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Supersonic Absorption and Stokes' Viscosity Relation

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It is pointed out that the reduction of the *two* viscosity coefficients to *one* according to the Stokes' relation $2\mu+3\lambda=0$ is not justified except in the special case of a monatomic gas. The generalization of this relation by the re-introduction of the second independent viscosity coefficient $\kappa=\frac{2}{3}\mu+\lambda$ makes it possible to develop the phenomenological theory of the absorption and dispersion of sound, in agreement with experiment in complete analogy to the corresponding optical phenomena. The connection of the well-known relaxation theory with classical hydrodynamics can be established and in the case of polyatomic gases κ is expressed by the characteristic constants of this theory. The case of liquids is discussed. In polyatomic gases and liquids one has generally $\kappa\gg\mu$. Other hydrodynamical consequences of the introduction of κ are discussed.

I. INTRODUCTION

It is a well-known fact that the supersonic absorption in polyatomic gases and in liquids exceeds by far the absorption predicted by the classical theory based on viscosity. For the very extended literature we refer to the detailed bibliography contained in the recent review of Richards.[1] The effect of heat conductivity on absorption is in general still smaller; we shall not discuss it in the following.

The "anomalous" absorption in gases is accompanied by a dispersion of sound velocity. Both absorption and dispersion were interpreted with success by the relaxation theory first proposed by Herzfeld and Rice[2] and developed by many others.[1]

This theory is based on the hypothesis that the molecular vibration requires a much larger number of collisions for reaching the state of thermal equilibrium than the translation and rotation. In other words, the relaxation time τ for the vibrational degrees of freedom is much greater than the relaxation time for the Maxwell distribution for the translational degrees of freedom. The latter is under ordinary conditions of the order of 10^{-9} sec. This hypothesis leads in a straight-forward way to a complex and frequency dependent specific heat making it possible to account for the absorption and dispersion of sound.

The persistence of the excited vibrational states over a period covering many thousand collisions has been proved through direct spectroscopic evidence by R. J. Dwyer.[3] On the other hand, τ could be calculated theoretically from molecular data by Landau and Teller.[4]

We therefore may consider it an unquestioned fact that there is a time lag in the establishment of equilibrium for the internal degrees of freedom and consequently a dissipation of energy. The purpose of the present paper is to show that the classical hydrodynamical equations can be easily generalized so as to include this phenomenon. One has merely to re-introduce the second viscosity coefficient which appeared automatically in the hydrodynamical equations but which was eliminated by the well-known relation of Stokes.

For perfect polyatomic gases the relaxation theory may be considered as a kinetic calculation of this viscosity coefficient. Our phenomenological scheme remains of course valid for liquids, too, while the relaxation theory encounters in this case the characteristic difficulties of the kinetic theory.

II. THE STOKES' RELATION

The so-called second approximation of the hydrodynamical equations is based on the hypothesis of Newton according to which the stress tensor p_{ik} is a linear function of

$$u_{ik}=\tfrac{1}{2}(\partial u_i/\partial x_k+\partial u_k/\partial x_i),$$

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[1] W. T. Richards, Rev. Mod. Phys. **11**, 36 (1939).

[2] K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1929).

[3] R. J. Dwyer, J. Chem. Phys. **7**, 40 (1939).

[4] L. Landau and E. Teller, Physik. Zeits. Sowjetunion **10**, 34 (1936).

the time derivative of the deformation tensor (u_i is the ith component of the flow velocity). The most general relation of this kind is[5]

$$p_{ik}=p_0\delta_{ik}-2\mu u_{ik}-\lambda\delta_{ik}\sum\nolimits_\alpha u_{\alpha\alpha}, \tag{1}$$

where δ_{ik} is the Kronecker symbol, p_0 the pressure in the first approximation (the hydrostatic pressure), and μ, λ are the viscosity coefficients. The first one is the ordinary shearing viscosity, the second is sometimes called compression coefficient. Defining in the usual manner the scalar pressure p as the mean value of the diagonal elements of the stress tensor, we obtain

$$p=\tfrac{1}{3}\sum\nolimits_\alpha p_{\alpha\alpha}=p_0-(\tfrac{2}{3}\mu+\lambda)\sum\nolimits_\alpha u_{\alpha\alpha}. \tag{2}$$

