

Nonlinear Influence of Sound on the Vibrational Energy of Molecules in a Relaxing Gas

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Dynamics of a weakly nonlinear and weakly dispersive flow of a gas where molecular vibrational relaxation takes place is studied. Variations in the vibrational energy in the field of intense sound is considered. These variations are caused by a nonlinear transfer of the acoustic energy into energy of vibrational degrees of freedom in a relaxing gas. The final dynamic equation which describes this is instantaneous, it includes a quadratic nonlinear acoustic source reflecting the nonlinear character of interaction of high-frequency acoustic and non-acoustic motions in a gas. All types of sound, periodic or aperiodic, may serve as an acoustic source. Some conclusions about temporal behavior of the vibrational mode caused by periodic and aperiodic sounds are made.

Keywords: relaxing gas, non-equilibrium media, nonlinear effects of sound.

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1. Introduction. Basic equations and starting points

The attention of physicists to non-equilibrium phenomena, particularly to non-equilibrium gases, was attracted by some fundamental results, both experimental and theoretical. In the sixties, these results provided a laser revolution (ZELDOVICH, RAIZER, 1966; GORDIETS *et al.*, 1973; OSIPOV, UVAROV, 1992). The establishment of a non-equilibrium molecular physics began due to the progress in laser technique and research in physics and chemistry that followed. Non-equilibrium gases embrace not only active gases used in lasers but discharge plasma, rarified levels of the upper atmosphere, interstellar media, and so on. The mechanism of a retarded energy exchange between the internal and translational degrees of freedom of the molecules is the reason for an anomalous dispersion and absorption of ultrasonic waves (ZELDOVICH, RAIZER, 1966; OSIPOV, UVAROV, 1992; KOGAN, MOLEVICH, 1986). Interest in non-equilibrium phenomena in the physics of gases was first connected with studies of these anomalies (OSIPOV, UVAROV, 1992; KOGAN, MOLEVICH, 1986; MOLEVICH *et al.*, 2005). The general theory of thermodynamic relaxation was created by MANDELSHTAM and LEON-

TOVICH (1947). The hydrodynamics of non-equilibrium fluids is a quickly developing area of a scientific knowledge.

This paper is devoted to a nonlinear phenomenon caused by a high-frequency sound in a vibrationally relaxing gas. This is an interaction of the sound with a non-acoustic vibrational mode leading to a nonlinear generation of a non-wave part of the vibrational energy by the dominative sound. As far as the author knows, it is a new subject to study. Losses in the acoustic energy in a standard thermoviscous fluid always increase the background temperature, and this phenomenon is called acoustic heating (RUDENKO, SOLUYAN, 1977; MAKAROV, OCHMANN, 1996). It was first discovered by Molevich that the nonlinear exchange of energy between the sound and the thermal mode may lead to a cooling instead of heating in a gas where non-equilibrium relaxation takes place (MOLEVICH, 2002). The sound itself enhances anomalously (MOLEVICH, 2003).

We start from a linear determination of modes as specific types of fluid motion in a simple case of motions in a gas whose steady but non-equilibrium state is maintained by pumping the energy into the vibrational degrees of freedom by the power I and heat withdrawal from the translational degrees of freedom of the power

Q , both I and Q refer to the unit mass (Sec. 2). The relaxation equation for the vibrational energy per unit mass complements the system of conservation equations in the differential form. It has the form:

$$\frac{d\varepsilon}{dt} = -\frac{\varepsilon - \varepsilon_{eq}(T)}{\tau(\rho, T)} + I. \quad (1)$$

The equilibrium value for the vibrational energy at a given temperature T is denoted by $\varepsilon_{eq}(T)$, and $\tau(\rho, T)$ is the vibrational relaxation time. For a system of harmonic oscillators,

$$\varepsilon_{eq}(T) = \frac{\hbar\Omega}{m(\exp(\hbar\Omega/k_B T) - 1)}, \quad (2)$$

where m is the molecule mass, $\hbar\Omega$ is the magnitude of the vibrational quantum, and k_B is the Boltzmann constant. Equation (2) is valid over the temperatures where one can neglect anharmonic effects, i.e., below the characteristic temperatures which are fairly high for most molecules (ZELDOVICH, RAIZER, 1966; GORDIETS *et al.*, 1973; OSIPOV, UVAROV, 1992). The mass, momentum and energy conservation equations governing the thermoviscous flow in a vibrationally relaxing gas read:

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \nabla(\rho \mathbf{v}) &= 0, \\ \rho \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \nabla) \mathbf{v} \right] &= -\nabla p + \eta \Delta \mathbf{v} + \frac{\eta}{3} \nabla(\nabla \mathbf{v}), \\ \rho \left[\frac{\partial(e + \varepsilon)}{\partial t} + (\mathbf{v} \nabla)(e + \varepsilon) \right] + p \nabla \mathbf{v} &= \chi \Delta T \\ &+ \rho(I - Q) + \frac{\eta}{2} \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} - \frac{2}{3} \delta_{ik} \frac{\partial v_l}{\partial x_l} \right)^2, \end{aligned} \quad (3)$$

