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ON VOLUME VISCOSITY AND ACOUSTIC DISPERSION PHENOMENA

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ABSTRACT

Our bulk-visco-elastic theory is extended to the case, as recently discovered in ultrasonic absorption measurements, in which there are present more than one relaxation times. This multi-relaxational theory is applied to the study of acoustic dispersion phenomena. The bearing of our relaxational theory in general on classical hydrodynamics is further examined. Illustrative calculations from certain available experimental data are given and their indications discussed.

It seems now well accepted that the excessive absorption of sound in fluids is due to relaxational molecular processes. A relaxational bulk-visco-elastic theory, assuming a single relaxational process, has been given by the writer[1]. Certain ultrasonic experimental data on sound absorption[2, 3] have shown the existence of more than one relaxation times for a single fluid-substance. More than one relaxational molecular processes are, indeed, to be expected in view of the existence of several vibration modes in the case of a gas and of the possible existence of several ways of molecular rearrangement in the case of a liquid. This fact necessitates an extension of our relaxational theory previously given.

1. MULTI-RELAXATIONAL VISCO-ELASTIC THEORY

Assume the simultaneous existence of several components or alternative molecular processes with different relaxation times $\tau_1, \tau_2, \ldots, \tau_i, \ldots$. Let n_i/n be the fractional occurrence of the ith relaxational process. Then $\sum_i n_i = n$. Recollecting that the compressibility, β_o, of a fluid element due to a constant change of the applied pressure is composed of two parts, one, β_∞,

1. Hoff Lu, *Chinese J. Phys.* **7** (1950), 365.
2. W. H. Pielemeier, *Jour. Acous. Soc. Am.* **15** (1943), 25.
3. E. A. Alexander and J. D. Lambert, *Proc. Roy. Soc.* A, **179** (1942), 499.

representing an instantaneous compression and another, β_r representing a relaxational compression due to volume viscosity, the time variation of relative compression, $s = -\triangle V/V$, may be represented by

$$\frac{ds}{dt} = \frac{1}{n} \sum_i n_i \frac{ds_i}{dt} , \tag{1}$$

with

$$\frac{ds_i}{dt} = \beta_\infty \frac{dp}{dt} + \frac{s_o - s_i}{\beta_o \eta_{2i}} , \tag{2}$$

where $s_o = \beta_o (p - p_o)$ is the equilibrium value of s ultimately produced by a constant pressure $p = p(\rho)$. As before, we may formally arrive at (2) if we define the ith coefficient of volume viscosity η_{2i} by

$$\bar{p} - p_i' = \eta_{2i} \left(\frac{ds_i}{dt} \right)_{\text{vis}} , \tag{3}$$

where

$$\left(\frac{ds_i}{dt} \right)_{\text{vis}} = \frac{ds_i}{dt} - \frac{ds_\infty}{dt} = \frac{ds_i}{dt} - \beta_\infty \frac{dp}{dt} ,$$

$\bar{p}$ is the mean dynamic pressure of hydrodynamics, being equivalent to a static pressure p as far as the steady value of s is concerned, and $p_i' = p_i' (\rho)$ is an effective dynamic pressure that determines the actual s_i according to

$$s_i = \beta_o (p_i' - p_o) . \tag{4}$$

Equation (2) shows a relaxation time

$$\tau_{2i} = \beta_o \eta_{2i} \tag{5}$$

for the part of compressional strain depending on η_{2i}.

Since obviously

$$s = \frac{1}{n} \sum_i n_i s_i = \frac{1}{n} \beta_o \sum_i n_i (p_i' - p_o)$$

$$= \beta_o \left(\frac{1}{n} \sum n_i p_i' - p_o\right) = \beta_o (p' - p_o) ,$$

the effective dynamic pressure is

$$p' = \frac{1}{n} \sum_i n_i p_i' \tag{6}$$

The overall volume viscosity η_2 as defined by

$$\bar{p} - p' = \eta_2 \left(\frac{ds}{dt} \right)_{\text{vis}} \tag{7}$$

is, by (3) and (6),

$$\eta_2 = \frac{1}{n} \sum_i n_i \eta_{2i} \left(\frac{ds_i}{dt} \right)_{\text{vis}} \Big/ \left(\frac{ds}{dt} \right)_{\text{vis}} . \tag{8}$$