Introducing the notation

$$\tfrac{2}{3}\mu+\lambda=\kappa \tag{3}$$

and making use of the continuity equation, we have

$$p=p_0+\kappa(1/\rho)d\rho/dt. \tag{2a}$$

That is, the constant κ—which we shall prefer to use instead of λ—has a simple meaning: It gives the second-order correction to the hydrostatic pressure, arising as a consequence of a compression or dilatation.[6]

A difficulty arises, however, in the determination of κ, because the pressure of the first approximation p_0 is properly defined for the hydrostatic case only. We may extend the definition to our non-static case by the following convention:

We define $p_0(\rho)$ as the pressure which would result from an *adiabatic compression* starting from the equilibrium state $p_0(\rho_0)$. Obviously p_0 is a function of *one* independent variable, of the density. Therefore, there exists a function $\mathbf{P}=\int 1/\rho dp_0$, such that $d\mathbf{P}/dx_i=1/\rho dp_0/dx_i$.

The second approximation of the hydrodynamical equations may then be written in our notation:

$$du_i/dt=-\partial/\partial x_i(\mathbf{P}+U)+\mu\nabla^2u_i +(\mu/3+\kappa)\partial/\partial x_i\sum\nolimits_\alpha \partial u_\alpha/\partial x_\alpha \tag{4}$$

where U is the potential of the external mass forces. We see that our decomposition (2a) of the pressure into two terms is reasonable, because the first term gives rise to forces of *conservative* and the second term to forces of *dissipative* character.

It has to be noted that (2a) and (4) are not the most general formulae, because non-adiabatic processes as heat conduction and radiative transfer of heat also give rise to additional terms to the hydrostatic pressure. Consequently, heat conduction gives dissipative effects as sound absorption. The non-adiabatic radiative heat transfer is particularly important in meteorology, where we have to add to the hydrostatic pressure $p_0(\rho)$ a term which is a function of two variables ρ, T. This case has been thoroughly discussed by V. Bjerknes.[7] In the present paper we are concerned only with the viscous effects.

In general it is usual to specialize (2a) and (4) by the relation

$$3\kappa=2\mu+3\lambda=0. \tag{5}$$

This relation has been the object of much controversy. Most of the hydrodynamical textbooks introduce it by referring simply to Stokes.[8] It is sometimes maintained that (5) is only an arbitrary convention for the definition of the scalar pressure.[9] In other textbooks the inadequacy of this relation has been pointed out,[10] but so far as we know, its generalization has never been thoroughly discussed.

For monatomic gases, (5) can be rigorously derived from the kinetic theory. But, as we saw in the introduction, for polyatomic gases there is a time lag for the establishment of equilibrium of the internal degrees of freedom, and similar conditions may be expected in general for any system where the energy is distributed over different kinds of degrees of freedom, i.e., for any system except a monatomic gas. In the case of the existence of such a relaxation time τ, the pressure of the fluid will depend not only on the instantaneous value of the density, but also on

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[5] E.g., H. Lamb, *Hydrodynamics* (1932), sixth edition, p. 574.

[6] We would prefer to call this term a "first-order correction," but this would be in contradiction with the usual expression of "hydrodynamical equations of the first approximation," for the equations without any viscosity term.

[7] Reference 5, p. 247.

[8] E.g., "It has been argued with great force by Professor Stokes . . ." Lord Rayleigh, *The Theory of Sound*, second edition, Vol. 2, p. 315.

[9] E.g. Enc. Math., third edition, Vol. 4, p. 69.

