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SOUND PROPAGATION IN GAS MIXTURES

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Abstract

An earlier treatment of the propagation of sound in mixtures of two gases is generalized and simplified somewhat. The essential point of the theory is the consideration of the internal energy variations by the assignment of fictitious internal state temperatures which, in the simplest case assumed here, are taken to be constant for each of the component gases. The long wave-length velocity expression is directly interpretable as a Laplace formula for a gas of mean reciprocal mass and averaged specific heat. From a more general point of view the velocity of propagation of infinitesimal waves is always given by the Laplace result provided a frequency variation of specific heats be recognized. Explicit mention is made of the detailed effect of viscosity and the two conductivities. Experimental data support theory.

In A recent paper,[1] the writer presented a theory of the propagation of sound in a single gas and mixtures of two gases. The present article extends the results on mixtures to the case of n gases and provides simpler forms for some of the earlier formulae. It also comments from a kinetic standpoint on the roles of viscosity and translational and internal energy conductivities.

The point of view taken is that the internal energy fluctuations of the various types of molecules are not of the same amount or synchronous in phase with the translational energy variations. We suppose however that each gas W may be characterized by a parameter ω_W such that if the translational temperature variation in a given region be δT the changes in the number of molecules in the various energy levels correspond to a temperature change $\omega_W \delta T$. The assumption that ω_W is independent of the quantum state considered, is, of course, a strong restriction. (An assumption tantamount to it for one gas has been used by Herzfeld and Rice[2] in their important work on sound propagation in a pure gas.) The very general analysis in I for the case of a single gas shows that some arbitrary postulate regarding the dependence of ω_W on the internal state considered is essential in order to make headway. It would seem worthwhile to investigate the consequences of various other functional relations between internal state r and ω_{W_r}.

The symbols to be used exclusive of those whose connotations seem sufficiently obvious are: M = number of distinct gases comprising the mixture. m_W = mass of molecule of gas W. N_W = number of type W molecules. N_{W_r} = number of type W molecules in the quantum state r. $S/N = \Sigma N_W / N m_W$ = mean value of the reciprocal molecular mass of the mixture. β_W = half the

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[1] D. G. Bourgin, Phil. Mag. Vol. **7**, 821, (1929). This paper will be referred to as I.

[2] K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928).

number of normal coordinates[3] in the internal energy of a type W molecule. $N_W N_R L_{WR}$ = energy increment in gas W/ unit time due to collisions of W and R type molecules, for unit energy difference $(3k/2)$ between translational and internal energy of the gas W molecules[4]. $\phi_W = \sum^M N_W N_R L_{WR}$. K_W = kinetic energy of a type W molecule. The equipartition principle indicates $K_W \underset{W}{\equiv} K$. $\dot{x} = dx/dK$. $\nu = 2\pi n$, where n is the frequency.

The equations for this work[5] are written for a one dimensional problem (i.e., an infinite plane source)

$$\frac{\partial}{\partial t} N_W = -\frac{\partial}{\partial x} N_W v \tag{1.1}$$

$$\frac{\partial}{\partial t} Nv = -\frac{\partial}{\partial x} \frac{2}{3} S\,K + \frac{4}{3} \mu \frac{S}{N} \frac{\partial^2 v}{\partial x^2} \tag{1.2}$$

$$\frac{\partial}{\partial t} NK = -\frac{\partial}{\partial x} \frac{5}{3} NKv + \Delta K + \psi \frac{\partial^2 K}{\partial x^2} \tag{1.3}$$

$$\frac{\partial}{\partial t} N_{W_r} = -\frac{\partial}{\partial x} N_{W_r} v + \Delta N_{W_r} + \gamma_{W_r} N_W \frac{\partial^2}{\partial x^2} N_{W_r}/N_W \tag{1.4}$$

μ is the coefficient of viscosity. The last terms in Eqs. (1.3) and (1.4) are the heat conduction terms and it will be observed that because of the use of K instead of T, ψ is $2k/3$ times the value of the usual conduction coefficient. The presence of the coefficients of conduction and viscosity outside the double differentiation is justified by the order of the approximations we shall make. For the same reason terms representing the interdiffusion effect and the dissipation[6] function have been omitted from Eq. (1.3). It is, of course, clear that μ, ψ and γ_{W_r}[7] are functions of $N_1, \cdots, N_M$.