2. DISPERSION AND ABSORPTION OF SOUND

Writing $$s_i = C_i e^{-\alpha_i x} e^{i\omega (t - x/v_i)} = C_i e^{i\omega (t - x/v_i^*)} ,$$

we have, for the practical case $\omega \gg \alpha_i v_i$, approximately.

$$v_i^{*2} \simeq v_i^2 + 2i\alpha_i v_i^3 / \omega , \tag{9}$$

and

$$v_i^{*2} = (k_i^* + \frac{4}{3} \mu^*)/\rho , \tag{10}$$

where $k_i^* = 1/\beta_i^*$ is the complex bulk modulus and μ^* the complex shear modulus. (2) yields

$$\beta_i^* = \beta_\infty + \frac{\beta_r}{1 + i\omega\tau_{2i}} , \tag{11}$$

while μ^* has been found[1] for two cases.

In the case of a gas or a more gas-like liquid, $\mu^* = i\omega\eta_1$, and we find, by comparing the real parts of (9) and (10),

$$v_i^2 = \frac{1}{\rho}\frac{\beta_o + \beta_\infty\,\omega^2\tau_{2i}^2}{\beta_0^2 + \beta_\infty^2\,\omega^2\tau_{2i}^2}\,. \tag{12}$$

Thus, there are as many sound velocities as there are relaxational processes causing the volume viscosity. However, in the following limiting cases, these velocities all merge into one, viz.,

$$\text{as}\quad \omega\tau_{2i}\text{'s} \longrightarrow 0\,, \qquad v \longrightarrow v_o = 1/(\rho\,\beta_o)^{\frac{1}{2}}\,; \tag{13}$$

$$\text{as}\quad \omega\tau_{2i}\text{'s} \longrightarrow \infty\,, \qquad v \longrightarrow v_\infty = 1/(\rho\,\beta_\infty)^{\frac{1}{2}}\,; \tag{14}$$

giving

$$\rho\,v_0^2\,\beta_o = \rho\,v_\infty^2\,\beta_\infty = 1\,. \tag{15}$$

The inflectional point of each dispersion curve, v_i^2 versus $\log\omega$, is found to be at the frequency $(\omega_i)_i = \beta_o/\beta_\infty\tau_{2i} = v_\infty^2/v_o^2\tau_{2i}$.

Comparing the imaginary parts of (9) and (10), we find

$$\alpha_i = \frac{\omega^2}{2\rho v_i^3}\left[\frac{4}{3}\eta_1 + \frac{\beta_o\beta_r}{\beta_0^2 + \beta_\infty^2\,\omega^2\tau_{2i}^2}\eta_{2i}\right]. \tag{16}$$

The experimentally measured coefficient of absorption is usually the intensity coefficient per wave length, i.e., γ as defined in $I = I_o e^{-\gamma x/\lambda} = I_o e^{-2\alpha x}$ so that $\gamma = 2\lambda\alpha$. Thus, we have

$$\gamma_i = \gamma_{1i} + \gamma_{2i} = 2\pi\,\omega\,\beta_o\left[\frac{4}{3}\eta_1\frac{\beta_0^2 + \beta_\infty^2\,\omega^2\tau_{2i}^2}{\beta_o\{\beta_o + \beta_\infty\,\omega^2\tau_{2i}^2\}} + \eta_{2i}\frac{\beta_r}{\beta_o + \beta_\infty\,\omega^2\tau_{2i}^2}\right] \tag{17}$$

The observed absorption coefficient per wave length is

$$\gamma = \frac{1}{n}\sum_i n_i\gamma_i\,, \tag{18}$$

$$\text{As}\quad \omega\tau_{2i}\text{'s} \longrightarrow 0, \qquad \gamma \longrightarrow \gamma_o = 2\pi\,\omega\,\beta_o\left[\frac{4}{3}\eta_1 + \frac{\beta_r}{\beta_o}\sum_i\frac{n_i}{n}\eta_{2i}\right]; \tag{19}$$

$$\text{as}\quad \omega\tau_{2i}\text{'s} \longrightarrow \infty\,, \quad \gamma \longrightarrow \gamma_\infty = 2\pi\,\omega\,\beta_\infty\left[\frac{4}{3}\eta_1 + \frac{\beta_r}{\beta_o\beta_\infty^2\,\omega^2}\sum_i\frac{n_i}{n}\frac{1}{\eta_{2i}}\right]. \tag{20}$$

The part of γ due to η_{2i} has its maximum value equal to

$$\frac{n_i}{n}(\gamma_2)_{max} = \frac{n_i}{n}\pi\frac{\beta_r}{(\beta_o\beta_\infty)^{1/2}} = \frac{n_i}{n}\pi\frac{v_\infty^2 - v_0^2}{v_\infty v_o}, \tag{21}$$

and at the frequency

$$(\omega_m)_i = (\beta_o/\beta_\infty)^{\frac{1}{2}}/\tau_{2i} = v_\infty/v_o\tau_{2i}\ . \tag{22}$$

These equations are found to be satisfactory in representing the observed dispersion phenomena. An illustrative calculation of η_{2i}, β_o, and β_∞, in the case of dry CO_2, is given in § 4.