[10] E.g., M. Brillouin, *Leçons sur la Viscosité* (Paris, 1907). Report of the Committee on Hydrodynamics. Bull. Nat. Research Comm. No. 84 (1932).

the "history" of the system. The Newton hypothesis (1) or (2a), claiming proportionality of the pressure with the first time derivative of the density, means that only the dependence on the *near past* is considered. This is justified if the times involved in the phenomenon are small compared to the relaxation time, or if one has $\omega \ll \tau^{-1}$ where ω is the sound frequency.

If the last condition is not satisfied, we may proceed as in the similar case in optics and consider the "constant" κ as a complex function of frequency.

Finally, we must discuss the view according to which the relation (5) is merely a convention. Indeed, it is possible to introduce (5) as a definition of $p_0(\rho)$, instead of defining it by our above-mentioned convention. According to (2a) one has then $p=p_0$: first- and second-order pressures are identical, i.e., one cannot introduce the concept of the "pressure in first approximation" and has to allow the pressure to depend on other variables than the density alone. Though this procedure is not less justified than that proposed by us, the introduction of the constant κ and the clean separation of conservative and dissipative forces seem to be useful for many hydrodynamical problems.

Before going over to the discussion of the consequences of the introduction of κ, we will quote two passages of the papers of Stokes. These will make it evident that Stokes himself did not consider the relation (5) as a definition, but foresaw the possibility of the present generalization in case experiment would demand it.

". . . Of course we may at once put $\kappa=0$ if we assume that in the case of a uniform motion of dilatation the pressure at any instant depends only on the actual density and temperature at that instant and not on the rate at which the former changes with the time. In most cases to which it would be interesting to apply the theory of the friction of fluids, the density of the fluid is either constant or may without sensible error be regarded as constant, or else changes slowly with the time. In the first two cases the results would be the same and in the third nearly the same whether κ were equal to zero or not. Consequently, if theory and experiments should in such cases agree, the experiments must not be regarded as confirming that part of the theory which relates to supposing κ to be equal to zero."[11]

". . . I have always felt that the correctness of the value $\frac{1}{3}\mu$ for the coefficient of the last term of (4) does not rest on as firm a basis as the correctness of the equation of motion of an incompressible fluid, for which the last term does not come in at all. If the supposition made above be not admitted, we must replace the coefficient $\frac{1}{3}\mu$ by a different coefficient which has to be written $\frac{1}{3}\mu+\kappa$ and κ must be positive as otherwise the more alternate expansion and compression, alike in all directions, of a fluid, instead of demanding the exertion of work upon it, would cause it to give out work. . . ."[12]

III. ABSORPTION AND DISPERSION OF SOUND

The additional term in the equation of motion will give rise to a new term in the dissipation function

$$\kappa \int\int\int \left(\sum_{\alpha} \frac{\partial u_\alpha}{\partial x_\alpha} \right)^2 dxdydz. \tag{6}$$

In particular it will give rise to an additional absorption of sound which we are going to consider.

We shall restrict ourselves to small amplitudes and derive from (4) and the equation of continuity in the usual approximation the wave equation of sound

$$\ddot{\rho} - V_0^2 \nabla^2 \rho - (4\mu/3+\kappa) 1/\rho \nabla^2 \dot{\rho} = 0, \tag{7}$$

where $V_0 = (\partial p/\partial \rho)^{\frac{1}{2}}$ is the sound velocity in the absence of viscosity. In the plane wave solution

$$\rho = \rho_0 + \rho_1 e^{i(\omega t - kx)} \tag{8}$$

k is complex, with the real and imaginary parts giving the sound velocity V and the absorption coefficient per unit length for the amplitude α. In other words we have

$$\text{real part } (k) = \omega/V, \text{ imaginary part } (k) = -\alpha. \tag{9}$$

Neglecting the quadratic term in the viscosity we have

$$k = \omega/V_0 [1 - (4\mu/3+\kappa) i\omega / 2\rho V_0^2], \tag{10}$$

i.e.,

$$V = V_0, \quad \alpha = (4\mu/3+\kappa)\omega^2/2\rho_0 V_0^3. \tag{11}$$

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[11] G. G. Stokes, Math. Phys. Papers **1**, p. 88.

