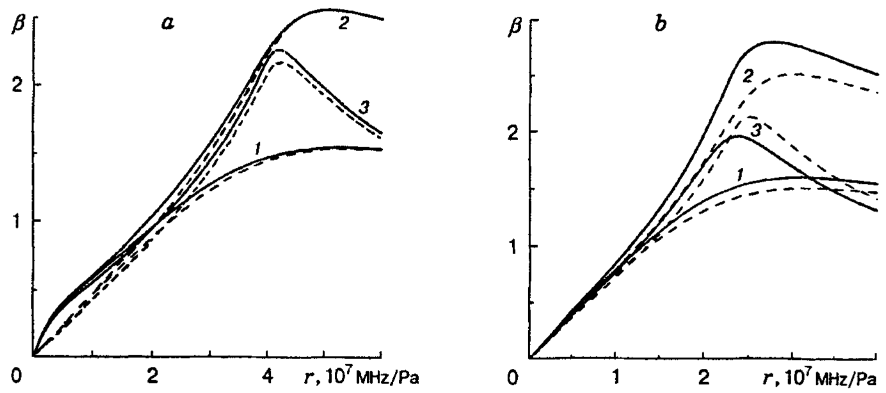

Fig. 4

of r close to r^*, where the above features of the behavior of dispersion curves are caused by the slow exchange of energy and momentum between hydrogen and xenon molecules, the rotations of hydrogen molecules are completely frozen, and the system can be considered as a mixture of monatomic gases [the functions $\bar{u}(r)$ with and without account of rotational relaxation are almost indistinguishable]. In the He–I_2 mixture, the rotations of iodine molecules I_2 lead to a downward shift of the dispersion curves, which is observed almost within the entire frequency range under study because of the high rate of rotational relaxation. The model of a mixture of monatomic gases is invalid for such a system.

Figure 4 shows the absorption factor for the H_2–Xe (a) and He–I_2 (b) mixtures (the notation corresponds to that used in Fig. 3). The rotations of H_2 molecules lead to an increase in the absorption factor, and the maximum of the rotational increment is in the range of frequencies close to the characteristic frequency of rotational relaxation. The character of this increment corresponds to the additive effect of the relaxation process on the absorption of sound. In this case, the contributions to β caused by different mechanisms of energy dissipation can be considered independently.

The effect of rotations of iodine molecules in the He–I_2 mixture is manifested in a different way. For low concentrations of the light component, this effect is comparatively small. For compositions close to the critical one, it is manifested more clearly and leads to a significant increase in the absorption factor in the range of r close to the critical value and to a shift of the maximum of the function $\beta(r)$. This indicates that the process of rotational relaxation of iodine molecules depends on the temperature–velocity relaxation of the components, i.e., a single process of "rotational–temperature–velocity" relaxation occurs, and the influence regions of individual nonequilibrium processes in the frequency scale are not separated.

The above considerations allow the following conclusions.

1. Rotational–translational relaxation does not lead to significant qualitative changes in the frequency dependence of the speed of sound and the absorption factor, which are typical of gas mixtures with disparate molecular masses [1, 2].

2. If the time of rotational relaxation of diatomic molecules is much greater than the mean free time (in the H_2–Xe mixture), the influence region of rotational relaxation is located within the range of comparatively low frequencies (of the order of the characteristic frequency of this process). In this case, the changes in acoustic characteristics of the mixture near the critical frequency occur at the frozen rotational energy of the molecules, as happens in monatomic gas mixtures, and the influence of molecular rotations on the critical composition of the mixture and the critical value of the parameter r is insignificant. If the time of rotational relaxation is little different from the mean free time (in the He–I_2 mixture), the effect of this process on the speed of sound and the absorption factor is significant within the entire range of frequencies and leads to a noticeable change in the critical value r^*.

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