For a more solid-like liquid, we had[1] $\mu^* = \mu i\omega\tau_1/(1+i\omega\tau_1)$, where τ_1 is Maxwell's relaxation time for the shearing process, i.e. $\tau_1=\eta_1/\mu$. Likewise, we may find the corresponding expressions for v_i and γ, the results being as follows:

$$v^2 = \frac{1}{\rho}\left(\frac{4}{3}\frac{\mu\omega^2\tau_1^2}{1+\omega^2\tau_1^2} + \frac{\beta_o+\beta_\infty\omega^2\tau_{2i}^2}{\beta_0^2+\beta_\infty^2\omega^2\tau_{2i}^2}\right). \tag{23}$$

As $\omega\tau_1 \longrightarrow 0$, and $\omega\tau_{2i}$'s $\longrightarrow 0$, $\quad v \longrightarrow v_o = 1/(\rho\,\beta_o)^{\frac{1}{2}}$; (24)

as $\omega\tau_1 \longrightarrow \infty$, and $\omega\tau_{2i}$'s $\longrightarrow \infty$, $\quad v \longrightarrow v_\infty = \left[(k_\infty + \frac{4}{3}\mu)/\rho\right]^{\frac{1}{2}}$. (25)

$$\alpha_i = \frac{\omega^2}{2\rho v_i^3}\left[\frac{4}{3}\frac{1}{1+\omega^2\tau_1^2}\eta_1 + \frac{\beta_o\beta_r}{\beta_0^2+\beta_\infty^2\omega^2\tau_{2i}^2}\eta_{2i}\right]. \tag{26}$$

As $\omega\tau_1 \longrightarrow 0$, and $\omega\tau_{2i}$'s $\longrightarrow 0$,

$$\gamma \longrightarrow \gamma_o = 2\pi\omega\beta_o\left[\frac{4}{3}\eta_1 + \frac{\beta_r}{\beta_o}\sum_i\frac{n_i}{n}\eta_{2i}\right]; \tag{27}$$

as $\omega\tau_1 \longrightarrow \infty$, and $\omega\tau_{2i}$'s $\longrightarrow \infty$,

$$\gamma \longrightarrow \gamma_\infty = \frac{2\pi\beta_\infty}{\omega(1+\frac{4}{3}\mu\beta_\infty)}\left[\frac{4}{3}\frac{\mu^2}{\eta_1} + \frac{\beta_r}{\beta_o\beta_\infty^2}\sum_i\frac{n_i}{n}\frac{1}{\eta_{2i}}\right]. \tag{28}$$

There does not exist absorption data of solid-like liquids at frequencies near the dispersion region to allow a test of these equations.

3. ON THE GENERALIZED CLASSICAL HYDRODYNAMICS

Classical hydrodynamics has been generalized[1] to embody the effect of η_2 by assuming

$$\bar{p} - p' = (\lambda + \frac{2}{3}\eta_1)\left(\frac{ds}{dt}\right)_{\text{vis}} = (\lambda + \frac{2}{3}\eta_1)\left(\frac{ds}{dt} - \frac{ds_\infty}{dt}\right)$$

$$= -(\lambda + \frac{2}{3}\eta_1)\left(\nabla \cdot \boldsymbol{v} + \beta_\infty \frac{dp}{dt}\right),$$

where λ and η_1 are Lamé's type coefficients. The equation of motion then becomes

$$\rho \frac{d\boldsymbol{v}}{dt} = \rho \boldsymbol{f} - \nabla p' + (\frac{1}{3}\eta_1 + \eta_2)\nabla\nabla\cdot\boldsymbol{v} + \eta_1\nabla^2\boldsymbol{v} + \eta_2\beta_\infty\nabla\frac{dp}{dt}. \quad (29)$$

