

ON THE THEORY OF THE MECHANICAL PROPERTIES OF LIQUIDS IN THE SUPERSONIC AND HYPERSONIC REGION

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Introduction

In recent years, the many experimental evidences that liquids show for extremely rapid deformation the more or less different characters from the one expressed by the well-known Naville-Stokes' equation, which holds good for common hydro-dynamical problems, have been accumulated. Of these discrepancies, the large absorption of supersonic waves, which is seen for most liquids and is incomprehensible from the classical theory, is most remarkable and the quantitative explanation of this phenomenon from the modern molecular-kinetic theory has not appeared up to the present.

On the other hand, the phenomenological derivation of the oscillatory characters by modifying the classical stress-strain relations so as to fit the rapid motion is to be tried, and this is the main object with which we intend to deal in the following.

More than eighty years ago, famous James Clerk Maxwell had suggested in his theory of viscosity that liquids have a rigidity dissipating rapidly with time.¹⁾ Recently this idea that liquids have elasticity as well as plasticity even for shear have taken as a starting point by Frenkel and Obratzov and by the present author to construct the stress-strain relations of plasto-elastic bodies.

Frenkel and Obratzov²⁾ have extended Maxwell's theory by introducing a reversible relaxation deformation besides the purely viscous and the purely elastic components for shear. Moreover, they have introduced the corresponding three components for volume dilatation besides the static compressibility being of undecaying nature, so that an isotropic body has seven rheological constants.

The present author³⁾ developed independently a simpler theory to explain the high velocity of hypersonic waves, or the waves of thermal motion, found by Raman and Venkateswaran. The author's theory, containing only three constants, i.e. the volume modulus, the viscosity and the rigidity, is simpler, but was insufficient to discuss the mechanical properties of liquids over wide variation of frequency.

In this paper, a generalization of the preceding work is brought forward by postulating arbitrarily many times of relaxation for the stresses occurring liquids and a general stress-strain relation for plasto-elastic bodies is obtained. It contains most of hitherto presented theories, including that of the author and of Frenkel and Obratzov, as special cases. The mechanical behaviour of liquids for the supersonic and hypersonic frequencies can be mostly explained according to this theory. The re-

lation to the molecular-kinetic process is also discussed.

Derivation of the Stress-Strain Relations

Let us derive the general stress-strain relations in a plasto-elastic body by extending directly Maxwell's original idea itself as far as we can. When a shear s is suddenly produced at a point in the body, the shearing stress S being proportional to the shear accompanies with it:

$$S = \mu s, \quad \dots\dots\dots (1)$$

where μ is the rigidity modulus. To treat the matter generally, it would be better to think the stress S consists of many components, S_1, S_2, \dots each of them being proportional to the strain S with different coefficients μ_1, μ_2, \dots . Namely, if we take n components,

$$S = S_1 + S_2 + \dots + S_n, \quad \dots\dots\dots (2)$$

$$S_i = \mu_i s \quad (i = 1, 2, \dots, n). \quad \dots\dots\dots (3)$$

Here μ_i 's are the constants which express, so to speak, the partial rigidities.

If the substance is purely elastic, (3) holds also in its differential form:

$$\frac{dS_i}{dt} = \mu_i \frac{ds}{dt} \quad (i = 1, 2, \dots, N). \quad \dots\dots\dots (4)$$

Owing to the plasticity, however, the stresses decay with time. Although the process of the relaxation is incomprehensible in detail in the present state, it is natural to take different time of relaxation for different mechanism.⁴⁾ So we denote the time of relaxation of the i -th component as τ_i , and put in place of (3)

$$S_i = \mu_i s \exp(-t/\tau_i). \quad \dots\dots\dots (3)'$$

On differentiation, we have

$$\frac{dS_i}{dt} = -\frac{1}{\tau_i} \mu_i s \exp(-t/\tau_i) = -\frac{S_i}{\tau_i}, \quad \dots\dots\dots (5)$$

which represents the rate of the dissipation of the stress by plastic flow. Combining the elastic term (4) and the plastic one (5), we have Maxwell's relation for plasto-elastic substance, that is

$$\frac{dS_i}{dt} = \mu_i \frac{ds}{dt} - \frac{S_i}{\tau_i}. \quad \dots\dots\dots (6)$$

Using the operational notation D for the differentiation with time d/dt , this is written as

$$S_i = \frac{\mu_i D}{1/\tau_i + D} s. \quad \dots\dots\dots (7)$$

If we deal with steady flow, both the strain velocity ds/dt and the stress S_i should be constant, and we have from (6)

$$S_i = \mu_i \tau_i \frac{ds}{dt}.$$

Accordingly we see that $\mu_i \tau_i$ means a sort of coefficient of viscosity, which we de-

note μ_i' ; i.e.

$$\mu_i \tau_i = \mu_i', \quad \text{or} \quad \tau_i = \mu_i' / \mu_i. \quad \dots\dots\dots (8)$$

Then (7) becomes

$$S_i = \frac{\mu_i' D}{1 + \tau_i D} \quad \dots\dots\dots (7)'$$

and substituting (7)' into (2), we have the resultant stress-strain relation

$$S = \left(\sum_{i=1}^n \frac{\mu_i' D}{1 + \tau_i D} \right) s. \quad \dots\dots\dots (9)$$