where \mathbf{v} denotes the velocity of the fluid, ρ , p are the density and pressure, e marks the internal energy per unit mass of the translation motion of molecules, η is the shear viscosity, χ denotes the thermal conductivity (η and χ supposed to be constants), x_i ($i = 1, 2, 3$) are space coordinates, δ_{ik} is the Kronecker symbol, it equals 1 if $i = k$ and 0 otherwise. Two thermodynamic functions $e(p, \rho)$ and $T(p, \rho)$ complete the system (3). Thermodynamics of ideal gases provides

$$e(p, \rho) = \frac{R}{\mu(\gamma - 1)} T(p, \rho) = \frac{p}{(\gamma - 1)\rho}, \quad (4)$$

where $\gamma = C_{P,\infty}/C_{V,\infty}$ is the isentropic exponent with no account of vibrational degrees of freedom ($C_{P,\infty}$ and $C_{V,\infty}$ denote “frozen” heat capacities correspondent to very quick processes), R is the universal gas constant, and μ is the molar mass of a gas.

2. Dispersion relations. One-dimensional motions of infinitely small amplitude and their decomposing

Let us start with considering the motion of a gas with infinitely small amplitude when $\eta = 0$, $\chi = 0$, $I = Q$. Every quantity q is represented as a sum of an unperturbed value q_0 (in the absence of the background flows, $v_0 = 0$) and its variation q' . The flow is supposed to be one-dimensional along the axis Ox . First, relations of excess perturbations specific for every mode should be established. These relations will be fixed going to a weakly nonlinear flow. That makes it possible to decompose equations governing the sound and non-wave modes accounting for their interactions correctly (Sec. 3). Following Molevich (MOLEVICH, 2003; 2004; MAKARYAN, MOLEVICH, 2007), we consider a weak transversal pumping which may vary the background quantities in the transversal direction of the axis Ox . It is assumed that the background stationary quantities are constant along the axis Ox .

The governing equations of continuity and the momentum and energy balance may be easily rearranged into the following ones:

$$\begin{aligned} \frac{\partial v'}{\partial t} + \frac{1}{\rho_0} \frac{\partial p'}{\partial x} &= 0, \\ \frac{\partial p'}{\partial t} + \gamma p_0 \frac{\partial v'}{\partial x} - (\gamma - 1) \rho_0 \frac{\varepsilon'}{\tau} &+ (\gamma - 1) \rho_0 T_0 \Phi_1 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right) = 0, \\ \frac{\partial \rho'}{\partial t} + \rho_0 \frac{\partial v'}{\partial x} &= 0, \\ \frac{\partial \varepsilon'}{\partial t} + \frac{\varepsilon'}{\tau} - T_0 \Phi_1 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right) &= 0, \end{aligned} \quad (5)$$

where

$$\begin{aligned} \Phi_1 &= \left(\frac{C_{V,eq}}{\tau} + \frac{\varepsilon - \varepsilon_{eq}}{\tau^2} \frac{d\tau}{dT} \right)_0, \\ C_{V,eq} &= \left(\frac{d\varepsilon_{eq}}{dT} \right)_0. \end{aligned} \quad (6)$$

The expansions in the series of equations of state (4) was used in the second and fourth equations from (5):

$$e' = \frac{R}{\mu(\gamma - 1)} T' = \frac{p_0}{(\gamma - 1)\rho_0} \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right). \quad (7)$$

The last equation in the set (5) follows from Eqs. (1) and (7):

$$\begin{aligned} \frac{\partial \varepsilon'}{\partial t} + \frac{\varepsilon'}{\tau} &= \left(\frac{C_{V,eq}}{\tau} + \frac{\varepsilon - \varepsilon_{eq}}{\tau^2} \frac{d\tau}{dT} \right)_0 T' \\ &= T_0 \left(\frac{C_{V,eq}}{\tau} + \frac{\varepsilon - \varepsilon_{eq}}{\tau^2} \frac{d\tau}{dT} \right)_0 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right). \end{aligned} \quad (8)$$

The relaxation time in the most important cases may be thought as a function of the temperature according to Landau and Teller in the form: $\tau(T) = A \exp(BT^{-1/3})$, where A and B are some positive constants, which gives negative values of $d\tau/dT$ (ZELDOVICH, RAIZER, 1966; GORDIETS *et al.*, 1973; OSIPOV, UVAROV, 1992). It is the simplest but most physically justified model (ZELDOVICH, RAIZER, 1966).

Let us start the study of motions with infinitely small amplitudes with representing of all perturbations as a sum of planar waves, where $\tilde{q}(k) \exp(i\omega(k)t)$ is the Fourier-transform of any perturbation q' :

$$q'(x, t) = \int_{-\infty}^{\infty} \tilde{q}(k) \cdot \exp i(\omega t - kx) dk + \text{complex conjugate.} \quad (9)$$

The dispersion equation follows from Eqs. (5):

$$\omega (i\Phi_1(\gamma - 1)T_0\tau(c^2k^2 - \gamma\omega^2) + c^2(c^2k^2 - \omega^2)(i - \omega\tau)) = 0, \quad (10)$$

where $c = \sqrt{\frac{\gamma RT_0}{\mu}} = \sqrt{\gamma p_0/\rho_0}$ is the “frozen”, infinitely small signal sound speed in an ideal uniform gas.

