

## Research Paper

**Excitation of the Secondary Modes by the Broad Spectrum Sound  
in a Liquid with Relaxation Losses**

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Features of nonlinear phenomena and, in particular, acoustic excitation of the entropy and relaxation modes in a liquid electrolyte with a chemical reaction are examined. The total range of frequencies of an exciter is considered, and the instantaneous dynamic equations are derived which govern perturbations in the secondary modes. The instantaneous leading-order acoustic forces of the secondary modes are evaluated. Examples of harmonic and nearly harmonic acoustic exciter are considered in detail. The difference in the nonlinear acoustic phenomena in an electrolyte and gases with relaxation mechanisms are specified and discussed.

**Keywords:** relaxation; dispersive media; acoustic heating.



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## 1. Introduction

The frequency-dependent attenuation of sound in fluids is of importance in many technical and medical applications, especially in medical imaging and tissue specification. It is well-known that the Newtonian attenuation often does not match the experimental data of attenuation in tissues (PARKER, 1983; DUCK *et al.*, 1998). There are variety of mechanisms of relaxation leading to dispersion and attenuation of sound, such as chemical reactions and vibrational relaxation of the molecules. The comprehensive review concerning various mechanisms of absorption in gases can be found in the book written by PIERCE (1981).

The mechanisms of relaxation and absorption in liquids in the context of wave dynamics, is still unresolved issue since the problem was first mentioned (LIEBERMANN, 1948). The composition of a liquid has a key role in a variety of relaxation processes. Typically, several kinds of relaxation take place in a liquid (PIERCE, MAST, 2021). Sound absorption in the sea water is dominated by chemical relaxations with contribution of magnesium sulfate at high frequencies of oscillations and boric acid at low frequencies of oscillations. There is an intermediate-frequency relaxation due to magnesium and carbonic acid (YEAGER, FISHER, 1973; MELLEN *et al.*, 1979). A detail

description of wave processes in the sea water is of importance in view of fishery, naval, and biological applications. The experimental studies of wave processes in water, aqueous solutions and other liquids, including electrolytes, confidently indicate the kinds of relaxation in a liquid and its composition. The dispersion which follows relaxation in fluids, makes the sound speed and attenuation frequency-dependent. Theoretical foundations of spatially distributed relaxation processes with the frequency power law attenuation have been discussed recently by PIERCE and MAST (2021). Shear viscosity and thermal conduction also contribute to the total attenuation.

Whereas, attenuation due to relaxation is the most important case of attenuation in liquid tissues, the first justified wave equation considering several relaxation mechanisms, was published by NACHMAN *et al.* (1990). It relies on absorption dominated by relaxation. Until this, the studies have focused mostly on attenuation in the presence of relaxation, but did not develop the linear wave theory (all the more so the nonlinear wave theory). NACHMAN *et al.* (1990) made use of a set of classical dynamic equations supplemented by thermodynamic and constitutive relations for an electrolyte (LIEBERMANN, 1949; EIGEN, TAMM, 1962). This requires involving into consideration quantities specifying chemical relaxation and enlargement of number of

equations and variety of modes in a flow. NACHMAN *et al.* (1990) considered spatial inhomogeneities in material compressibility, density, and parameters of relaxation and pointed the difference of relaxation processes and wave features in liquids and gases. The different kind of relaxation in liquids provides especial features of nonlinear distortions of a waveform, nonlinear excitation of the non-wave modes (that is, the entropy and the vortex modes) by the intense wave perturbations (PERELOMOVA, 2015).

An exact solution to the dynamic nonlinear equation with frequency-dependent relaxation in the wide range of wave frequencies is still unresolved issue (HAMILTON *et al.*, 1998). As for dynamic equations which describe secondary nonlinear effects induced by sound in electrolytes, they have been derived in the limiting cases of high and low frequencies of an exciter. This concerns excitation of the relaxation mode and acoustic streaming and heating, i.e., nonlinear excitation of vorticity and entropy modes due to losses in momentum and energy of the intense sound (PERELOMOVA, 2015). In general, the nonlinear effects of sound in a relaxing fluid are poorly studied theoretically and rely only on a few papers (MOLEVICH, 2001; PERELOMOVA, PELC-GARSKA, 2010). This theoretical study considers the nonlinear effects of sound in liquid electrolytes with relaxation due to chemical reactions in all frequency regimes.