[12] G. G. Stokes, Math. and Phys. Papers **3**, p. 136. We have slightly changed the notation.

The κ viscosity gives an absorption coefficient proportional to ω^2 and no dispersion, just as the μ viscosity does.

In the case of a perfect polyatomic gas the fraction of the absorption proportional to κ must be identical with the value given by the relaxation theory in the limit of low frequencies. The result of this theory can be expressed in the following form:[1]

$$\omega^2/k^2=p/\rho_0\left[1+(\gamma-1)\left(1-\eta+\frac{\eta}{1+i\omega\tau}\right)^{-1}\right], \quad (12)$$

where $\gamma=c_p/c_v$ is the ratio of the (static) specific heats at constant pressure and volume and $\eta=c_i/c_v$ is the fraction of the specific heat at constant volume corresponding to the internal degrees of freedom for which the equilibrium is established with the relaxation time τ. (More generally one would have to consider different η and τ values for every normal vibration.)

We obtain from (12) on neglecting the square of the second term,

$$k=\frac{\omega}{V_0}\left[1-\frac{1}{2}\cdot\frac{i\omega\tau(\gamma-1)}{(1+i\omega\tau(1-\eta))\gamma}\right]. \quad (13)$$

In the limit of small frequencies $\omega\tau\ll1$ we have

$$k=\omega/V_0[1-\tfrac{1}{2}i\omega\tau\eta(\gamma-1)/\gamma]. \quad (14)$$

The comparison (14) with the last term of (10) yields

$$\kappa=\rho_0V_0^2\tau\eta(\gamma-1)/\gamma. \quad (15)$$

We obtain a very simple form for κ if we remember that $V_0^2=\frac{1}{8}\pi\gamma\bar{v}^2$ where $\bar{v}$ is the mean thermal velocity and if we define the mean free path l' relative to the excitation of the vibration in question by the relation $l'=\tau\bar{v}$ we have thus

$$\kappa=\tfrac{1}{8}\pi\rho_0\bar{v}(\gamma-1)l'\eta. \quad (16)$$

More generally one has

$$\kappa=\tfrac{1}{8}\pi\rho_0\bar{v}(\gamma-1)\textstyle\sum_i l'_i\eta_i, \quad (16a)$$

where the sum is taken over the different internal degrees of freedom, e.g., the different normal vibrations.

Equations (16) or (16a) can be easily compared to the ordinary viscosity, given by the well-known elementary formula

$$\mu=\tfrac{1}{3}\rho_0\bar{v}l, \quad (17)$$

where l is the mean free path in the ordinary sense.

These results cease to be valid for $\omega\gtrsim\tau^{-1}$. In this frequency region the pressure will depend not only on the density and the rate of compression, as claimed by the relation of Newton, but on the whole history of the system. (A "non-Newtonian" behavior occurs also with respect to the shearing viscosity μ.) One can proceed, however, as in the analogous case in optics and introduce formally a coefficient $\kappa(\omega)$ depending on frequency. Comparing now (10) with (13) rather than with (14), we get

$$\kappa(\omega)=\rho_0V_0^2(\gamma-1)/\gamma[1+i\omega\tau(1-\eta)]^{-1}. \quad (18)$$

Separating real and imaginary parts:

$$\kappa=\kappa_1-i\kappa_2$$

we have according to (9) (10)

$$\alpha=\kappa_1\omega^2/2\rho_0V_0^3,\quad V=V_0(1+\kappa_2\omega/2\rho_0V_0^2). \quad (19)$$

Using (18) we get

$$\alpha=\frac{(\gamma-1)\eta\omega\tau}{2V_0\gamma[1+(1-\eta)^2\omega^2\tau^2]} \quad (20)$$

and

$$V=V_0\left[1+\frac{(\gamma-1)\eta(1-\eta)\omega^2\tau^2}{2\gamma[1+(1-\eta)^2\omega^2\tau^2]}\right]. \quad (21)$$