Approximate roots of the dispersion equation for both acoustic branches, progressive in the positive and negative directions of the axis Ox , are well known under the simplifying condition $\omega\tau \gg 1$ which restricts consideration by the high-frequency sound (OSIPOV, UVAROV, 1992; MOLEVICH, 2003)

$$\begin{aligned} \omega_1 &= ck + \frac{i(\gamma - 1)^2 T_0}{2c^2} \Phi_1, \\ \omega_2 &= -ck + \frac{i(\gamma - 1)^2 T_0}{2c^2} \Phi_1. \end{aligned} \quad (11)$$

The last term in the both dispersion relations manifests an amplification of the sound in a non-equilibrium regime (if $\Phi_1 < 0$) which does not depend on the wavenumber k . The amplification effect increases with a growth of $|d\tau/dT|$ and vibrational disequilibrium $m(\varepsilon - \varepsilon_{eq})/k_B T$. The two last roots of the dispersive equation, estimated without the limitation $\omega\tau \gg 1$, have the following form:

$$\begin{aligned} \omega_3 &= i \left(\frac{1}{\tau} + \frac{(\gamma - 1)(\gamma + c^2 k^2 \tau^2) T_0}{c^2 (1 + c^2 k^2 \tau^2)} \Phi_1 \right), \\ \omega_4 &= 0. \end{aligned} \quad (12)$$

The third mode comes from the vibrational relaxation. The fourth root represents the thermal, or entropy, mode. In an equilibrium gas, this type of a non-wave motion specifies perturbation in the background temperature and correspondent variation in its density. It is well established that nonlinear losses in the acoustic energy in a gas with typical thermoviscous attenuation lead to heating of the background, and by means

of that, influence on the sound velocity in a fluid. The last two roots manifest slow varying and stationary, non-wave motions of a gas.

In accordance to Eqs. (5) and the roots (11), (12), the Fourier transforms of the dynamic variables may be represented as linear combinations of four specific Fourier transforms of the excess density $\tilde{\rho}_1, \tilde{\rho}_2, \tilde{\rho}_3, \tilde{\rho}_4$ as follows:

$$\begin{aligned} \tilde{v} &= \sum_{n=1}^4 \omega_n \tilde{\rho}_n / (k\rho_0), \\ \tilde{p} &= \sum_{n=1}^4 \omega_n^2 \tilde{\rho}_n / k^2, \\ \tilde{\rho} &= \sum_{n=1}^4 \tilde{\rho}_n, \\ \tilde{\varepsilon} &= \frac{T_0 \Phi_1}{\rho_0 c^2} \sum_{n=1}^2 \left(\frac{\gamma \omega_n^2}{k^2} - c^2 \right) \frac{\tilde{\rho}_n}{i\omega_n} + \left(\frac{\gamma \omega_3^2}{k^2} - c^2 \right) \cdot \frac{T_0 \Phi_1}{\rho_0 c_\infty^2} \frac{\tilde{\rho}_3}{i\omega_3 + 1/\tau} + \frac{\tau T_0 \Phi_1}{\rho_0 c^2} \left(\frac{\gamma \omega_4^2}{k^2} - c^2 \right) \tilde{\rho}_4. \end{aligned} \quad (13)$$

Thus, perturbation in the velocity, pressure, or energy of every dynamic variable may be expressed in terms of specific excess densities. The correspondent formulas in the (x, t) space follow from Eqs. (13) and the roots of the dispersion equation, i.e., Eqs. (11), (12), keeping in mind that the overall excess velocity, pressure, density, and internal energy are sums of specific parts:

$$\begin{aligned} v'(x, t) &= \sum_{n=1}^4 v'_n(x, t), p'(x, t) \\ &= \sum_{n=1}^4 p'_n(x, t), \rho'(x, t) = \sum_{n=1}^4 \rho'_n(x, t), \varepsilon'(x, t) \\ &= \sum_{n=1}^4 \varepsilon'_n(x, t). \end{aligned} \quad (14)$$

Relations of acoustic right- and leftwards progressive waves in the high-frequency regime ($ck\tau \gg 1$) follow from the dispersion relations $\omega_1(k), \omega_2(k)$, i.e., Eqs. (11), and Eqs. (13):

$$\begin{aligned} v'_1(x, t) &= \frac{c}{\rho_0} \left(1 - B \int dx \right) \rho'_1(x, t), \\ p'_1(x, t) &= c^2 \left(1 - 2B \int dx \right) \rho'_1(x, t), \\ \varepsilon'_1(x, t) &= \frac{2Bc^2}{(\gamma - 1)\rho_0} \int dx \rho'_1(x, t), \\ v'_2(x, t) &= -\frac{c}{\rho_0} \left(1 + B \int dx \right) \rho'_2(x, t), \\ p'_2(x, t) &= c^2 \left(1 + 2B \int dx \right) \rho'_2(x, t), \\ \varepsilon'_2(x, t) &= -\frac{2Bc^2}{(\gamma - 1)\rho_0} \int dx \rho'_2(x, t), \end{aligned} \quad (15)$$

where

$$B = -\frac{(\gamma - 1)^2 T_0}{2c^3} \Phi_1. \quad (16)$$

The sound is imposed to be a wave process, so that it attenuates (or amplifies, in dependence to the sign of B) weakly over the wavelength, $|B|k \ll 1$. The third mode possesses the following leading-order relationships:

$$\begin{aligned} v'_3(x, t) &= \frac{1}{\rho_0 \tau} \int dx \rho'_3(x, t), \\ p'_3(x, t) &= 0, \\ \varepsilon'_3(x, t) &= \frac{c^2}{(\gamma - 1)\rho_0} \rho'_3(x, t). \end{aligned} \quad (17)$$