The mathematical concept of derivation of coupling nonlinear equations for interacting modes is explained and discussed in details by LEBLE and PERELOMOVA (2018). In essence, it is immediate projection of the initial equations onto dynamic equations governing different modes. The first step is to determine modes as specific types of motion in a fluid. That allows to establish projecting operators and to derive the leading-order coupling equations governing every mode in a weakly nonlinear flow. These equations take into account interaction of modes. As usual, some wave modes are considered as dominative and hence contribute predominantly to the “forces” in excitation of the secondary modes. The method was proposed, tested and applied by the author in analysis of nonlinear phenomena in fluids with the standard attenuation and different mechanisms of relaxation (LEBLE, PERELOMOVA, 2018). This method operates on instantaneous quantities, does not require averaging over the sound period at any stage and is valid for both periodic and aperiodic sound. It allows to distribute the nonlinear terms between dynamic equations for the individual modes correctly. This study investigates weakly nonlinear dynamics of the secondary entropy and relaxation modes in electrolyte with a chemical reaction in the total frequency range of the acoustic exciting perturbations. The peculiarity of this type of relaxation in comparison with relaxation in gases, is explained and discussed in the Concluding Remarks. Relaxation of this kind

brings also unusual nonlinear relations between acoustic perturbations.

## 2. Weakly nonlinear dynamics of a flow

### 2.1. Starting points and basic equations

We start from consideration of governing equations for a fluid flow with relaxation:

$$\frac{D\rho}{Dt} + \rho(\nabla \cdot \mathbf{v}) = 0, \quad (1)$$

(conservation of mass;  $\rho$  and  $\mathbf{v}$  are density and particle velocity, and  $\frac{D}{Dt}$  designates the total time derivative operator),

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla p, \quad (2)$$

(conservation of momentum;  $p$  is the total pressure), and the energy balance equation. The Gibbs relation for the rate of variation of entropy  $s$  is as follows:

$$T \frac{Ds}{Dt} = \frac{Du}{Dt} - \frac{p}{\rho^2} \frac{D\rho}{Dt} + \sum_l A_l \frac{Dn_l}{Dt}, \quad (3)$$

where  $u$  is the internal energy per unit mass,  $A_l$  are affinities, and  $n$  designates the number of molecules of species  $l$  per unit mass (LIEBERMANN, 1949; EIGEN, TAMM, 1962). The entropy is a sum of an equilibrium part  $s^e$  and of an irreversible part (EIGEN, TAMM, 1962; NACHMAN *et al.*, 1990; PIERCE, 2021):

$$s(p, \rho, n) = s^e(p, \rho) + \frac{C_p}{\beta T} \sum_l \kappa_l \Delta \xi_l, \quad (4)$$

where

$$\Delta \xi_l = \frac{n - n_l^e(p, T)}{\partial n_l^e(p, T) / \partial p},$$

$\kappa_l$  designates the contribution of the dissolved molecules of species  $l$  to the isothermal compressibility (reciprocal of the bulk modulus), and the appropriate thermodynamic coefficients (the heat capacity under constant pressure and the volumetric coefficient of thermal expansion) are determined as

$$C_p = T_0 \left( \frac{\partial s^e}{\partial T} \right)_p, \quad \beta = -\frac{1}{\rho_0} \left( \frac{\partial \rho}{\partial T} \right)_p,$$

where  $T_0$  and  $\rho_0$  denote temperature and density of a medium in equilibrium. Finally, the entropy balance equation takes the leading-order form as follows (NACHMAN *et al.*, 1990):

$$\frac{Dp}{Dt} - c^2 \frac{D\rho}{Dt} - \frac{B}{2\rho_0^2} \frac{D\rho^2}{Dt} + \rho c^2 \sum_l \kappa_l \frac{D\Delta \xi_l}{Dt} = \sum_l \frac{\kappa_l \beta c^2}{\tau_l C_p} \Delta \xi_l^2, \quad (5)$$

where  $c$  is the equilibrium speed of infinitely-small magnitude sound,  $\tau_l$  is the relaxation time for the process in species  $l$  and  $B$  is determined by an equality

(RUDENKO, SOLUYAN, 1977; MAKAROV, OCHMANN, 1996):

$$\left(\frac{\partial^2 p}{\partial \rho^2}\right)_{se} = \frac{B}{\rho_0^2}.$$

Our primary objective is to derive dynamic equations valid at order  $M^2$ , where the Mach number  $M$  is a ratio of magnitude of a fluid velocity to the sound speed. The Mach number measures degree of nonlinearity of a flow. A linear flow corresponds to the infinitely small Mach number. Assuming constant equilibrium quantities  $\rho_0$  and  $p_0$ , and a lack of the bulk flow and a planar geometry of a flow, we arrive to the system (PERELOMOVA, 2015):