We can set up a similar relation between the pressure P and the volume dilatation ε , but there exists an important difference. Namely, if the shear produced is kept constant, the shearing stress S gradually diminishes and approaches to zero with time, as shown in (3)'. However, it is not the case for volume dilatation. After sufficiently long time, the pressure does not vanish, but approaches to a constant value which is determined from the equation of state of the substance. Since this thermodynamical value is proportional to the volume dilatation, we can write as

$$p \rightarrow -k_0 \varepsilon,$$

where k_0 means the statical volume modulus. Accordingly we may apply the law of dissipation being of the same type as (9) for the residual pressure $p - (-k_0 \varepsilon)$, but not for the pressure p itself. It is

$$-k_0 \varepsilon - p = \left(\sum_{i=1}^m \frac{k_i' D}{1 + \tau_i' D} \right) \varepsilon,$$

or

$$p = - \left(k_0 + \sum_{i=1}^m \frac{k_i' D}{1 + \tau_i' D} \right) \varepsilon. \quad \dots\dots\dots (10)$$

Here k_i' means the partial coefficient of viscosity for volume dilatation corresponding to μ_i' for shearing deformation, and $\tau_i' = k_i' / k_i$ a time of relaxation, where k_i means the partial modulus of compression corresponding to μ_i for shear.

Now we can construct the general stress-strain relations for the plasto-elastic body under consideration on the ground of (9) and (10). According to the general usage, we denote the components of the stress tensor and the strain tensor referring to Cartesian coordinates as

$$X_x, Y_y, Z_z, Y_z = Z_y, Z_x = X_z, X_y = Y_x \quad \dots\dots\dots (11)$$

and

$$\left. \begin{aligned} x_x &= \frac{\partial u}{\partial x}, & y_y &= \frac{\partial v}{\partial y}, & z_z &= \frac{\partial w}{\partial z}, \\ \frac{y_z}{2} &= \frac{z_y}{2} = \frac{1}{2} \left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right), \\ \frac{z_x}{2} &= \frac{x_z}{2} = \frac{1}{2} \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right), \\ \frac{x_y}{2} &= \frac{y_x}{2} = \frac{1}{2} \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right), \end{aligned} \right\} \quad \dots\dots\dots (12)$$

respectively, where u, v and w are the components of a displacement.

For the tangential tractions $-Y_z$, $-Z_x$ and $-X_y$, we can apply directly the relation (9) for shear, i.e.

$$Y_z = - \left(\sum_i \frac{\mu_i' D}{1 + \tau_i D} \right) y_z, \quad \text{etc.} \quad \dots\dots\dots (13)$$

However, for the three normal component tractions $-X_x$, $-Y_y$ and $-Z_z$, the situation is not so simple. Considering that for an isotropic body the stress tensor should be obtained from the strain tensor by multiplying a scalar factor containing the elastic constants. Since the factor is as a matter of course common for the all component, the normal component tractions may be written as

$$\left. \begin{aligned} X_x &= - \left(\sum \frac{2 \mu_i' D}{1 + \tau_i D} \right) x_x + K, \\ Y_y &= - \left(\quad \quad \quad \right) y_y + K, \\ Z_z &= - \left(\quad \quad \quad \right) z_z + K, \end{aligned} \right\} \dots\dots\dots (14)$$

where K is a common additive scalar quantity being proportional to the strain. On addition we have

$$X_x + Y_y + Z_z = - \left(\sum \frac{2 \mu_i' D}{1 + \tau_i D} \right) \epsilon + 3 K,$$

if we recognize that for the cubical dilatation

$$\epsilon = x_x + y_y + z_z.$$

Defining the pressure by

$$p = \frac{1}{3} (X_x + Y_y + Z_z),$$

we obtain

$$p = - \left(\sum \frac{2}{3} \cdot \frac{\mu_i' D}{1 + \tau_i D} \right) \epsilon + K.$$

Since this must coincide with (10),

$$K = - \left(k_0 + \sum \frac{k_i' D}{1 + \tau_i' D} - \frac{2}{3} \sum \frac{\mu_i' D}{1 + \tau_i D} \right) \epsilon.$$

And on substitution in (14) we have the stress-strain relations. These are, together with (13),

$$\left. \begin{aligned} X_x &= - \left(k_0 + \sum_{i=1}^m \frac{k_i' D}{1 + \tau_i' D} - \frac{2}{3} \sum_{i=1}^n \frac{\mu_i' D}{1 + \tau_i D} \right) \epsilon - \left(\sum_{i=1}^n \frac{2 \mu_i' D}{1 + \tau_i D} \right) x_x, \\ Y_y &= - \left(\quad \quad \quad \right) \epsilon - \left(\quad \quad \quad \right) y_y, \\ Z_z &= - \left(\quad \quad \quad \right) \epsilon - \left(\quad \quad \quad \right) z_z, \\ Y_z &= Z_y = - \left(\sum_{i=1}^n \frac{\mu_i' D}{1 + \tau_i D} \right) y_z, \\ Z_x &= X_z = - \left(\quad \quad \quad \right) z_x, \\ X_y &= Y_x = - \left(\quad \quad \quad \right) x_y. \end{aligned} \right\} \dots (15)$$

If we put $m = 0$, $n = 1$ the results of the author's previous work are obtained. It is natural because of there considered only one sort of relaxation and assumed tacitly

the absence of volume viscosity.