The equalities defining the thermal mode correspond to an isobaric motion:

$$\begin{aligned} v'_4(x, t) &= 0, \quad p'_4(x, t) = 0, \\ \varepsilon'_4(x, t) &= -\frac{T_0 \Phi_1 \tau}{\rho_0} \rho'_4(x, t). \end{aligned} \quad (18)$$

Relations (15)–(18) along with the linear property of superposition, Eq. (14), point out a way of combining four equations from (5) in order to get dynamic equations for perturbation of only one specific mode. Application of a matrix operator on the vector of overall perturbations (v' p' ρ' ε') actually decomposes the correspondent specific mode:

$$P_n \begin{pmatrix} v'(x, t) \\ p'(x, t) \\ \rho'(x, t) \\ \varepsilon'(x, t) \end{pmatrix} = \begin{pmatrix} v'_n(x, t) \\ p'_n(x, t) \\ \rho'_n(x, t) \\ \varepsilon'_n(x, t) \end{pmatrix}, \quad n = 1, \dots, 4. \quad (19)$$

Within the accuracy up to the terms of the first order in $(ck\tau)^{-1}$, ($|B|k$), projectors take the form as follows ($n = 1, \dots, 4$):

$$P_n = \begin{pmatrix} P_{n(1,1)} & P_{n(1,2)} & P_{n(1,3)} & P_{n(1,4)} \\ P_{n(2,1)} & P_{n(2,2)} & P_{n(2,3)} & P_{n(2,4)} \\ P_{n(3,1)} & P_{n(3,2)} & P_{n(3,3)} & P_{n(3,4)} \\ P_{n(4,1)} & P_{n(4,2)} & P_{n(4,3)} & P_{n(4,4)} \end{pmatrix}, \quad (20)$$

where

$$\begin{aligned} P_{1(1,1)} &= \frac{1}{2} + \frac{B}{2} \int dx, \\ P_{1(1,2)} &= \frac{1}{2c\rho_0} - \frac{B}{c\rho_0(\gamma - 1)} \int dx, \\ P_{1(1,3)} &= \frac{Bc}{\rho_0(\gamma - 1)} \int dx, \\ P_{1(1,4)} &= -\frac{(\gamma - 1)}{2c^2\tau} \int dx, \end{aligned}$$

$$\begin{aligned} P_{1(2,1)} &= \frac{c\rho_0}{2}, \\ P_{1(2,2)} &= \frac{1}{2} - \frac{(\gamma + 1)B}{2(\gamma - 1)} \int dx, \\ P_{1(2,3)} &= \frac{B}{(\gamma - 1)c^2} \int dx, \\ P_{1(2,4)} &= -\frac{\rho_0}{2c\tau} \int dx, \\ P_{1(3,1)} &= \frac{\rho_0}{2c} + \frac{B\rho_0}{c} \int dx, \\ P_{1(3,2)} &= \frac{1}{2c^2} + \frac{B(\gamma - 3)}{2(\gamma - 1)c^2} \int dx, \\ P_{1(3,3)} &= \frac{B}{(\gamma - 1)} \int dx, \\ P_{1(3,4)} &= \frac{(\gamma - 1)\rho_0}{2c^3\tau} \int dx, \\ P_{1(4,1)} &= \frac{Bc}{(\gamma - 1)} \int dx, \\ P_{1(4,2)} &= \frac{B}{\rho_0(\gamma - 1)} \int dx, \\ P_{1(4,3)} &= P_{1(4,4)} = 0, \\ P_{2(1,1)} &= \frac{1}{2} - \frac{B}{2} \int dx, \\ P_{2(1,2)} &= -\frac{1}{2c\rho_0} - \frac{B}{c\rho_0(\gamma - 1)} \int dx, \\ P_{2(1,3)} &= \frac{Bc}{\rho_0(\gamma - 1)} \int dx, \\ P_{2(1,4)} &= -\frac{(\gamma - 1)}{2c^2\tau} \int dx, \\ P_{2(2,1)} &= -\frac{c\rho_0}{2}, \\ P_{2(2,2)} &= \frac{1}{2} + \frac{(\gamma + 1)B}{2(\gamma - 1)} \int dx, \\ P_{2(2,3)} &= -\frac{B}{(\gamma - 1)c^2} \int dx, \\ P_{2(2,4)} &= \frac{\rho_0}{2c\tau} \int dx, \\ P_{2(3,1)} &= -\frac{\rho_0}{2c} + \frac{B\rho_0}{c} \int dx, \\ P_{2(3,2)} &= \frac{1}{2c^2} - \frac{B(\gamma - 3)}{2(\gamma - 1)c^2} \int dx, \\ P_{2(3,3)} &= -\frac{B}{(\gamma - 1)} \int dx, \\ P_{2(3,4)} &= -\frac{(\gamma - 1)\rho_0}{2c^3\tau} \int dx, \\ P_{2(4,1)} &= \frac{Bc}{(\gamma - 1)} \int dx, \end{aligned}$$