Equations (20) and (21), though somewhat different in notation, are of course identical with the corresponding formulae of the relaxation theory and are in general agreement with experiment. It should be possible to determine from the measurements the numerical values of the constants τ, η and so of κ. Unfortunately, there is a considerable deviation between the measurements of different laboratories, and keeping in mind the criticisms of W. T. Richards,[1] we would not attempt to fix the numerical values of these constants. We remark merely for orientation that on the basis of the experimental results obtained and compiled by Kneser[13] one has for CO_2 and N_2O $\kappa/\mu\sim2\times10^3$. For air κ and μ seem to be of the same order of magnitude.

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[13] H. O. Kneser, Ann. d. Physik 16, 337 (1933).

The "anomalous" absorption of supersonics in liquids has been first observed by Biquard,[14] and has been corroborated since by many workers.[1] According to more recent results, V and α/ω^2 are for most liquids constant over wide ranges of frequencies,[15,16] i.e., we find very often a "Newtonian" behavior and can operate with a constant, real κ.

Kneser[17] proposed to interpret the absorption in liquids exactly as in the case of gases by the relaxation time connected with the internal molecular vibration. Herzfeld has shown recently[18] that, at least for water, the vibrational energy is insufficient to account for the effect. Herzfeld mentions the possibility that the relaxation time connected with the configurational energy might be of importance, as it was previously suggested by Debye. He proposes tentatively an equation which is equivalent to our Eq. (3).

The question may be put somewhat more generally. Roughly speaking, the energy of a liquid can be considered as consisting of molecular and intermolecular vibrations, of Debye quanta and of configurational energy (quasi-crystalline structure). This does not mean, of course, that we assume any strict additivity between these types of energies. In any case these types of energies will be distinct from the translational energy of the sound wave, and one will have to attribute different relaxation times to them. Therefore, practically the whole thermal energy of the liquid will contribute to the absorption ($\eta \sim 1$), whereas under ordinary conditions for gases ($\eta \ll 1$). On the other hand, because of the strong interaction in the liquid the relaxation time will be smaller than in the case of the gases. Although we cannot assume the formula (16a) to hold quantitatively for liquids, the experimental evidence of values of κ varying widely from one liquid to the other is not too surprising.

As concerns the determination of the numerical value of κ for the different liquids from experiment, we are faced with still greater difficulties than in the case of gases. Should we assume that the observed loss in the propagation of supersonics is owing entirely to the ***true absorption*** given by our formula (11) then we could determine κ out of the relation

$$L = \mu + \tfrac{3}{4}\kappa, \tag{22}$$

where L is the experimental "loss factor" defined and tabulated for the different liquids by Willard.[15] We would thus get values up to 2000 for κ/μ. It has to be kept in mind, however, that losses are not always caused by true absorption (energy converted into heat) but also to the scattering of the supersonic wave by density fluctuations.[19] As we do not see the possibility of an independent measurement of κ, the absorption measurements ought to be carefully analyzed as to the possibility of an evaluation of κ.

In the cases where α/ω^2 and V vary with the frequency, κ has to be chosen again as a function of ω. It is, however, not surprising that the formula (16a) derived for gases cannot quantitatively account for the experiments.

It is obvious that the knowledge of κ could prove useful in the investigation of liquid structure. The molecular interpretation of the experimental results would, however, be difficult in view of the different mechanisms contributing to κ. The situation is not very much different, though still more complicated, than in the case of the ordinary μ viscosity. The monatomic liquids would, therefore, be of special interest. The only monatomic liquid studied is mercury with an absorption which does not exceed considerably the classical value[20] ($\kappa/\mu \sim 1.5$). It is not quite certain, however, that mercury is a typical case.