The work of Frenkel and Obratzov cited above is also included as a special case. To show this, we use the notation S_{ik} for a component of the stress-tensor and γ_{ik} for that of the strain tensor, namely,

$$S_{11} = X_x, \quad S_{12} = X_y, \dots; \quad \gamma_{11} = x_x, \quad \gamma_{12} = \frac{x_y}{2}, \dots,$$

and consequently

$$\frac{1}{3} \sum S_{ii} = p, \quad \sum \gamma_{ii} = \epsilon.$$

On applying these notations to our result (15), this is transformed into

$$\left. \begin{aligned} p &= -A \frac{\epsilon}{3} \\ S_{ik} - \delta_{ik} p &= -B \left(\gamma_{ik} - \delta_{ik} \frac{\epsilon}{3} \right), \end{aligned} \right\} \dots\dots\dots (16)$$

where A and B are the operators

$$\left. \begin{aligned} A &= 3 \left(k_0 + \sum \frac{k'_i D}{1 + \tau'_i D} \right), \\ B &= \sum \frac{2 \mu'_i D}{1 + \tau_i D} \end{aligned} \right\} \dots\dots\dots (17)$$

respectively. On the other hand, the theory of Frenkel and Obratzov gives

$$\left. \begin{aligned} p &= -\frac{N}{P} \frac{\epsilon}{3}, \\ S_{ik} - \delta_{ik} p &= -\frac{L}{M} \left(\gamma_{ik} - \delta_{ik} \frac{\epsilon}{3} \right), \end{aligned} \right\} \dots\dots\dots (18)$$

where L, M, N and P are the operators,

$$\left. \begin{aligned} L &= 2(G_i + \eta_1 D) \\ M &= \left(1 + \frac{G_1}{G} + \frac{\eta_1}{\eta} \right) + \frac{\eta_1}{G} D + \frac{G_1}{\eta} D^{-1}, \\ N &= \frac{1}{\kappa_s} + \eta_2 D, \\ P &= \frac{1}{3} \left(1 + \eta_2 \kappa D \right), \end{aligned} \right\} \dots\dots\dots (19)$$

consisting of the time differential operator $D = d/dt$ and the seven material constants $G, G_1, \eta_1, \eta_2, \kappa, \kappa_s, \eta$. Comparing (18) with (16), there must exist the correspondence

$$\frac{N}{P} \rightarrow A \quad \text{and} \quad \frac{L}{M} \rightarrow B. \quad \dots\dots\dots (20)$$

From (19) we have

$$\frac{N}{P} = 3 \left(\frac{1/\kappa_s + \eta_2 D}{1 + \eta_2 \kappa D} \right)$$

and

$$\frac{L}{M} = \frac{2(G_1 + \eta_1 D)}{\left(1 + \frac{G_1}{G} + \frac{\eta_1}{\eta}\right) + \frac{\eta_1}{G} D + \frac{G_1}{\eta} \frac{1}{D}} = \frac{2 \frac{\eta}{G_1} (G_1 + \eta_1 D) D}{1 + \frac{\eta}{G_1} \left(1 + \frac{G_1}{G} + \frac{\eta_1}{\eta}\right) D + \frac{\eta \eta_1}{G G_1} D^2} \dots\dots\dots (21)$$

On the other hand, if we put $m = 1$ and $n = 2$ in (17), our theory leads to

$$\left. \begin{aligned} A &= 3 \left(k_0 + \frac{k_1' D}{1 + \tau_1' D} \right) = 3 \frac{k_0 + (k_0 \tau_1' + k_1') D}{1 + \tau_1' D}, \\ B &= \frac{2 \mu_1' D}{1 + \tau_1' D} + \frac{2 \mu_2' D}{1 + \tau_2' D} = \frac{2 \{ (\mu_1' + \mu_2') + (\mu_1' \tau_2' + \mu_2' \tau_1') D \}}{1 + (\tau_1' + \tau_2') D + \tau_1' \tau_2' D^2}, \end{aligned} \right\} \dots\dots (22)$$

which is entirely of the same form with (21), as (20) requires, and we can derive from the correspondence the relations among the constants included in the two theories if needed. These are

$$\eta_2 \rightarrow k_0 \tau_1' + k_1', \quad \kappa \rightarrow \frac{1}{k_0 + k_1'}, \quad \kappa_s \rightarrow \frac{1}{k_0},$$

$$\eta_1 \rightarrow \mu_1' + \mu_2', \quad G \rightarrow \mu_1 + \mu_2,$$

$$\left. \begin{aligned} \frac{\eta}{G} \cdot \frac{\eta_1}{G_1} &= \tau_1 \tau_2 \\ \frac{\eta}{G} + \frac{\eta_1}{G_1} &= \frac{\mu_1' \tau_1 + \mu_2' \tau_2}{\mu_1' + \mu_2'} \end{aligned} \right\} \text{are obtainable from}$$

Application to the Supersonic Waves

In (15) if the relaxation of a component of the normal traction and that of a component of the tangential traction are to be attried to a same cause, it is natural to give them the equal time constant, e.g.

$$\tau_i' = \frac{k_i'}{k_i} = \frac{\mu_i'}{\mu_i} = \tau_i. \dots\dots\dots (23)$$

Putting thus the times of relaxation for the both i -th components equal, (15) becomes

$$\left. \begin{aligned} X_x &= - \left\{ k_0 + \sum \left(k_i' - \frac{2}{3} \mu_i' \right) \frac{D}{1 + \tau_i D} \right\} \varepsilon - \left(\sum \frac{2 \mu_i' D}{1 + \tau_i D} \right) x_x, \\ Y_y &= - \left(\begin{array}{ccc} & & \end{array} \right) \varepsilon - \left(\begin{array}{ccc} & & \end{array} \right) y_y, \\ Z_z &= - \left(\begin{array}{ccc} & & \end{array} \right) \varepsilon - \left(\begin{array}{ccc} & & \end{array} \right) z_z, \\ Y_z &= Z_y = - \left(\sum \frac{\mu_i' D}{1 + \tau_i D} \right) y_z, \\ Z_x &= X_z = - \left(\begin{array}{ccc} & & \end{array} \right) z_x, \\ X_y &= Y_x = - \left(\begin{array}{ccc} & & \end{array} \right) x_y. \end{aligned} \right\} \dots\dots (24)$$

Since k_i' or μ_i' can vanish for some mechanisms, the generality of (15) is never lost in (24). We shall principally adopt this form in the following.