$$\begin{aligned}
 P_{2(4,2)} &= -\frac{B}{\rho_0(\gamma-1)} \int dx, \\
 P_{2(4,3)} &= P_{2(4,4)} = 0, \\
 P_{3(1,1)} &= 0, \\
 P_{3(1,2)} &= \frac{2B}{c\rho_0(\gamma-1)} \int dx, \\
 P_{3(1,3)} &= -\frac{2Bc}{\rho_0(\gamma-1)} \int dx, \\
 P_{3(1,4)} &= \frac{(\gamma-1)}{c^2\tau} \int dx, \\
 P_{3(2,1)} &= P_{3(2,2)} = P_{3(2,3)} = P_{3(2,4)} = 0, \\
 P_{3(3,1)} &= -\frac{2B\rho_0}{c} \int dx, \\
 P_{3(3,2)} &= \frac{2B\tau}{(\gamma-1)c}, \\
 P_{3(3,3)} &= -\frac{2B\tau c}{(\gamma-1)}, \\
 P_{3(3,4)} &= \frac{(\gamma-1)\rho_0}{c^2} + \frac{2B\rho_0\tau}{c}, \\
 P_{3(4,1)} &= -\frac{2Bc}{(\gamma-1)} \int dx, \\
 P_{3(4,2)} &= \frac{2Bc\tau}{\rho_0(\gamma-1)^2}, \\
 P_{3(4,3)} &= -\frac{2Bc^3\tau}{\rho_0(\gamma-1)^2}, \\
 P_{3(4,4)} &= 1 + \frac{2B\tau c}{(\gamma-1)}, \\
 P_{4(1,1)} &= P_{4(1,2)} = P_{4(1,3)} = P_{4(1,4)} = 0, \\
 P_{4(2,1)} &= P_{4(2,2)} = P_{4(2,3)} = P_{4(2,4)} = 0, \\
 P_{4(3,1)} &= 0, \\
 P_{4(3,2)} &= -\frac{1}{c^2} - \frac{2B\tau}{(\gamma-1)c}, \\
 P_{4(3,3)} &= 1 + \frac{2B\tau c}{\gamma-1}, \\
 P_{4(3,4)} &= -\frac{(\gamma-1)\rho_0}{c^2} - \frac{2B\rho_0\tau}{c}, \\
 P_{4(4,1)} &= 0, \\
 P_{4(4,2)} &= -\frac{2Bc\tau}{\rho_0(\gamma-1)^2}, \\
 P_{4(4,3)} &= \frac{2Bc^3\tau}{\rho_0(\gamma-1)^2}, \\
 P_{4(4,4)} &= -\frac{2B\tau c}{(\gamma-1)}.
 \end{aligned}$$

Projectors P_1, \dots, P_4 form a full orthogonal set of projectors:

$$\begin{aligned}
 P_n \cdot P_m &= P_n, \quad P_n \cdot P_m = \bar{0} \quad (n \neq m), \\
 \sum_{n=1}^4 P_n &= \bar{E}, \quad n, m = 1, \dots, 4,
 \end{aligned} \quad (21)$$

where $\bar{0}$ and \bar{E} denote the zero and unit matrix operators, correspondingly. The remarkable property of projectors is that then decompose the dynamic equations governing the correspondent mode by an immediate appliance on the linear system (5):

$$\begin{aligned}
 P_n \left(\frac{\partial}{\partial t} \begin{pmatrix} v' \\ p' \\ \rho' \\ \varepsilon' \end{pmatrix} + \bar{L} \begin{pmatrix} v' \\ p' \\ \rho' \\ \varepsilon' \end{pmatrix} \right) \\
 = \frac{\partial}{\partial t} \begin{pmatrix} v'_n \\ p'_n \\ \rho'_n \\ \varepsilon'_n \end{pmatrix} + \bar{L} \begin{pmatrix} v'_n \\ p'_n \\ \rho'_n \\ \varepsilon'_n \end{pmatrix} = 0.
 \end{aligned} \quad (22)$$

where \bar{L} is the matrix operator correspondent to the system (5). Employment of the second rows of P_1 or P_2 on the system (5) distinguishes the governing equations for the specific acoustic pressures p'_1 or p'_2 , respectively:

$$\begin{aligned}
 \frac{\partial p'_1}{\partial t} + c \frac{\partial p'_1}{\partial x} - cBp'_1 &= 0, \\
 \frac{\partial p'_2}{\partial t} - c \frac{\partial p'_2}{\partial x} - cBp'_2 &= 0,
 \end{aligned} \quad (23)$$

which obviously coincide with the roots of the dispersion equation, i.e., ω_1 and ω_2 from Eqs. (11). Application of the last rows of P_3 or P_4 on Eqs. (5) decomposes the equations for the excess specific energies as follows, correspondingly:

$$\frac{\partial \varepsilon'_3}{\partial t} + \left(\frac{1}{\tau} - \frac{2Bc}{\gamma-1} \right) \varepsilon'_3 = 0, \quad \frac{\partial \varepsilon'_4}{\partial t} = 0. \quad (24)$$

These equations coincide with ω_3 and ω_4 established by Eqs. (15). Projecting in problems of weakly nonlinear flows was worked out and applied by the author in the studies of acoustic streaming and heating in standard thermoviscous flows (PERELOMOVA, 2003; 2006), as well as in some weakly dispersive flows.