Since double and higher frequency terms are to be neglected we may assume that the variables vary sinusoidally about equilibrium values and that coefficients of products of harmonic functions are vanishingly small. The amplitudes of the harmonic terms are distinguished by the customary variation symbol δ as prefix. It can be shown, Cf. I, that the collision increments may be written

$$\Delta K = \delta K \sum^M \phi_W(\omega_W - 1) \tag{2.1}$$

$$\Delta N_{W_r} = \delta K(1 - \omega_W)\ \dot{N}_{W_r} \sum^M C_{WR}\, N_R. \tag{2.2}$$

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[3] This definition is preferable to the one involving the ambiguous term degrees of freedom used in I.

[4] Cf. I, Eq. (28), for the expression in terms of transition probabilities.

[5] Cf. I for the most important terms in these equations.

[6] Lamb, Hydrodynamics, p. 518.

[7] That γ_{W_r} is of the nature of a heat conductivity coefficient for the internal energies is immediately obvious on multiplying Eq. (1.4) by ϵ_r and summing over r and W. We should then get the internal energy change equation. The ratio N_{W_r}/N_W occurs with the differentiating operator because this term is obviously to be independent of change in concentration alone.

Another useful relation is

$$\delta N_{Wr} = N_{Wr}\frac{\delta \dot{N}}{N} + \omega_W \dot{N}_{Wr}\,\delta K .$$

The solution for ω_W is

$$\omega_W = \frac{\dot{N}_{Wr} \sum C_{WR} N_R}{j\nu \dot{N}_{Wr} + \dot{N}_{Wr} \sum C_{WR} N_R + \gamma_{W_r W_r} \dot{N} \nu^2 / V^2} . \tag{3.1}$$

An argument given in I leads to

$$C_{WR} = 3L_{WR}/2\beta_W .$$

Hence

$$\omega_W = 1 - j\nu\frac{2}{3}\,\frac{\beta_W}{\sum N_R L_{WR}} - \frac{4}{9}\,\frac{\nu^2 \beta_W{}^2}{(\sum N_R L_{WR})^2} - \frac{2}{3}\nu^2 \frac{\gamma_{W_r}}{V_0{}^2} + j\nu^3 \left[\partial_W{}^3 + \frac{\partial_W{}^2 \gamma_W}{V_0{}^2} + \frac{\partial_W \gamma_W d_1}{V_0{}^2} \right] \tag{3.2}$$

where

$$\partial_W = 1/\sum C_{WR} N_R$$

$$\frac{1}{V^2} = \frac{1}{V_0{}^2}\,1 - j\nu d_1 \cdots d_1 > 0$$

It is to be remembered that the internal energy change* is $\int_{T_0}^{T} (1-\omega_W)\phi_W \delta K dT$ and is to be compared with the translational energy increment detailed by the terms exclusive of ΔK in Eq. (1.3). In both cases the lowest order term is the one in ν. Accordingly the† *in phase* increase of internal energy depends for its rate on the specific heat and finite transition time; the lag, or ν^2 term, on internal conduction besides. Viscosity and external conduction appear in d_1 (Cf. Eq. (3.2)) to modify the relative amplitude of internal energy changes in the next higher term.

The fiction of an internal temperature may be waived and instead one may employ a variable specific heat $B(\nu)$ determined either from the fact that the internal energy increases by an amount $B_W(\nu)k\delta T$ for a change δT or that the rate of variation in internal energy is $\nu B(\nu) k \delta T \cos \nu t$. There result the two equivalent definitions

$$B_W(\nu) = \omega_W B_W(0) \left(= \tfrac{2}{3}\omega_W \beta_W\right)$$

$$= (1-\omega_W) \sum^{M} N_R L_{WR} \tag{4}$$

After some not very difficult eliminations of the amplitude terms in Eqs. (1.1) $\cdots$ (1.4) we may write the key equation

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* It may be pointed out that if ω_W is to be independent of r to the second order in ν, it is necessary to drop the subscript r from γ_{W_r}.