The equations of motion are

$$\rho \frac{d^2 u}{dt^2} = - \left(\frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \right)$$

$$= - \left\{ k_0 + \sum \frac{(k_i' - 2/3 \mu_i') D}{1 + \tau_i D} \right\} \frac{\partial \varepsilon}{\partial x} + \left(\sum \frac{2 \mu_i' D}{1 + \tau_i D} \right) \frac{\partial x_x}{\partial x} + \left(\sum \frac{\mu_i' D}{1 + \tau_i D} \right) \left(\frac{\partial x_y}{\partial y} + \frac{\partial x_z}{\partial z} \right), \text{ etc.}$$

where ρ is density. Expressing the components of shear in terms of the displacements u, v, w , by (12), and neglecting the second power of the displacements, which are assumed to be small, we have

$$\rho D^2 n = \left\{ k_0 + \sum \left(k_i' - \frac{2}{3} \mu_i' \right) \frac{D}{1 + \tau_i D} \right\} \frac{\partial \varepsilon}{\partial x} + \left(\sum \frac{\mu_i' D}{1 + \tau_i D} \right) \left(2 \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 v}{\partial x \partial y} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} + \frac{\partial^2 w}{\partial x \partial z} \right), \text{ etc.}$$

or introducing the components of rot (u, v, w), i.e.

$$\tilde{\omega}_1 = \frac{1}{2} \left(\frac{\partial w}{\partial y} - \frac{\partial v}{\partial z} \right),$$

$$\tilde{\omega}_2 = \frac{1}{2} \left(\frac{\partial u}{\partial z} - \frac{\partial w}{\partial x} \right),$$

$$\tilde{\omega}_3 = \frac{1}{2} \left(\frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} \right),$$

we obtain

$$\left. \begin{aligned} \rho D^2 u &= \left\{ k_0 + \sum \left(k_i' + \frac{4}{3} \mu_i' \right) \frac{D}{1 + \tau_i D} \right\} \frac{\partial \varepsilon}{\partial x} - \left(\sum \frac{2 \mu_i' D}{1 + \tau_i D} \right) \left(\frac{\partial \tilde{\omega}_3}{\partial y} - \frac{\partial \tilde{\omega}_2}{\partial z} \right), \\ \text{and similarly} \\ \rho D^2 v &= \left\{ \begin{array}{c} \text{''} \\ \text{''} \end{array} \right\} \frac{\partial \varepsilon}{\partial y} - \left(\begin{array}{c} \text{''} \\ \text{''} \end{array} \right) \left(\frac{\partial \tilde{\omega}_1}{\partial z} - \frac{\partial \tilde{\omega}_3}{\partial x} \right), \\ \rho D^2 w &= \left\{ \begin{array}{c} \text{''} \\ \text{''} \end{array} \right\} \frac{\partial \varepsilon}{\partial z} - \left(\begin{array}{c} \text{''} \\ \text{''} \end{array} \right) \left(\frac{\partial \tilde{\omega}_2}{\partial x} - \frac{\partial \tilde{\omega}_1}{\partial y} \right). \end{aligned} \right\} (25)$$

To discuss the dilatational wave we differentiate these three equations with x, y and z respectively and add, resulting

$$\rho D^2 \varepsilon = \left\{ k_0 + \sum \left(k_i' + \frac{4}{3} \mu_i' \right) \frac{D}{1 + \tau_i D} \right\} \mathcal{P}^2 \varepsilon. \quad \dots\dots\dots (26)$$

Consider a wave propagating toward + x -direction with the frequency $\nu = \omega/2\pi$,

$$\varepsilon = \text{const. exp} (i\omega t - \beta x), \quad \dots\dots\dots (27)$$

the velocity v and the absorption coefficient κ for intensity per wave-length of which are given by

$$v = \frac{\omega}{\Im(\beta)}, \quad \dots\dots\dots (28)$$

and

$$\kappa = \frac{2 \Re(\beta)}{\Im(\beta)} \quad \dots\dots\dots (29)$$

Here $\Re(\beta)$ and $\Im(\beta)$ express the real and the imaginary parts of β respectively. Substitution of (27) in (26) means mere replacement of D or $\partial/\partial t$ by $i\omega$ and $\mathcal{P}^2 = \partial^2/\partial x^2$ by β^2 , as is familiar in operational calculus. We have, therefore, the equation

$$-\rho \omega^2 = \beta^2 \left\{ k_0 + \sum \left(k_i' + \frac{4}{3} \mu_i' \right) \frac{i\omega}{1 + i\tau_i \omega} \right\},$$

from which β is determined as

$$\beta = i\omega\rho^{1/2} \left\{ k_0 + \sum_{i=1}^n \left(k_i' + \frac{4}{3}\mu_i' \right) \frac{i\omega}{1 + i\tau_i\omega} \right\}^{-1/2} \dots\dots\dots (30)$$

If we consider only one kind of relaxation, that is, put $n = 1$, we get

$$\beta = i\omega\rho^{1/2} \left\{ k_0 + \left(k_1' + \frac{4}{3}\mu_1' \right) \frac{i\omega}{1 + i\tau_1\omega} \right\}^{-1/2} = i\omega\sqrt{\frac{\rho}{k_0} \cdot \frac{1 + i\tau_1\omega}{1 + \left(1 + \frac{k_1 + \frac{4}{3}\mu_1/3}{k_0} \right) i\tau_1\omega}}$$

which, taking $k = 0$, coincides with the result formerly obtained. The velocity v and the absorption coefficient κ versus frequency calculated from (28) and (29) for the three cases for which the ratio $\left(k_1 + \frac{4}{3}\mu_1 \right) : k_0$ equals to $\frac{1}{2}$, 1 and 2 respectively are shown in Fig. 1.