3. Interaction of the dominative sound and non-acoustic types of motion in a weakly nonlinear flow

3.1. Decomposition of dynamic equations in a weakly nonlinear flow

Account for the nonlinear terms of the second order in the relaxation Eq. (1) and the state Eqs. (4) yields the leading order equalities:

$$\begin{aligned}
 T' &= T_0 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} + \frac{\rho'^2}{\rho_0^2} - \frac{p'\rho'}{p_0\rho_0} \right), \\
 \frac{d\varepsilon'}{dt} &= -\frac{\varepsilon'}{\tau} + T_0 \left(\frac{1}{\tau^2} \frac{d\tau}{dT} \right)_0 \varepsilon' \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right) \\
 &\quad + T_0\Phi_1 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} + \frac{\rho'^2}{\rho_0^2} - \frac{p'\rho'}{p_0\rho_0} \right) \\
 &\quad + T_0\Phi_2 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right)^2, \tag{25}
 \end{aligned}$$

where

$$\begin{aligned}
 \Phi_2 &= T_0 \left(-\frac{1}{\tau^2} C_{V,eq} \frac{d\tau}{dT} - \frac{(\varepsilon_0 - \varepsilon_{eq})}{\tau^3} \left(\frac{d\tau}{dT} \right)^2 \right. \\
 &\quad \left. + \frac{1}{2\tau} \frac{dC_{V,eq}}{dT} + \frac{(\varepsilon_0 - \varepsilon_{eq})}{2\tau^2} \frac{d^2\tau}{dT^2} \right)_0.
 \end{aligned}$$

The governing dynamic system with the account for quadratic nonlinear terms differs from (5) by the quadratic right-hand side:

$$\frac{\partial v'}{\partial t} + \frac{1}{\rho_0} \frac{\partial p'}{\partial x} = -v' \frac{\partial v'}{\partial x} + \frac{\rho'}{\rho_0^2} \frac{\partial p'}{\partial x},$$

$$\begin{aligned}
 \frac{\partial p'}{\partial t} + \gamma p_0 \frac{\partial v'}{\partial x} - (\gamma - 1) \rho_0 \frac{\varepsilon'}{\tau} \\
 + (\gamma - 1) \rho_0 T_0 \Phi_1 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right) &= -v' \frac{\partial p'}{\partial x} - \gamma p' \frac{\partial v'}{\partial x} \\
 + (\gamma - 1) \rho' \left(\frac{\varepsilon'}{\tau} - T_0 \Phi_1 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right) \right) \\
 - (\gamma - 1) \rho_0 \left(T_0 \left(\frac{1}{\tau^2} \frac{d\tau}{dT} \right)_0 \varepsilon' \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right) \right. \\
 \left. + T_0 \Phi_1 \left(\frac{\rho'^2}{\rho_0^2} - \frac{p'\rho'}{p_0\rho_0} \right) + T_0 \Phi_2 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right)^2 \right), \tag{26}
 \end{aligned}$$

$$\frac{\partial \rho'}{\partial t} + \rho_0 \frac{\partial v'}{\partial x} = -v' \frac{\partial \rho'}{\partial x} - \rho' \frac{\partial v'}{\partial x},$$

$$\begin{aligned}
 \frac{\partial \varepsilon'}{\partial t} + \frac{\varepsilon'}{\tau} - T_0 \Phi_1 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right) \\
 = T_0 \left(\frac{1}{\tau^2} \frac{d\tau}{dT} \right)_0 \varepsilon' \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right) \\
 + T_0 \Phi_1 \left(\frac{\rho'^2}{\rho_0^2} - \frac{p'\rho'}{p_0\rho_0} \right) \\
 + T_0 \Phi_2 \left(\frac{p'}{p_0} - \frac{\rho'}{\rho_0} \right)^2 - v' \frac{\partial \varepsilon'}{\partial x}.
 \end{aligned}$$

The left-hand sides of Eqs. (26) may be successfully decomposed into specific parts by projecting. The right-hand nonlinear terms become distributed between specific dynamic equations by projecting in the correct way as well: a sum of all projectors is the unit operator. The non-linear right-hand parts of Eqs. (26) include terms of all modes, and further analysis depends on the portion of every mode there.

3.2. Weakly nonlinear equation governing sound

The most important problems relate to dominative (intense) sound and nonlinear phenomena in its field. The mode is dominative with respect to other modes if amplitudes of its perturbations are much larger than that of other modes. The equation governing the sound may be readily obtained by applying of acoustic projectors on the system (26). It is valid over the temporal and spatial domains where sound holds dominative, because a weak nonlinearity presupposes a slow growth of the secondary modes, and they may become comparable in the amplitude with the dominative sound. We will consider the first acoustic mode and nonlinear generation of the third mode in its field. Applying of the second row of P_1 on Eqs. (26) and replacing all nonlinear terms by those specific for the sound one readily obtains the following equation:

$$\frac{\partial p'_1}{\partial t} + c \frac{\partial p'_1}{\partial x} - c B p'_1 = \frac{\gamma + 1}{2\rho_0 c} p'_1 \frac{\partial p'_1}{\partial x}. \tag{27}$$