† I contains a minor error of statement as regards this point.

$$V^2=\frac{SK}{3N}\;\frac{\frac{10}{3}Nj\nu+2\sum(1-\omega_W)\phi_W+\frac{2\psi\nu^2}{V^2}+j\frac{4\mu\nu}{KN}\mathbf{N}}{Nj\nu+\sum(1-\omega_W)\phi_W+\frac{\phi\nu^2}{V^2}} \tag{5}$$

where

$$\mathbf{N}=N_{j\nu}+\sum(1-\omega_W)\,\phi_W+\frac{\psi\nu^2}{V^2}$$

From Eq. (5) the low frequency velocity is approximately

$$V_0{}^2=\frac{SK}{3N}\;\frac{\frac{10}{3}N+\frac{4}{3}\sum N_W\beta_W}{N+\frac{2}{3}\sum N_W\beta_W}\,. \tag{5.1}$$

The first order approximation for V_0, as contrasted with the absorption term, is practically independent of the assumptions made about the dependence of ω_{W_r} on r (Cf. I). To the next approximation

$$V=V_0\left[1+j\nu\frac{2}{3}\left(\frac{\frac{4}{9}N\sum^{M}\frac{N_W\beta_W{}^2}{\sum^{M}N_RL_{WR}}+\frac{N}{V_0{}^2}\left\{\psi+\frac{2}{3}\sum\gamma_WN_W\beta_W\right\}}{\left(N+\frac{2}{3}\sum N_W\beta_W\right)\left(\frac{10}{3}N+\frac{4}{3}\sum N_W\beta_W\right)}+\frac{\mu S}{N^2V_0{}^2}\right)+\cdots\right] \tag{5.2}$$

The interpretation of the remarkably simple result for the long wavelength velocity is that the mixture behaves like a single gas of averaged specific heat and averaged reciprocal mass* and that Eq. (5.1) is the Laplace value for the velocity in this hypothetical single gas[8] (clearly the ratio in Eq. (5.1) is proportional to the effective specific heats at constant pressure and constant volume).

It is instructive to make a further step and to look upon Eq. (5.2) as a Laplace formula still, with specific heats, functions of the frequency. More explicitly the translational specific heat at constant volume ($3k/2$) is affected to the next order by the translational conductivity while the numerator which refers to constant pressure involves, due to the relative motions implied in expansion and contraction, the viscosity term as well. Similarly the internal specific heat $\beta(\nu)$ which has already been explicitly characterized (Cf. Eq. (4)) depends on transition times and internal conductivity and to a still higher order on viscosity and translational conductivity.

This point of view makes the study of sound propagation more intuitive. It is, then, only necsesary to know how the internal and trans-

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* Not as has sometimes been supposed the averaged mass (Cf. H. Benndorf, Phys. Zeits. **4**, 97 (1929)).

[8] The form of the analogous expression (which is now seen to be reducible) appearing in I obscured this direct generalization of the Laplace formula and the above interpretation was given there for the case $L_{WR}\underset{R}{\equiv}L_W$, only.

lational energies change at constant volume and constant pressure respectively. Inclusion of new terms or modifications of the theory can start directly with the extended Laplace formula and the real meaning of the changes seen immediately without necessity of recourse to the original differential equations.

Chapman[9] has given the value of ψ and μ for a mixture of monatomic gases. From the form of his results it seems that to a first approximation in the general case the coefficients would involve the ratio of quadratic forms in the concentrations at the least.[10] Even for the comparatively simpler problem assumed by Chapman a theoretical computation would be most awkward—hence for a test of Eq. (5.2) it would be necessary to obtain μ, γ_W and ψ experimentally as functions of the concentrations of the gases.

The absorption term[11] depends on the ratio of a cubic to a biquadratic in the concentrations (not including the change in V_0).[12] The extreme assumption $L_W \underset{R}{\equiv} L_W$ would allow us to treat the mixture as a single gas of averaged β^2/L so that experiments on the component gases might be used to predict that part of the absorption due to the finite time required for internal energy transitions. This should be a fair working assumption for gases of similar natures.

One of the first tests of a theory of sound in mixtures ought to be the derivation of the velocity of sound in air. Clearly since β is the same for O_2 and N_2 we have

$$\frac{V_{12}}{V_2} = \frac{1}{m_{12}} \Big/ \frac{1}{m_1} = \frac{1}{5} \, \frac{4m_2 + m_1}{m_1 m_2} \Big/ \frac{1}{m_1} \tag{6}$$

1, 2 and 12 refer to N_2, O_2 and air respectively.