$$\begin{aligned} \frac{\partial v}{\partial t} + \frac{1}{\rho_0} \frac{\partial p'}{\partial x} &= -v \frac{\partial v}{\partial x} + \frac{\rho'}{\rho_0^2} \frac{\partial p'}{\partial x}, \\ \frac{\partial p'}{\partial t} + \rho_0 c^2 \frac{\partial v}{\partial x} + \rho_0 c^2 \sum_l \kappa_l \frac{\partial}{\partial t} \Delta \xi_l &= -v \frac{\partial p'}{\partial x} \\ &\quad - \frac{c^2 \rho_0 + B}{\rho_0} \rho' \frac{\partial v}{\partial x} + \frac{\beta c^2}{C_p} \sum_l \frac{\kappa_l}{\tau_l} \Delta \xi_l^2 \\ &\quad - \rho' c^2 \sum_l \kappa_l \frac{\partial}{\partial t} \Delta \xi_l - \rho_0 c^2 v \frac{\partial}{\partial x} \sum_l \kappa_l \Delta \xi_l, \quad (6) \\ \frac{\partial \rho'}{\partial t} + \rho_0 \frac{\partial v}{\partial x} &= -\rho' \frac{\partial v}{\partial x} - v \frac{\partial \rho'}{\partial x}, \\ \frac{\partial \Delta \xi_l}{\partial t} + \frac{\Delta \xi_l}{\tau_l} + \frac{\partial p'}{\partial t} &= -v \frac{\partial p'}{\partial x} - v \frac{\partial}{\partial x} \Delta \xi_l. \end{aligned}$$

The linear version of this system was derived by NACHMAN *et al.* (1990).

### 2.2. Dispersion relations and modes of a linear flow

Studies of motions of infinitely-small magnitudes begin usually by representing all perturbations as a sum of planar waves:

$$f'(x, t) = \int \tilde{f}(k) \exp(i\omega(k)t - ikx) dk,$$

where  $k$  is the wave vector,  $\tilde{f}(k) \exp(i\omega(k)t)$  denotes the Fourier transform of  $f'(x, t)$ ,  $\tilde{f}(k, t) = \frac{1}{2\pi} \int f(x, t) e^{ikx} dx$ . The number of dispersion relations, i.e., number of modes, coincides with the number of initial equations in partial derivatives which include the first derivative with respect to time. Only one relaxation process is considered for simplicity. There are two sound modes ( $i = 1$  and  $i = 2$ ), one entropy mode ( $i = 3$ ) and one relaxation mode ( $i = 4$ ). The dispersion relations  $\omega_i$  ( $i = 1, \dots, 4$ ) take the leading-order forms:

$$\begin{aligned} \omega_{1,2} &= \pm ck + i \frac{c^4 k^2 \rho_0 \tau}{2(1 + ick\tau)} \kappa, & \omega_3 &= 0, \\ \omega_4 &= \frac{i}{\tau} \left( 1 + \frac{\kappa c^2 \rho_0}{1 + c^2 k^2 \tau^2} \right). \quad (7) \end{aligned}$$

We consider weakly dispersive flows which are characterized by a small dimensionless parameter responsible for relaxation:

$$\alpha = \kappa c^2 \rho_0 \ll 1.$$

All formulae are derived with an accuracy up to  $\alpha^1$ . It is convenient to express all Fourier transforms in terms of the Fourier transform of excess density  $\tilde{\rho}$  for the first three modes:

$$\begin{aligned} \tilde{v}_i &= \frac{\omega_i \tilde{\rho}_i}{k \rho_0}, \\ \tilde{p}_i &= \frac{\omega_i^2 \tilde{\rho}_i}{k^2}, \quad (8) \\ \tilde{\Delta \xi}_i &= -i \frac{\omega_i^3 \tilde{\rho}_i}{k^2 (i\omega_i + 1/\tau)}, \quad (i = 1, 2, 3), \end{aligned}$$

and to make use of  $\tilde{\Delta \xi}_4$  as the reference variable for the relaxation mode:

$$\begin{aligned} \tilde{\rho}_4 &= \frac{k^2 (i - \tau\omega_4)}{\tau\omega_4^3} \tilde{\Delta \xi}_4, \\ \tilde{p}_4 &= \frac{i - \tau\omega_4}{\tau\omega_4} \tilde{\Delta \xi}_4, \quad (9) \\ \tilde{v}_4 &= \frac{k (i - \tau\omega_4)}{\tau\rho_0\omega_4^2} \tilde{\Delta \xi}_4. \end{aligned}$$