3.3. Equation governing the relaxation mode

At this point we make routine manipulations to decompose the dynamic equation for the specific excess energy of the vibrational mode by applying on the system (26) of the fourth row of projector P_3 and collecting together terms of the leading order. Only dominative acoustic terms are held in the right-hand non-linear part, which may be expressed in terms of the acoustic excess pressure in view of Eqs. (15):

$$\begin{aligned}
 \frac{\partial \varepsilon'_3}{\partial t} + \left(\frac{1}{\tau} - \frac{2Bc}{\gamma - 1} \right) \varepsilon'_3 &= -\frac{2B\tau(\gamma + 1)}{\rho_0^2(\gamma - 1)^2} p'_1 \frac{\partial p'_1}{\partial x} \\
 + T_0 \left(\frac{1}{\tau^2} \frac{d\tau}{dT} \right)_0 \frac{2B}{\rho_0^2 c^2} p'_1 \int p'_1 dx \\
 + \frac{T_0 \Phi_2 (\gamma - 1)^2 p_1'^2}{\rho_0^2 c^4}. \tag{28}
 \end{aligned}$$

The acoustic pressure in the right-hand side should itself satisfy the dynamic Eq. (27). Equation (28) is instantaneous and applies to the periodic or aperiodic high-frequency sound. It is the leading-order equation accounting for a weak nonlinearity and dispersion.

4. Examples

4.1. Periodic sound

A solution of the linear wave equation may be preliminary considered for the acoustic pressure:

$$p'_1(x, t) = P_0 \sin(\omega_1(t - x/c)), \tag{29}$$

where P_0 is a constant. Equation (28) after averaging over the sound period $2\pi/\omega_1$ rearranges in the leading order into:

$$\frac{\partial \langle \varepsilon'_3 \rangle}{\partial t} + \left(\frac{1}{\tau} - \frac{2Bc}{\gamma - 1} \right) \langle \varepsilon'_3 \rangle = \frac{T_0 \Phi_2 (\gamma - 1)^2}{2\rho_0^2 c^4} P_0^2, \quad (30)$$

where square brackets denote averaging over the sound period.

After integrating with the initial condition $\langle \varepsilon'_3 \rangle|_{t=0} = 0$, a variation in the vibrational energy of the third mode takes the form:

$$\langle \varepsilon'_3 \rangle \approx \varepsilon'_3 = \frac{T_0 \Phi_2 (\gamma - 1)^2}{2\alpha \rho_0^2 c^4} P_0^2 (1 - e^{-\alpha t}), \quad (31)$$

$$\alpha = \frac{1}{\tau} - \frac{2Bc}{\gamma - 1},$$

if $\alpha \neq 0$. For small αt , $\varepsilon'_3 \approx \frac{T_0 \Phi_2 (\gamma - 1)^2}{2\rho_0^2 c^4} P_0^2 t$. Equation (31) is valid over the temporal domain where the sound still remains dominant:

$$\begin{aligned} \text{Max} |\varepsilon_1(x, t)| &= \text{Max} \left| \frac{2B}{(\gamma - 1)\rho_0} \int dx p'_1 \right| \\ &= \left| \frac{2BcP_0}{(\gamma - 1)\rho_0 \omega_1} \right| \gg |\langle \varepsilon_3(x, t) \rangle|. \end{aligned} \quad (32)$$

The sound is dominant comparatively to the non-acoustic modes but the excess pressure caused by it must be small due to a weak nonlinearity of the flow: $P_0 \ll p_0$. The sign of α determines whether the relaxation mode enhances in time ($\alpha < 0$) or tends to a limit value ($\alpha > 0$). It may be readily concluded that the condition of increase for the third mode magnitude is much more rigorous than that of the sound. In view of $1 \leq \frac{(\gamma + c^2 k^2 \tau^2)}{(1 + c^2 k^2 \tau^2)}$ for any wavenumber k , the condition of the third mode amplification is as follows:

$$\frac{\varepsilon - \varepsilon_{eq}}{\tau} \approx I \geq - \frac{R}{\frac{\mu(\gamma - 1)^2}{d\tau/dT} + C_{V,eq}}. \quad (33)$$

Thus the threshold quantity of the third mode amplification is

$$I_{th,3} = - \frac{R}{\frac{\mu(\gamma - 1)^2}{d\tau/dT}} + I_{th,a}, \quad (34)$$

where the threshold quantity for the sound amplification, corresponding to $\Phi_1 = 0$, is $I_{th,a} = \frac{-C_{V,eq}}{d\tau/dT}$.