When the ratio is very small, viz. $\left(k_1 + \frac{4}{3}\mu_1 \right) / k_0 \ll 1$, we have by expansion the approximative formulae for the velocity,

$$v = v_0 \frac{1 + \tau_1^2\omega^2}{1 + \left(1 - \frac{k_1 + \frac{4}{3}\mu_1/3}{2k_0} \right) \tau_1^2\omega^2}$$

and that for the absorption coefficient per unit length

$$\alpha = \Re(\beta) = \frac{\omega}{2v_0^2\rho} \cdot \frac{\tau_1\omega}{1 + \tau_1^2\omega^2},$$

where

$$v_0 = \left(\frac{k_0}{\rho} \right)^{1/2}, \dots (31)$$

respectively the velocity for sufficiently small frequencies. These formulas and curves resemble very much that derived on the basis of the molecular theory by Kneser.⁵⁾

If the more sorts of relaxations are taken into account, β is given by (30), that is

$$\beta = i\omega\rho^{1/2} \left\{ k_0 + i\omega \sum_{i=1}^n \frac{\left(k_i + \frac{4}{3}\mu_i \right) \tau_i}{1 + i\tau_i\omega} \right\}^{-1/2} \dots\dots\dots (32)$$

For continuous distribution of the times of relaxation, we may replace the summation by the integration.

However, to write up generally and explicitly the real and the imaginary parts of β , and therefore the velocity and the absorption coefficient, is rather tedious and of little use. Let us make the assumption that the component instantaneous elastic moduli, k_1, k_2, \dots, k_n and $\mu_1, \mu_2, \dots, \mu_n$ are considerably small compared with the static k_0 , i.e.

$$\left(k_i + \frac{4}{3}\mu_i \right) / k_0 \ll 1 \quad (i = 1, 2, \dots, n).$$

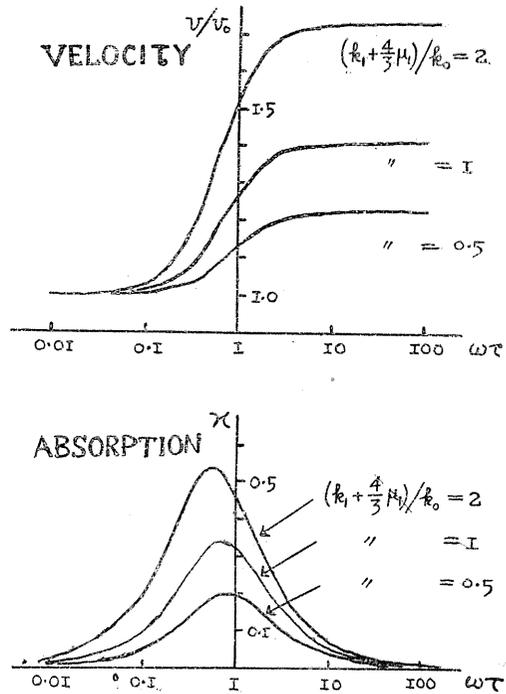


Fig. 1

Then we can expand (32) in power series in terms of this ratio, and, neglecting the higher terms, we have

$$\Re(\beta) = \omega \left(\frac{\rho}{k_0}\right)^{1/2} \sum_{i=1}^n \frac{\left(k_i + \frac{4}{3}\mu_i\right)\omega\tau_i}{2k_0(1 + \tau_i^2\omega^2)}, \quad \dots\dots\dots (33)$$

$$\Im(\beta) = \omega \left(\frac{\rho}{k_0}\right)^{1/2} \left[1 - \sum_{i=1}^n \frac{\left(k_i + \frac{4}{3}\mu_i\right)\omega^2\tau_i^2}{2k_0(1 + \omega^2\tau_i^2)} \right]. \quad \dots\dots\dots (34)$$

The absorption coefficient per unit length becomes

$$\alpha = \Re(\beta) = \frac{\omega^2}{2v_0^3\rho} \sum_{i=1}^n \frac{k_i' + \frac{4}{3}\mu_i'}{1 + \tau_i^2\omega^2} \quad \dots\dots\dots (35)$$

For sufficiently low frequencies this reduces to

$$\alpha = \frac{2\omega^2}{3v_0^3\rho} \left(\mu_1' + \frac{3}{4}k_1' + \mu_2' + \frac{3}{4}k_2' + \dots \right) \quad \dots\dots\dots (36)$$

If we identify μ_1' with the ordinary coefficient of viscosity, the first term

$$\alpha = \frac{2\omega^2\mu_1'}{3v_0^3\rho} \quad \dots\dots\dots (37)$$

gives the classical dissipation, arising from the ordinary viscosity, which was derived by Stokes. Then k_1' is what was called by Kirchhoff the second coefficient of viscosity, and is considered to vanish for gases. Owing to the additional viscosity μ_2' , k_2' and so on, the absorption generally becomes larger than the classical value, giving a phenomenological explanation of the large absorption of the supersonic wave.