In particular, the leading-order links for the Fourier transforms of perturbations in the first sound mode, the entropy mode and the relaxation mode are as follows:

$$\begin{aligned} \tilde{p}_1 &= c^2 \tilde{\rho}_1 + \frac{i\alpha c^3 k \tau}{1 + ick\tau} \tilde{\rho}_1, \\ \tilde{v}_1 &= \frac{c}{\rho_0} \left( 1 + \frac{i\alpha ck\tau}{2(1 + ick\tau)} \right) \tilde{\rho}_1, \\ \tilde{\Delta \xi}_1 &= -\frac{ic^3 k \tau}{1 + ick\tau} \left( 1 + \frac{\alpha(3ick\tau - 2c^2 k^2 \tau^2)}{2(1 + ick\tau)^2} \right) \tilde{\rho}_1, \\ \tilde{p}_3 &= 0, \quad \tilde{v}_3 = 0, \quad \tilde{\Delta \xi}_3 = 0, \quad (10) \\ \tilde{\rho}_4 &= \frac{\alpha k^2 \tau^2}{1 + c^2 k^2 \tau^2} \tilde{\Delta \xi}_4, \\ \tilde{p}_4 &= -\frac{\alpha}{1 + c^2 k^2 \tau^2} \tilde{\Delta \xi}_4, \\ \tilde{v}_4 &= \frac{i\alpha k \tau}{(1 + c^2 k^2 \tau^2) \rho_0} \tilde{\Delta \xi}_4. \end{aligned}$$

Equations (10) determine relations of perturbations in  $x$  space at any moment  $t$  unequivocally. The total small-magnitude perturbations and their Fourier transforms are the sums of all specific ones:

$$\begin{aligned} \tilde{v} &= \sum_{i=1}^4 \tilde{v}_i, & \tilde{p} &= \sum_{i=1}^4 \tilde{p}_i, \\ \tilde{\rho} &= \sum_{i=1}^4 \tilde{\rho}_i, & \tilde{\Delta\xi} &= \sum_{i=1}^4 \tilde{\Delta\xi}_i. \end{aligned} \quad (11)$$

An equation governing excess density in an acoustic planar wave which propagates in the positive direction of the axis  $OX$ ,  $\rho_1(x, t)$ , may be reconstructed by the use of  $\omega_1$  (Eq. (7)):

$$\frac{\partial \rho_1}{\partial t} + c \frac{\partial \rho_1}{\partial x} - \frac{\alpha c}{2} \int_x^\infty \exp\left(\frac{x-x'}{c\tau}\right) \frac{\partial^2 \rho_1}{\partial x'^2} dx' = 0. \quad (12)$$

The linear equation specifying perturbations in the relaxation mode, takes the form

$$\frac{\partial \Delta\xi_4}{\partial t} + \frac{\Delta\xi_4}{\tau} + \frac{\alpha}{2c\tau^2} \int_{-\infty}^\infty \exp\left(-\frac{|x-x'|}{c\tau}\right) \Delta\xi_4(x', t) dx' = 0. \quad (13)$$

In derivation of Eqs. (12) and (13), we make use of conformity of operators in  $k$  and  $x$  spaces:

$$\begin{aligned} -ik &\Leftrightarrow \frac{\partial}{\partial x}, \\ \frac{1}{1+ick\tau} &\Leftrightarrow \frac{1}{c\tau} \int_x^\infty dx' \exp\left(\frac{x-x'}{c\tau}\right), \\ \frac{1}{1-ick\tau} &\Leftrightarrow \frac{1}{c\tau} \int_{-\infty}^x dx' \exp\left(-\frac{x-x'}{c\tau}\right), \\ \frac{1}{1+c^2k^2\tau^2} &\Leftrightarrow \frac{1}{2c\tau} \int_{-\infty}^\infty dx' \exp\left(-\frac{|x-x'|}{c\tau}\right). \end{aligned} \quad (14)$$

The approximate solutions to an equation similar to Eq. (12) are discussed by HAMILTON *et al.* (1998). Apart from the dispersion relations and links specifying every mode, we are able to evaluate operators which distinguish the specific perturbation from the vector of total disturbances in a linear flow. Solving algebraic equations:

$$\begin{aligned} \tilde{P}_1(\tilde{v} \ \tilde{p} \ \tilde{\rho} \ \tilde{\Delta\xi})^T &= \tilde{\rho}_1, \\ \tilde{P}_3(\tilde{v} \ \tilde{p} \ \tilde{\rho} \ \tilde{\Delta\xi})^T &= \tilde{\rho}_3, \\ \tilde{P}_4(\tilde{v} \ \tilde{p} \ \tilde{\rho} \ \tilde{\Delta\xi})^T &= \tilde{\Delta\xi}_4, \end{aligned}$$

one arrives at operator rows which distinguish every specific Fourier transform of excess quantities for these three modes:

$$\begin{aligned} \tilde{P}_1 &= \begin{pmatrix} \frac{\rho_0}{2c} + \frac{\alpha ck^2 \tau^2 \rho_0}{4(1+ick\tau)^2} \\ \frac{1}{2c^2} - \frac{ia k \tau (1+2ick\tau)}{4c(1+ick\tau)^2} \\ 0 \\ \frac{\alpha}{2c^2(1+ick)} \end{pmatrix}^T, \\ \tilde{P}_3 &= \begin{pmatrix} 0 \\ -\frac{1}{c^2} \\ 1 \\ -\frac{\alpha}{c^2} \end{pmatrix}^T, \\ \tilde{P}_4 &= \begin{pmatrix} \frac{ic^2 k \rho_0 \tau}{1+c^2 k^2 \tau^2} + \frac{4i\alpha c^4 k^3 \rho_0 \tau^3}{(1+c^2 k^2 \tau^2)^3} \\ \frac{c^2 k^2 \tau^2}{1+c^2 k^2 \tau^2} + \frac{\alpha c^2 k^2 \tau^2 (3c^2 k^2 \tau^2 - 1)}{(1+c^2 k^2 \tau^2)^3} \\ 0 \\ 1 + \frac{2\alpha c^2 k^2 \tau^2}{(1+c^2 k^2 \tau^2)^2} \end{pmatrix}^T. \end{aligned} \quad (15)$$

They are evaluated with accuracy up to terms proportional to  $\alpha^0$  and  $\alpha^1$  but without any restrictions concerning spatial spectrum of perturbations. The elements of  $\tilde{P}_3$  and  $\tilde{P}_4$  determine some integro-differential spatial operators  $P_3$  and  $P_4$  in the  $x$  space accordingly to Eq. (14). When  $P_3$ ,  $P_4$  apply at the system of conservation Eq. (6), they distinguish equations for the excess specific densities of the entropy and relaxation modes, respectively.

### 2.3. Nonlinear dynamics of sound

Equation (12) may be expanded by inclusion of the nonlinear term. For this purpose, it is sufficient to apply  $P_1$  on the system Eq. (6) with the leading-order result:

$$\begin{aligned} \frac{\partial \rho_1}{\partial t} + c \frac{\partial \rho_1}{\partial x} - \frac{\alpha c}{2} \int_x^\infty \exp\left(\frac{x-x'}{c\tau}\right) \frac{\partial^2 \rho_1}{\partial x'^2} dx' \\ + \frac{\varepsilon c}{\rho_0} \rho_1 \frac{\partial \rho_1}{\partial x} = 0. \end{aligned} \quad (16)$$

The nonlinear distortion of a wave is conditioned by the positive parameter of nonlinearity  $\varepsilon$ :

$$\varepsilon = \frac{B}{2c^2 \rho_0} + 1.$$

Links (Eq. (10)) specifying acoustic perturbations, may be corrected by involving nonlinear terms. As for links connecting  $p_1$ ,  $v_1$  and  $\rho_1$ , they are as follows:

$$\begin{aligned}
 p_1 &= c^2 \rho_1 - c^2 \alpha \int_x^\infty \exp\left(\frac{x-x'}{c\tau}\right) \frac{\partial \rho_1}{\partial x'} dx' + \frac{B}{2\rho_0^2} \rho_1^2, \\
 v_1 &= \frac{c}{\rho_0} \rho_1 + c^2 \int_x^\infty \exp\left(\frac{x-x'}{c\tau}\right) \frac{\partial \rho_1}{\partial x'} dx' + \frac{B-2c^2\rho_0}{4c\rho_0^3} \rho_1^2.
 \end{aligned}
 \tag{17}$$

The nonlinear correction to  $\xi_1$  may be readily derived in two limiting cases:

$$\text{low-frequency: } \Delta \xi_1 = c^3 \tau \frac{\partial \rho_1}{\partial x} + \frac{Bc\tau}{2\rho_0^2} \rho_1 \frac{\partial \rho_1}{\partial x}, \tag{18}$$

$$\text{high-frequency: } \Delta \xi_1 = -c^2 \rho_1. \tag{19}$$

Hence, nonlinearity introduces nothing in “high-frequency” links (if  $c\tau \left| \frac{\partial \rho_1}{\partial x} \right| \gg |\rho_1|$ ), but contributes in the “low-frequency” ones (if  $c\tau \left| \frac{\partial \rho_1}{\partial x} \right| \ll |\rho_1|$ ). The nonlinear correction is unusual. The links which determine  $v_1$  and  $p_1$  are proportional to  $\rho_1^2$  in the Riemann wave.