A simple estimation for a typical laser mixture $\text{CO}_2 : \text{N}_2 : \text{He} = 1 : 2 : 3$ at the pressure $p_0 = 1$ atm and temperature $T_0 = 300$ K (GORDIETS, OSIPOV, 1992; MAKARYAN, MOLEVICH, 2007), possessing an averaged molar mass $\mu \approx 18.7 \cdot 10^{-3}$ kg/mol, $\tau \approx 5 \cdot 10^{-5}$ s, $d\tau/dT \approx -6 \cdot 10^{-7}$ s/K, yields in quantities: $I_{th,a}\rho_0 = 1.5$ W/cm³, $I_{th,3}\rho_0 = 5 \cdot 10^3$ W/cm³. The threshold level for the third mode is much greater than that for

the both acoustic branches, and, even without considering an experimental possibility of such a large intensity, for the valid description of the motion it becomes necessary to account for gradients in the background parameters. The conclusions above are no longer valid because the linearization should be proceeded with respect to the background with non-zero spatial gradients of pressure and density. This alters the very definition of modes and further analysis, making it complex. Investigation devoted to amplification of the sound in the flat layer of a non-equilibrium gas reveals some new properties as compared to the case of a uniform gas (KOLTSOVA *et al.*, 1994). In particular, the area of instability becomes smaller in the plane pumping intensity vs. the inverse time of relaxation. Features of non-acoustic modes and governing equations for them may alter essentially. Unfortunately, mathematical difficulties do not allow to consider the problem in general.

The sign of the excess vibrational energy is defined by Φ_2 (Eq. (25)). Evaluation of it for the mentioned mixture $\text{CO}_2 : \text{N}_2 : \text{He} = 1 : 2 : 3$ at the pressure $p_0 = 1$ atm yields quantities from $6 \cdot 10^6$ to $193 \cdot 10^6$ J/(kg K s) at temperatures varying from 300 K to 2000 K. It is also positive for other gases. Thus, an averaged excess vibrational energy generated by periodic sound is positive for any α . Its absolute value increases in time for a typically positive α and achieves maximum $\left| \frac{T_0 \Phi_2 (\gamma - 1)^2}{2\alpha \rho_0^2 c^4} P_0^2 \right|$.

4.2. Impulse sound

In the case of the sound being a solution of a linear wave equation in the role of an acoustic source, $p'_1 = p'_1(\eta = (t - x/c)/\theta, \mu t)$, where $\theta \ll \tau$ is a characteristic duration of a pulse, μ is a generic small parameter that characterizes the smallness of $|B|k$ and the acoustic Mach number M . The meaning of the solution in the above form is that in the retarded frame (i.e., for an observer in a reference frame that moves at the speed c), nonlinearity and absorption separately produce only slow variations as functions of the distance. Equation (28) is rearranged in the leading order and may be readily integrated as follows:

$$\begin{aligned} \frac{\partial \varepsilon'_3}{\partial t} + \left(\frac{1}{\tau} - \frac{2Bc}{\gamma - 1} \right) \varepsilon'_3 &\approx \frac{2Bc\tau\theta(\gamma + 1)}{\rho_0^2(\gamma - 1)^2} p'_1 \frac{\partial p'_1}{\partial \eta}, \\ \varepsilon'_3(\eta, \mu t) &\approx \frac{2B\tau(\gamma + 1)}{\rho_0^2 c(\gamma - 1)^2} \exp(-\alpha\eta\theta) \\ &\cdot \int_{-\infty}^{\eta} p'_1(\eta', \mu t) \frac{dp'_1(\eta', \mu t)}{d\eta'} \exp(\alpha\eta'\theta) d\eta'. \end{aligned} \quad (35)$$

The trace after a pulse passing is namely $\varepsilon'_3(\eta \rightarrow \infty)$. Note that minus infinity in the lower limit of integration and the whole above formula are rather symbolic because this subsection considers confined pulses.

The part of the excess vibrational energy belonging to the third mode behaves differently in dependence on the sign of B and the shape of the acoustic pulse. It may be negative or positive but is hardly expected to achieve large values.

5. Concluding remarks

In this study, we consider a nonlinear generation of the vibrational mode by the high-frequency sound, $\omega\tau \gg 1$. The domain of frequencies satisfying this condition for a typical laser mixture $\text{CO}_2 : \text{N}_2 : \text{He} = 1 : 2 : 3$ at the pressure $p_0 = 1$ atm and temperature $T_0 = 300$ K is $\omega \gg 10^5 \text{ s}^{-1}$ (GORDIETS, OSIPOV, 1992; MAKARYAN, MOLEVICH, 2007). The standard thermal viscosity always leads to sound attenuation and nonlinear growth of the excess temperature belonging to the thermal mode. This excess temperature and excess energy associated with it may be negative if the non-equilibrium relaxation takes place. The behavior of a non-equilibrium gas over a wide range of variations of the parameters require to take into account influence of pumping and heat removal (OSIPOV, UVAROV, 1992; KOLTSOVA *et al.*, 1994). With increasing of the relaxation time, the amplification coefficient declines; however, a larger magnitude of pumping I is required to maintain the same degree of non-equilibrium, since $\varepsilon - \varepsilon_{eq} \approx I\tau$. That makes the non-equilibrium media inhomogeneous (OSIPOV, UVAROV, 1992; KOLTSOVA *et al.*, 1994; MOLEVICH, 2001).

This investigation is devoted to a nonlinear generation of the relaxation modes by the low-frequency dominative sound, periodic or aperiodic. The analysis is based on the method of a successful decomposition of weakly nonlinear equations worked out by the author. The main result is an instantaneous dynamic Eq. (28). The sound may increase or decrease a part of the vibrational energy in the total excess energy. As it was discovered in Sec. 4, a periodic sound results in a positive but finite excess vibrational energy. This may be useful in order to govern the degree of inhomogeneity of a gas and to influence the rate of the exchange process between the translational and vibrational energies of a molecule.

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