IV. HYDRODYNAMICAL CONSEQUENCES OF THE INTRODUCTION OF κ

We have seen that the experiments on supersonic absorption lead for many liquids and gases to the result that the newly introduced viscosity coefficient exceeds by far the ordinary viscosity

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[14] P. Biquard, Comptes rendus **193**, 226 (1931); Ann. d. Physik **6**, 195 (1936); Biquard indicated that the anomalous absorption might be due to the breakdown of Stokes' relation for high frequencies.

[15] G. W. Willard, J. Acous. Soc. Am. **12**, 438 (1941).

[16] F. E. Fox and G. D. Rock, J. Acous. Soc. Am. **12**, 505 (1941).

[17] H. O. Kneser, Ann. d. Physik **32**, 277 (1938).

[18] K. F. Hezfeld, J. Acous. Soc. Am. **13**, 33 (1941).

[19] R. Lucas, J. de Phys. **8**, 41 (1937). For a discussion of other sources of error cf. reference 15.

[20] R. Bär, Helv. Phys. Acta **10**, 332 (1937).

$\kappa \gg \mu$. The question arises, naturally, what are the other hydrodynamical consequences of the introduction of κ and why the usual method of ignoring it did not lead to more difficulties.

It can be seen from (6) and (8) and the continuity relation that the energy dissipation due to the κ viscosity for a periodic process of the frequency ω is of the order of

$$\kappa\omega^2(\rho_1/\rho_0)^2. \tag{22}$$

Hydrodynamics usually deals with problems where compressibility can be neglected, i.e., $\rho_1/\rho_0 \ll 1$. In fact, this was the chief reason why Stokes thought the value of κ was of secondary importance.[11] This circumstance can be, however, compensated if $\omega \gg 1$. This is the case of acoustical waves and still more of supersonics which have been amply discussed.

On the other hand, there are problems for which the compressibility cannot be neglected, when the flow velocities reach and exceed the sound velocity. These problems are treated by the so-called *gas dynamics*. In this case ρ_1/ρ_0 is of the order of unity and (22) can no more be neglected even if $\omega \sim 1$.

Not only the viscous, but also the turbulent dissipation has to be revised in the case of gas dynamics. The origin of turbulence has been studied chiefly for incompressible liquids. In this case a change in circulation may arise only as a consequence of the shearing viscosity near solid walls (Grenzschichttheorie of Prandtl). Computing the time derivative of circulation around a contour moving with the liquid on the basis of Eq. (4) one gets an additional term proportional to κ, which we shall consider now:

$$(d/dt)\oint \mathbf{u}\cdot d\mathbf{r} = \kappa \oint \frac{1}{\rho}\,\text{grad div}\,\mathbf{u}\cdot d\mathbf{r}. \tag{23}$$

This can be written in a more convenient form by using Stokes' theorem and the continuity equation:

$$\frac{d}{dt}\oint \mathbf{u}\cdot d\mathbf{r} = \kappa \int\int \text{grad}\,\frac{1}{\rho} \times \text{grad}\,\frac{d \ln \rho}{dt} dF, \tag{24}$$

where dF is the surface element of a surface F spanned by the contour.

Let us consider two series of surfaces with $1/\rho = \text{constant}$ and $(d/dt) \ln \rho = \text{constant}$, respectively. We choose the distances of the neighboring surfaces to be $1/h_1 = |\text{grad}\,1/\rho|$ and $1/h_2 = |\text{grad}\,d/dt \ln \rho|$. These surfaces form tubes which cut elementary surfaces f out of the surface F. It follows readily that

$$\frac{d}{dt}\oint \mathbf{u}\cdot d\mathbf{r} = \kappa \int\int \frac{dF}{f}, \tag{25}$$

i.e., the rate of change of the circulation around a contour is equal to the number of tubes cutting the surface F.

Equation (25) is in formal analogy to a formula of Bjerkness concerning the rate of change of circulation in a fluid where the pressure is not entirely determined by the density, which is important in meteorology.[7]

It is a pleasure for us to thank Professor K. F. Herzfeld for his critical remarks and Dr. Biquard for discussing the experiments on supersonic absorption.