### 3. Acoustic heating

We consider the dominant first acoustic mode as an exciter of secondary perturbations. The perturbations specifying all other modes are considered as negligibly small at the beginning of evolution. The leading-order linear links for the perturbations in this mode take the forms (Eqs. (10) and (14)):

$$\begin{aligned}
 p_1 &= c^2 \rho_1 - \alpha c^2 \int_x^\infty \exp\left(\frac{x-x'}{c\tau}\right) \frac{\partial \rho_1}{\partial x'} dx', \\
 v_1 &= \frac{c}{\rho_0} \rho_1 - \frac{\alpha c}{2\rho_0} \int_x^\infty \exp\left(\frac{x-x'}{c\tau}\right) \frac{\partial \rho_1}{\partial x'} dx',
 \end{aligned}
 \tag{20}$$

$$\Delta \xi_1 = c^2 \int_x^\infty \exp\left(\frac{x-x'}{c\tau}\right) \frac{\partial \rho_1}{\partial x'} dx'.$$

They make possible to express an acoustic source in terms of perturbation of density attributable to the acoustic mode. Application of  $P_3$  (Eq. (15)) at the system Eq. (6) reduces all acoustic and relaxation terms in the left-hand linear side and yields the leading-order equation which governs acoustic heating:

$$\begin{aligned}
 \frac{\partial \rho_3}{\partial t} &= -\frac{\alpha}{2cC_p\rho_0^2\tau} \left( 2\beta c^3 \rho_0 \left( \int_x^\infty e^{\frac{x-x'}{c\tau}} \frac{\partial \rho_1(x',t)}{\partial x'} dx' \right)^2 \right. \\
 &+ 2cC_p\rho_0\rho_1 \int_x^\infty e^{\frac{x-x'}{c\tau}} \frac{\partial \rho_1(x',t)}{\partial x'} dx' \\
 &+ C_p\tau\rho_1 \left( \frac{B}{c\tau} \int_x^\infty e^{\frac{x-x'}{c\tau}} \frac{\partial \rho_1(x',t)}{\partial x'} dx' \right. \\
 &\left. \left. - (B+2c^2\rho_0) \frac{\partial \rho_1(x',t)}{\partial x} \right) \right) = Q_{a,e}.
 \end{aligned}
 \tag{21}$$

The leading-order low- and high- frequency limits of  $Q_{a,e}$  have been preliminarily considered by PERELOMOVA (2015). They are the limiting cases of Eq. (21) if  $c\tau \left| \frac{\partial \rho_1}{\partial x} \right| \ll |\rho_1|$ ,  $c\tau \left| \frac{\partial \rho_1}{\partial x} \right| \gg |\rho_1|$ , respectively:

low-frequency:

$$Q_{a,e} = -\frac{\alpha\tau}{2C_p\rho_0^2} \left( 2\beta c^4 \rho_0 \left( \frac{\partial \rho_1}{\partial x} \right)^2 + BC_p\rho_1 \frac{\partial^2 \rho_1}{\partial x^2} \right),$$

high-frequency:

$$\begin{aligned}
 Q_{a,e} &= -\frac{\alpha}{2c^2\tau^3 C_p\rho_0^2} \left( 2\beta c^2 \rho_0 \left( \int \rho_1(x,t) dx \right)^2 \right. \\
 &+ 2c(2\beta c^2 - C_p)\rho_0\tau \left( \int \rho_1(x,t) dx \right) \rho_1 \\
 &- \tau^2 \rho_1 \left( (BC_p - 2\beta c^4 \rho_0 + 2c^2 C_p \rho_0) \rho_1 \right. \\
 &\left. \left. + cC_p(B + 2c^2 \rho_0)\tau \frac{\partial \rho_1}{\partial x} \right) \right).
 \end{aligned}$$

Equation (21) may be solved by the integration of  $Q_{a,e}$  over time.

#### 3.1. Nearly harmonic exciter

The most interesting case is the median domain of frequencies. Let the exciting perturbation in density takes the form

$$\begin{aligned}
 \rho_1 &= M\rho_0 \exp\left(-\frac{\alpha c^2 k^2 \tau}{1+c^2 k^2 \tau^2} t\right) \sin \\
 &\cdot \left( kx - \frac{ck(1+(1+0.5\alpha)c^2 k^2 \tau^2)}{1+c^2 k^2 \tau^2} t \right),
 \end{aligned}
 \tag{22}$$

where  $M$  is the Mach number, and  $\frac{ck(1+(1+0.5\alpha)c^2 k^2 \tau^2)}{1+c^2 k^2 \tau^2}$  is the quasi-frequency of an exciter. The amplitude of excess density decreases with time. The leading-order acoustic source averaged over period equals

$$\begin{aligned}
 \langle Q_{a,e} \rangle &= \exp\left(-\frac{\alpha c^2 k^2 \tau}{1+c^2 k^2 \tau^2} t\right) \\
 &\cdot \frac{\alpha M^2 k^2 \tau (BC_p + 2c^2(C_p - \beta c^2)\rho_0)}{4C_p(1+c^2 k^2 \tau^2)}.
 \end{aligned}
 \tag{23}$$