The time of relaxation τ_1 of ordinary viscosity is considered to be very short, being the order of 10^{-11} sec. for ordinary liquids. So $\omega\tau_1 \ll 1$ for the supersonic waves, whose frequencies lie between 10^5 and 10^8 sec.⁻¹ Then (35) becomes, if only one extra relaxation is considered,

$$\alpha = \frac{\omega^2}{2v_0^3\rho} \left(k_1' + \frac{3}{4}\mu_1' + \frac{k_2' + \frac{4}{3}\mu_2'}{1 + \tau_2^2\omega^2} \right). \quad \dots\dots\dots (38)$$

According to this α/v^2 decreases with increasing frequency from $\frac{2\pi^2}{v_0^3\rho} \left(k_1' + \frac{4}{3}\mu_1' + k_2' + \frac{4}{3}\mu_2' \right)$ to $\frac{2\pi^2}{v_0^3\rho} \left(k_1' + \frac{4}{3}\mu_1' \right)$. The fact that most liquids show no distinguishable change of α/v^2 with frequency can be interpreted as the second period τ_2 of relaxation is so small that the product $\omega\tau_2$ is also fairly smaller than unity.

A few liquids, including acetic acid, methyl acetate and ethyl acetate, however, show the apparent decrement of the absorption coefficients with increasing frequency. For acetic acid at about 20°C putting

$$\begin{aligned} \tau_2 &= 4.83 \times 10^{-8} \text{ sec.}, \\ k_1' + \frac{4}{3}\mu_1' &= 0.14 \text{ poises}, \\ k_2' + \frac{4}{3}\mu_2' &= 8.4 \text{ poises}, \end{aligned}$$

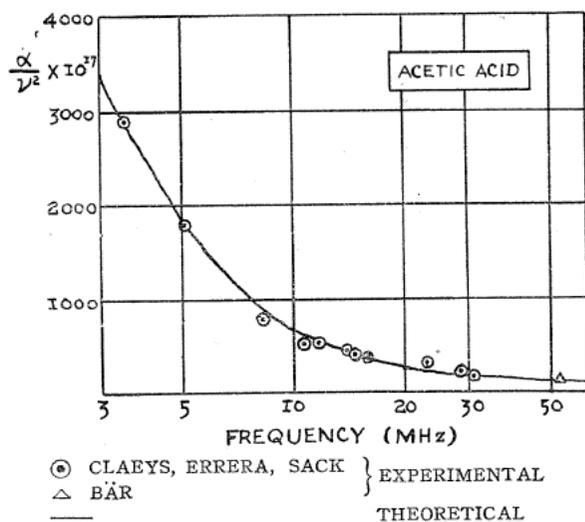


Fig. 2

(38) gives good agreements with the experimental data, as shown in Fig. 2. If we identify μ_1' with the ordinary coefficient of viscosity, which is 0.012 poises for acetic acid at 20°C, the second coefficient k_1' should be equal to $0.14 - 0.012 = 0.128$ poises.

In this case, the postulation, that

$$k_2 + \frac{4}{3}\mu_2 = \frac{1}{\tau_2} \left(k_2' + \frac{4}{3}\mu_2' \right) = 1.74 \times 10^8 \text{ dynes.cm.}^{-2}$$

is far smaller than k_0 , is fulfilled, because the latter is larger than 10^{10} dyne.cm.⁻²

The dispersion is always accompanied with absorption. From (34) we have, as the formula for sound velocity corresponding the absorption given by (38),

$$v = \frac{\omega}{\mathfrak{I}(\beta)} = v_0 \left[1 + \frac{\left(k_2 + \frac{4}{3}\mu_2 \right) \omega^2 \tau_2^2}{2k_0(1 + \omega^2 \tau_2^2)} \right]. \quad \dots\dots (39)$$

If the frequency becomes so large that $\omega\tau_2$ is much larger than unity, but still $\omega\tau_1 \ll 1$, the velocity comes to

$$v' = v_0 \left[1 + \frac{k_2 + \frac{4}{3}\mu_2}{2k_0} \right], \quad \dots\dots (40)$$

and the relative dispersion

$$\frac{v' - v_0}{v_0} = \frac{k_2 + \frac{4}{3}\mu_2}{2k_0}$$

for acetic acid becomes approximately 0.8% using the figures cited above. Spakovskij⁶⁾ found experimentally 0.9% relative dispersion for the frequency range from 0.24 to 2.7 MHz. Since $\omega\tau_2$ varies from 0.073 to 0.82 instead of from zero to a number sufficiently larger than unity, we can calculate from (39) the relative dispersion for this range to be about 0.3%. Though decided conclusion cannot be drawn, because of the sample used by Spakovskij was not pure, and of the ambiguity of the

figures above on which our calculation grounds, the theoretical and the experimental results are in agreement in order of magnitude, that is to say, at any rate, not contradictory each other.

The abnormal absorption of methyl acetate and ethyl acetate found by Claeys, Errera and Sack⁷⁾ is not easy to understand. According to Byer and Smith,⁸⁾ the absorption coefficient α for ethyl acetate is directly proportional to frequency from 3 to 40 MHz, and $2\alpha/\nu$ is approximately constant, being $(20 \sim 30) \times 10^{-9}$ c.g.s. unit. Such a fact cannot be explained by (38). A combination of three or more relaxations might reproduce the experimental result approximately, but we can hardly say anything about the reality of these individual relaxations. The exact comprehension of the fact remains, therefore, unsolved until the molecular mechanism is clarified.