This equation differs in form from the classical equation first explicitly given by Tisza[4] and also used by Eckart[5] merely in the presence of the extra term $\eta_2\beta_\infty\nabla\frac{dp}{dt}$. It is seen that Tisza's hydrodynamics neglects the instantaneous dilatational strain and corresponds to the approximation $\nabla\cdot\boldsymbol{v} \approx -(ds/dt)_{\text{vis}}$, implying that $ds_\infty/dt \ll (ds/dt)_{\text{vis}}$. We note that for an incompressible fluid, $\nabla\cdot\boldsymbol{v} = 0$ and $dp/dt = 0$, we have $p' = \bar{p}$ and (29) reduces to

$$\rho\frac{d\boldsymbol{v}}{dt} = \rho\boldsymbol{f} - \nabla\bar{p} + \eta_1\nabla^2\boldsymbol{v},$$

so that the effect of η_2 vanishes. Since hydrodynamics is ordinarily applied to fluids that may be regarded as incompressible, we see why η_2 remains unnoticed for so long. We further note that in (29) the effect of any shear modulus that may exist has been neglected. How this may be included has been indicated by Frenkel[6].

Classical hydrodynamics as here generalized according to (29) leads to[1] the approximate expression

$$\alpha = \frac{\omega^2}{2\rho v^3}\left(\frac{4}{3}\eta_1 + \frac{\beta_r}{\beta_o}\eta_2\right) \quad (30)$$

4. Tisza, L., *Phys. Rev.* **61** (1942), 531.
5. Eckart, C., *Phys. Rev.* **73** (1948), 68.
6. Frenkel, J., *Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1946), IV, 10, pp. 248-249.

for the amplitude coefficient of absorption at sufficiently low frequencies. This is seen to be the same as the limiting form of our visco-elastic theory for $\omega\tau_1 \to 0$ and $\omega\tau_{2i}$'s $\to 0$ with

$$\eta_2 = \frac{1}{n} \sum_i n_i \eta_{2i} \, . \tag{31}$$

It is to be noted that the hydrodynamical equation involving η_2 employed by Tisza[4], Eckart[5], and others is the one obtained from (29) by dropping the last term which represents the effect of instantaneous strain. Such an equation leads to the approximate expression

$$\alpha = \frac{\omega^2}{2\rho v^3}\left(\frac{4}{3}\eta_1 + \eta_2\right) \tag{32}$$

for sufficiently low frequencies. Comparing this with (16) and (26), we see that

$$\beta_o \beta_r \sum_i \frac{n_i}{n} \frac{\eta_{2i}}{\beta_0^2 + \beta_\infty^2 \omega^2 \tau_{2i}^2} \, , \tag{33}$$

or $\frac{\beta_r}{\beta_o} \sum_i \frac{n_i}{n} \eta_{2i}$ for sufficiently low frequencies, plays the role of an effective volume viscosity for such a hydrodynamical theory.

4. ILLUSTRATIVE CALCULATIONS

Results of calculations of the volume viscosity and the static and instantaneous compressibilities from the observed maxima of sound absorption in the case of a single relaxation time have been given elsewhere[7] for a number of polyatomic gases. It turns out that η_2 is several thousand times greater than η_1 and that $\beta_r \approx \beta_\infty / 10$.

Pielemeier[2] has shown that Fricke's absorption curve for dry CO_2 at 23°C may be resolved into two components, one having its peak of 0.215 at 17 kc while the other having its peak of 0.043 at about 37 kc. Assuming these values, let us calculate the two relaxation times and hence the two coefficients of volume viscosity of dry CO_2. Since, practically, we have $(n_1/n)\ (\gamma_2)_{max} = 0.215$ and $(n_2/n)\ (\gamma_2)_{max} = 0.043$, we get $(\gamma_2)_{max} = 0.258$, and $n_1/n = 5/6$ and $n_2/n = 1/6$. By (21), we find $v_\infty / v_o = 1.042$. Since

7. Hoff Lu, *Jour. Acous. Soc. Am.* **23** (1951), 12.

$(\omega_m)_1 = 2\pi \times 17\times10^3$ and $(\omega_m)_2 = 2\pi \times 37 \times 10^3$, we have, by (22), $\tau_{21} = 9.76\times10^{-6}$ second and $\tau_{22} = 4.48\times10^{-6}$ second. Taken from Handbook of Chemistry and Physics, $\rho = 1.81\times10^{-3}$ gm/cm^3, and $v_o = 268$ m/sec, so that, by (15), we get $\beta_o = 7.69\times10^{-7}$ cm^2/dyne and $\beta_\infty = 7.09\times10^{-7}$ cm^2/dyne, and, by (5), $(\eta_2)_1 = 12.7$ poises and $(\eta_2)_2 = 5.82$ poises. At frequencies much below those of the dispersion region (i.e., for $\omega \ll (\omega_m)_i$), we have, by (31), $\eta_2 = 11.5$ poises.