High-frequency limit  $ck\tau \gg 1$  results in

$$\langle Q_{a,e} \rangle = \exp\left(-\frac{\alpha t}{\tau}\right) \frac{\alpha M^2 (BC_p - 2c^2 C_p \rho_0 - 2c^4 \beta \rho_0)}{4c^2 C_p \tau}.
 \tag{24}$$

This leads to uniform generation of perturbation of density which starts at  $t = 0$  ( $\rho_3(0) = 0$ ):

$$\rho_3 = \left( 1 - \exp\left(-\frac{\alpha t}{\tau}\right) \right) \frac{M^2 (BC_p - 2c^2 C_p \rho_0 - 2c^4 \beta \rho_0)}{4c^2 C_p}.
 \tag{25}$$

The maximum absolute value of excess density which may be achieved in the course of acoustic heating, does not depend on  $\alpha$  and  $\tau$  (these parameters determine the rate of exciting of the entropy mode).

#### 4. Excitation of the relaxation mode.

##### Case of harmonic exciter

Recalling relations (Eq. (10)) and applying  $P_4$  at Eq. (6), one arrives at the leading-order dynamic equation for the perturbations in the relaxation mode:

$$\frac{\partial \Delta \xi_4}{\partial t} + \frac{1}{\tau} \Delta \xi_4 + \frac{\alpha}{c\tau^2} \int_{-\infty}^{\infty} \exp\left(-\frac{|x-x'|}{c\tau}\right) \cdot \Delta \xi_4(x', t) dx' = Q_{a,r}. \quad (26)$$

In view of the complex form of operators in  $P_4$  corresponding to  $\tilde{P}_4$  (Eq. (15)), we use the solution of the equation without account of dispersion and non-linearity,

$$\rho_1 = M\rho_0 \sin(\Omega(t - x/c)). \quad (27)$$

The averaged form of  $Q_{a,r}$  in the case of the harmonic exciter is as follows:

$$\begin{aligned} \langle Q_{a,r} \rangle &= \frac{\alpha \Omega^2 M^2}{64 C_p \tau (1 + \Omega^2 \tau^2)^3} (8 B C_p (1 + \Omega^2 \tau^2)^2 \\ &+ c^2 \rho_0 (C_p (16 + 93 \Omega^2 \tau^2 + 46 \Omega^4 \tau^4 + 9 \Omega^6 \tau^6)) \\ &- 18 \beta (1 + \Omega^2 \tau^2)^2 c^2). \end{aligned}$$

The limiting forms of coupling equations are

low-frequency:

$$\frac{\partial \Delta \xi_4}{\partial t} + \frac{1 + \alpha}{\tau} \Delta \xi_4 = \frac{\alpha M^2 \Omega^2 \tau}{8 C_p} \cdot (B C_p + 2c^2 (C_p \rho_0 - \beta c^2) \rho_0), \quad (28)$$

high-frequency:

$$\frac{\partial \Delta \xi_4}{\partial t} + \frac{1}{\tau} \Delta \xi_4 = \frac{9}{64} \alpha M^2 \rho_0 c^2 \Omega^2 \tau. \quad (29)$$

The efficiency of low-frequency harmonic excitation is fairly low. As for the high-frequency excitation, the absolute value of an acoustic force does not tend to any finite limit but enlarges with frequency of an exciter as  $\Omega^2$  in contrast to an acoustic source of the entropy mode. Equations (28) and (29) may be readily solved by direct integration over time making the use of the substitutions  $\Delta \xi_4 = f(x, t) \exp(-t(1 + \alpha)/\tau)$  and  $\Delta \xi_4 = f(x, t) \exp(-t/\tau)$ , respectively. There is non-zero variation in temperature which associates with the relaxation mode:

$$T_4 = \frac{\gamma}{\beta} p_4 - \frac{1}{\rho_0 \beta} \rho_4,$$

where

$$\gamma = \frac{1}{\rho_0} \left( \frac{\partial \rho}{\partial p} \right)_T$$

designates the isothermal compressibility. These variations are of the order  $\alpha^2 M^2$  in all ranges of frequencies. They are much smaller than in the entropy mode (the latter are of the order  $\alpha M^2$ ).