Thermal Condition. Relation to the Molecular Theory

We have hitherto disregarded the thermal condition for the sake of simplicity. Now, in this chapter, it will be treated in some detail, and, by the way, the relation of our theory to the molecular-kinetic theory, which we owe mainly Kneser, will be discussed.

If a cubical expansion ϵ is produced, isothermally in a purely elastic body, the pressure p is given by

$$p = -k_T \epsilon, \quad \dots\dots\dots (41)$$

where k_T is the isothermal volume modulus. However, in general, the process is not isothermal, but there occurs the change of the temperature T , and the pressure becomes

$$p = k_T \{a(T - T_0) - \epsilon\}, \quad \dots\dots\dots (42)$$

where a is the coefficient of cubical thermal expansion, and T_0 the original temperature before the expansion takes place. If the process is perfectly adiabatic, the rise of the temperature is, according to thermodynamics, given by

$$\rho c_v (T - T_0) = -ak_T T_0 \epsilon, \quad \dots\dots\dots (43)$$

c_v being the specific heat at constant volume. Substituting the temperature change in (42), we have

$$p = -k_T \left(1 + \frac{a^2 k_T T_0}{\rho c_v}\right) \epsilon. \quad \dots\dots\dots (44)$$

Comparing this to (41), we recognize that

$$k_S = k_T \left(1 + \frac{a^2 k_T T_0}{\rho c_v}\right) \quad \dots\dots\dots (45)$$

means the adiabatic volume modulus. In ordinary sound waves, it is well known that the change is almost adiabatic, and the velocity is given by

$$v_L = \sqrt{\frac{k_S}{\rho}} = \sqrt{\frac{k_T}{\rho} \left(1 + \frac{a^2 k_T T_0}{\rho c_v}\right)}, \quad \dots\dots\dots (46)$$

but not by

$$v_N = \sqrt{\frac{k_T}{\rho}}. \quad \dots\dots\dots (47)$$

There is, of course, the effect of the conduction of heat, which brings the process from the adiabatic to the isothermal one, but generally the effect is very small, and for a while we neglect it.

For such frequent repetition of expansion and contraction as the supersonic waves create, the situation is more complicated. Kneser⁹⁾ conceived that the energy supplied by the sudden compression is delivered at first to the translational and rotational motion of the molecules, and then after a finite time interval, it transfers to the internal degrees of freedom, that is the intramolecular vibration. Consequently the external and the internal motion of the molecules are not in thermal equilibrium. If T' denotes the temperature when only the translational and rotational motion of the molecules are considered, we have for a sudden compression or dilatation

$$\rho c_v'(T' - T_0) = -\alpha' k_T' T_0 \varepsilon$$

in the place of (43). Here c_v' , α' and k_T' mean the specific heat at constant volume, α' , the coefficient of cubical expansion and k_T' , the isothermal volume modulus respectively, all being the imaginary values that they would take when the internal degrees of freedom are frozen. The intramolecular vibration hardly contributes to the mechanical or to the thermal expansion, we can put $k_T' = k_T$, $\alpha' = \alpha$, and

$$T' - T_0 = -\frac{\alpha k_T T_0}{\rho c_v'} \varepsilon. \quad \dots\dots\dots (48)$$

If ε varies with time, we have the differential equality,

$$\frac{d}{dt}(T' - T_0) = -\frac{\alpha k_T T_0}{\rho c_v'} \frac{d\varepsilon}{dt} \quad \dots\dots\dots (49)$$

But, on the other hand, the temperature T' dissipates according to the energy conversion from the external to the internal motion. The rate of the conversion seems to be proportional to the temperature difference $T' - T''$, where T'' denotes the temperature corresponding to the internal energy, thus

$$\frac{d}{dt}(T' - T'') = -\frac{1}{\tau_K}(T' - T''). \quad \dots\dots\dots (50)$$

τ_K is a constant having the dimension of time, and is a measure of the velocity of this conversion. Since the total energy is conserved during the process,

$$\rho c_v'(T' - T_0) + \rho c_v''(T'' - T_0) = \rho c_v(T - T_0),$$

where c_v'' , being equal to $c_v - c_v'$, means the specific heat at constant volume when only the internal motion of the molecules is considered. Then

$$T'' - T_0 = \frac{c_v}{c_v''}(T - T_0) - \frac{c_v'}{c_v''}(T' - T_0) \quad \dots\dots\dots (51)$$

and, considering that the thermodynamical temperature $T - T_0$ retains constant value given by (43) during the process, we have by differentiation

$$\frac{d}{dt}(T'' - T_0) = -\frac{c_v'}{c_v''} \frac{d}{dt}(T' - T_0). \quad \dots\dots\dots (52)$$

Using (51) and (52) we can eliminate T'' from (50), and obtain

$$\frac{d}{dt}(T' - T_0) = -\frac{1}{\tau_K}(T' - T_0) + \frac{1}{\tau_K}(T - T_0).$$

Combining this and (49), we have the equation

$$\frac{d}{dt}(T' - T_0) = -\frac{ak_T T_0}{\rho c_{v'}} \frac{d\varepsilon}{dt} - \frac{1}{\tau_K}(T' - T_0) + \frac{1}{\tau_K}(T - T_0). \quad \dots (53)$$