For liquids, τ_2 is, in general, so small ($\sim 10^{-10}$ sec) that the dispersion region is usually at inaccessibly high frequencies. As a result, only the effective viscosity $\eta_2\, \beta_r/\beta_o$ can be calculated from the observed attenuation coefficient. The results[7] of such calculations for a number of liquids have shown that the value of $\eta_2\, \beta_r/\beta_o$ ranges from several to several ten times greater than η_1. Sensibly, the same values for $\eta_2\, \beta_r/\beta_o$ are obtained[7] from the results[8] of Liebermann's experiment on a hydrodynamical effect of the volume viscosity.

One case of Liebermann's data is of interest. Ethyl formate ($HCOOC_2H_5$) is the only liquid that has its dispersion region fall in the experimental range of frequencies in Liebermann's experiment. Hence, for this case, Liebermann's n'/n is

$$\frac{n'}{n} = \frac{\beta_o\, \beta_r}{\beta_0^2 + \beta_\infty^2\, \omega^2 \tau_2^2}\, \frac{\eta_2}{\eta_1} - \frac{2}{3} = \frac{1}{1 + \omega^2\, \beta_\infty^2\, \eta_2^2}\, \frac{\beta_r}{\beta_o}\, \frac{\eta_2}{\eta_1} - \frac{2}{3}\,.$$

Using the first and last data, this formula yields $\eta_2\, \beta_r/\beta_o = 2.3$ poises and $\beta_\infty\, \eta_2 = 1.9\times10^{-7}$ poise-cm^2/dyne. The theoretical curve thus given is drawn in Fig. 1, the experimental points being also given (crossed) for comparison.

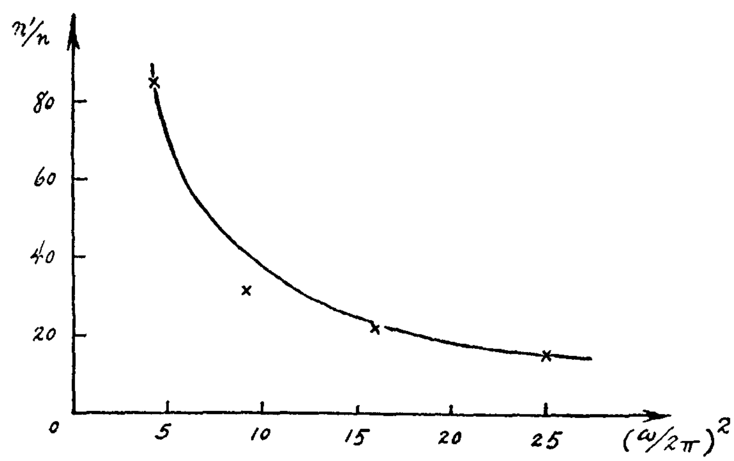

Fig. 1

8. L. N. Liebermann, *Phys. Rev.* **75** (1949), 1415.

Taking $\beta_o \approx 1\times 10^{-10}$ cm^2/dyne, we have, for ethyl formate at 17.4°C, $\eta_2 \approx 2000$ poises, $\tau \approx 2\times 10^{-7}$ sec, $\beta_\infty \approx \beta_o$, and $\beta_r \approx 1\times 10^{-13}$ cm^2/dyne. Unfortunately, there are too few experimental points to enable us say anything as to whether there exists an extra relaxation time that causes one of the point go off the theoretical curve considerably.

5. CONCLUDING REMARKS

We note that in all cases in which we have been able to calculate β_r and β_∞, it turns out that $\beta_r < \beta_\infty$, which means that $s_r < s_\infty$ so the we expect $(ds/dt)_{\rm vis} < ds_\infty/dt$ and, hence, Tisza's simplified type of generalized hydrodynamics will not be expected to apply in these cases, as is already known from the observed dependence of sound attenuation on frequency. However, for the more common fluids whose dispersion region is so remote that no appreciable effect of frequency is observable, Tisza's type of equation will be applicable, and for this case our theory would indicate that $\beta_r > \beta_\infty$, or $\beta_\infty \approx 0$.