#### 5. Concluding remarks

In this study, we consider weakly nonlinear effects of sound in an electrolyte. The total range of sound frequencies is considered. Nonlinearity of a flow and relaxation of thermodynamic processes are necessary conditions for interaction of modes and excitation of the secondary entropy and relaxation modes in the field of intense sound. The instantaneous equations which govern excitation of the relaxation and entropy modes in the field of intense sound wave, are derived (Eqs. (21), (26)). Thermodynamic parameters of the nonlinear phenomena slowly vary with time since they do not represent the wave processes. They are readily measured and may be useful in indication of relaxation processes in liquids. Theoretical conclusions may be employed in modeling of nonlinear scattering in applications such as image reconstruction in a liquid. The theory is of interest from the standpoint of understanding wave processes in the sea and in biological systems, and as a tool in studies of colloidal systems. In addition, studies of sound absorption in various fluids such as distilled water and electrolytic solutions, are of crucial importance in the understanding of their molecular structure. The nonlinear phenomena indicate the kind of relaxation in a fluid, its equilibrium thermodynamic properties and frequency of exciting wave perturbations. The mechanic viscosity and heat conduction are not considered in this study. In gases, these effects are well-studied (RUDENKO, SOLUYAN, 1977; MAKAROV, OCHMANN, 1996), and they are small compared to relaxation effects in liquids and biological tissues (MANDELSHTAM, LEONTOWICH, 1937; HERTZFELD, LITOWITZ, 1959; NYBORG, 1978).

There is an apparent difference of the considered case of relaxation in liquids and relaxation due to other processes of deviation from the thermodynamic equilibrium in gases, such as excitation of vibrational degrees of a molecule's freedom or exothermic chemical reactions. That concerns dispersion relations specifying wave and non-wave modes and, as a result, linear dynamic equations describing perturbations in these modes. The links of specific perturbations in wave and non-wave mode are also different. This has been indicated by PERELOMOVA (2015). In particular, the dispersion relation for the relaxation mode in a gas flow with vibrational relaxation looks different as compared with  $\omega_{4,V}$  from Eq. (7) ( $\tau_V$  is the characteristic time of vibrational relaxation, and

$T_0$  designates the equilibrium temperature of a gas) (PERELOMOVA, 2010):

$$\omega_{4,V} = \frac{i}{\tau_V} + \frac{i(\gamma - 1)(\gamma + c^2 k^2 \tau_V^2) T_0 C_v}{c^2 \tau_V (1 + c^2 k^2 \tau_V^2)}.$$

It describes different behavior especially at intermediate characteristic frequencies of exciting perturbations. The relaxation mode is isobaric in the case of relaxation processes in gases. An excess pressure in the relaxation mode in electrolytes is not zero and relates to excess density in the following manner

$$\rho_4 = \tau^2 \frac{\partial^2 p_4}{\partial x^2}.$$

Also, the dispersion relations for the high-frequency sound in a liquid which readily follow from Eq. (7):

$$\omega_{1,2} = \pm (ck + 0.5\kappa c^3 k \rho_0),$$

fundamentally differ from that in a gas with vibrational relaxation (OSIPOV, UVAROV, 1992; MOLEVICH, 2001):

$$\omega_{1,2} = \pm ck + 0.5i(\gamma - 1)^2 C_v T_0 / (\tau_V c^2).$$

There is an attenuation independent of frequency in the case of vibrational relaxation, while there is only pure dispersion without attenuation in the case of relaxation in electrolytes. The Newtonian attenuation is proportional to  $k^2$ . The links between acoustic pressure and excess density also look different. In particular:

$$p_1 = c^2 \rho_1 - \alpha c^2 \int_x^\infty e^{\frac{x-x'}{c\tau}} \frac{\partial \rho_1(x', t)}{\partial x'} dx'$$

in the case of relaxation in electrolytes, and

$$p_1 = c^2 \rho_1 - \frac{\theta c}{\tau} \int_x^\infty e^{\frac{x-x'}{c\tau}} \rho_1(x', t) dx'$$

in the case of vibrational relaxation in gases, where  $\theta$  is a dimensionless parameter reflecting vibrational relaxation in gases in view of inflow of energy (may be negative) (PERELOMOVA, 2019). The similar link specifies a gas flow with a chemical reaction (LEBLE, PERELOMOVA, 2018). The different behavior conditions different hysteresis acoustic curves (PERELOMOVA, 2013). The nonlinear effects of sound also look different in gases and liquids. The leading-order acoustic force is proportional to the squared Mach number  $M^2$  and  $\alpha$ , and is frequency-dependent. The high-frequency sound is effective in excitation of the secondary perturbations in presence of all kinds of relaxation, but the low-frequency exciters are not effective (PERELOMOVA 2010; 2019).

The nonlinear links of specific acoustic variables attract special attention. We face with the unusual

relations (Eq. (18)) for low-frequency sound perturbations with a nonlinear term proportional to  $\rho_1 \frac{\partial \rho_1}{\partial x}$ , not  $\rho_1^2$  which is specific for the flows over uniform fluids (RUDENKO, SPYAN, 1977). Hence, nonlinear links reveal the frequency-dependent character and may indicate sound frequency, characteristic time of relaxation and equilibrium parameters of an electrolyte.

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