Lechner's[13] value 315.5m/sec for V_2 leads to $V_{12} \sim 332.5\ m/\mathrm{sec}$ which is in very close agreement with Pierce's result 331.94 m/sec.

For application of Eq. (5.1) to a case where the gases are of different heat capacities we shall consider the influence of water vapor in air. It is readily substantiated that

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[9] Chapman, Phil. Trans. **98,** 252 (1915).

[10] The occurrence of ψ in higher order terms is due to its associated factor $1/V^2$ (Cf. Eq. (5)). The presence of γ_W is only partially due to an analogous cause (Cf. Eq. (3.2)). Hence although both conductivity coefficients enter the phase lag expression in a parallel way and may in fact be conveniently reduced to the single effective coefficient $\psi + (2/3)\sum N_W \beta_W \gamma_W$ the next and higher order approximations show asymmetry in their action.

[11] The form given is somewhat more perspicuous than the special expression occurring in I which is reducible Cf. note 9.

[12] Our theory has been illustrated for an infinite vibrating plane—a case which may not correspond to the experimental practice studied. For effects due to motion in two or three dimensions, slight modifications (amounting in general to symmetrizing the expressions as regards x, y, and z) are to be made in Eqs. (1.1) to (1.4). Then, retaining the harmonic form of the time factor, the space coordinate dependence may be obtained by solving the equations under the limitations of small variations and the appropriate initial and boundary conditions. In a very general case, besides the causes taken account of in our treatment, attenuation may be due to wave spreading, lateral and radial diffusion, vorticity, change of wave form, wall reactions, double frequency effects, etc.

[13] Lechner, Wiener Ber. **11,** 1035 (1909).

$$\frac{\delta V}{V}=\frac{N_2}{2N}\left[\frac{m_1-m_2}{m_2}-\frac{8(\beta_2-\beta_1)}{(4\beta_1+10)(2\beta_1+3)}\right] \tag{7}$$

where N_2/N is the moisture ratio of air, m_1 is the m_{12} defined in Eq. (6) and the subscripts 1, 2 refer to air and water vapor respectively. Substitution of the appropriate values leads to $\delta V/V \sim 0.006+$ for *N.T.P.* Recent[14] unpublished experimental work by Professor Pierce's students suggests a variation of almost 0.005. The two figures are satisfactorily close.

The writer is further informed by Professor Pierce that the latest work in his laboratory does not support a frequency dependence of the velocity in air.[15] This is in complete accord with theoretical prediction since the values of the dissipation terms in the case of air are very small. The previous positive results were due to the fact that the apparent measured velocity varies with distance from the source. This latter anomalous effect is probably a matter of experimental method rather than a characteristic of the physical situation though the energy dissipation progressively increases the wavelength very slightly. It may be that corrections for the displacement of the node from the boundary of the vibrating source or consideration of the sphericity of the waves forming the stationary wave pattern may account for the result but it is perhaps unprofitable to speculate in the absence of details.

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[14] Earlier negative results (Proc. Am. Ac. Arts and Sci. **60**, 271 (1925)), are explained as due to a hitherto unsuspected effect. Cf. the concluding remarks of this paper.

[15] A curve of the type published by Pierce for air, i.e., involving maxima or minima could be formally accounted for by a large fourth order effect of opposite sign to the second order term. In any particular case, however, the parameters involved could all be estimated from the low frequency velocity and absorption and independent data and hence the permissibility of the explanation tested. It is clear too that neglected terms in our equations would affect the higher approximations. Cf. also Note 12. In this connection it may be remarked that a falling velocity-frequency characteristic is not impossible, for Eq. (5) yields for the ν^2 velocity correction the following negative sum, besides the usually predominant positive terms

$$\frac{\nu^2}{V_0^2}\left\{\frac{\dfrac{\psi+\frac{2}{3}\Sigma\beta_W\gamma_W}{V_0^2}+\dfrac{4}{9}\sum\dfrac{N_W\beta_W^2}{\Sigma N_R L_{WR}}}{1+\frac{2}{3}\sum N_W\beta_W/N}\right\}^2$$

Comparison with the positive terms involving the conductivities indicates that in general their effect is in the direction of decreasing velocity (Compare Herzfeld-Rice, reference 2).