From the three equations, (43), (53) and

$$\dot{p} = k_T \{ a(T' - T_0) - \varepsilon \}, \quad \dots (54)$$

we can eliminate T and T' , and have the relation between ε and \dot{p} , that is

$$\dot{p} = -k_T \left(1 + \frac{a^2 k_T T_0 c_{v'} / c_v + \tau_K D}{\rho c_{v'} (1 + \tau_K D)} \right) \varepsilon \quad \dots (55)$$

$$= - \left(k_T + \frac{a^2 k_T^2 T_0}{\rho c_v} + \frac{a^2 k_T^2 T_0}{\rho c_v} \cdot \frac{c_{v''}}{c_{v'}} \cdot \frac{\tau_K D}{1 + \tau_K D} \right) \varepsilon. \quad \dots (56)$$

This is utterly of the same form with the phenomenological result (10), and by comparison, the following correspondence, which is in accordance with that of Frenkel¹⁰⁾, is obtained.

$$\left. \begin{aligned} k_0 &\rightarrow k_T + \frac{a^2 k_T^2 T_0}{\rho c_v}, \\ k_1 &\rightarrow \frac{a^2 k_T^2 T_0 c_{v''}}{\rho c_v c_{v'}}. \end{aligned} \right\} \quad \dots (57)$$

We recognize that k_0 corresponds to the adiabatic volume modulus k_s . Even when we consider many sorts of internal motion, as Richards,¹¹⁾ each of which has different τ_K , the generalization of the discussion above is not difficult.

For liquids and solids, however, it is sure that there exists another cause of stress relaxation, perhaps owing to the fact that the molecular rearrangement accompanied by deformation needs a finite time period. But the time period is presumably extremely short for ordinary liquids.

According to Eyring's theory of viscosity,¹²⁾ the rate of flow of liquids is regulated by the probability that a molecule jumps in unit time from a point of equilibrium, to another, adjacent one. The coefficient μ' of viscosity is proportional to the reciprocal of the probability, having dimension of time, and being expressed by τ_E , such as

$$\mu' = \frac{\lambda_1 k T}{\lambda_2 \lambda_3 \lambda^2} \tau_E, \quad \dots (58)$$

where λ is the distance between the two adjacent points of equilibrium, and $\lambda_1, \lambda_2, \lambda_3$ are the intermolecular distances, λ_2 being in the direction of flow, λ_3 being in the slip layers and being perpendicular to the flow, and λ_1 being perpendicular to the slip layers. For nearly spherical molecules, we can put approximately

$$\lambda = \lambda_1 = \lambda_2 = \lambda_3 = \left(\frac{V}{N} \right)^{1/3}, \quad \dots (59)$$

where V is molecular volume and N the Loschmidt's number. Introducing (59) in (58), we have

$$\tau_E = \frac{V\mu'}{RT} \quad \dots\dots\dots (60)$$

where R is the universal gas constant. It is sure that, for so rapid deformation, completes in a period shorter than τ_E the flow cannot take place and a liquid behaves as it were a non-plastic solid. Therefore we can identify τ_E with $\tau_1 = \mu'/\mu$, that is the coefficient viscosity divided by the coefficient of rigidity. Calculating τ_E for some liquids at 20°C, we have

for acetic acid	$\tau_E = 2.1 \times 10^{-11}$ sec.
carbon bisulphide	9.0×10^{-12} sec.
water	7.4×10^{-12} sec.
methyle alcohol	9.8×10^{-12} sec.
glycerine	4.5×10^{-8} sec.

From these figures we can see that for most liquids $\omega\tau_E$ is yet very small compared with unity even in the supersonic region. Nevertheless we take this mechanism of relaxation into account to make possible to go beyond the supersonic region.

Combining the two mechanisms, (54) and

$$Y_z = Z_y = -\frac{\mu\tau_1 D}{1 + \tau_1 D} y_z, \quad \text{etc.},$$

we obtain the stress-strain relations, as we have done in the preceding chapter,

$$\left. \begin{aligned} X_x &= k_T a(T' - T_0) - k_T \varepsilon + \frac{2}{3} \frac{\mu\tau_1 D}{1 + \tau_1 D} \varepsilon - \frac{2}{1 + \tau_1 D} \frac{\mu\tau_1 D}{1 + \tau_1 D} x_x, \\ Y_y &= k_T a(T' - T_0) - k_T \varepsilon + \frac{2}{3} \frac{\mu\tau_1 D}{1 + \tau_1 D} \varepsilon - \frac{2}{1 + \tau_1 D} \frac{\mu\tau_1 D}{1 + \tau_1 D} y_y, \\ Z_z &= k_T a(T' - T_0) - k_T \varepsilon + \frac{2}{3} \frac{\mu\tau_1 D}{1 + \tau_1 D} \varepsilon - \frac{2}{1 + \tau_1 D} \frac{\mu\tau_1 D}{1 + \tau_1 D} z_z, \\ Y_z &= Z_y = -\frac{\mu\tau_1 D}{1 + \tau_1 D} y_z, \\ Z_x &= X_z = -\frac{\mu\tau_1 D}{1 + \tau_1 D} z_x, \\ X_y &= Y_x = -\frac{\mu\tau_1 D}{1 + \tau_1 D} x_y. \end{aligned} \right\} \dots\dots (61)$$

It is easily seen that, by the aid of (56), this is of the same form with the phenomenological equations (15), putting $m = n = 1$.

Now we complete the temperature equations (43) and (53) by considering the conduction of heat. The heat inflow $K\nabla^2(T - T_0)$, where K is thermal conductivity, should be added to the differential form of (43), i.e.

$$\rho c_v \frac{\partial(T - T_0)}{\partial t} = -ak_T T_0 \frac{\partial \varepsilon}{\partial t},$$

expressing the rate of the production of heat by compression, namely

$$\rho c_v \frac{\partial(T - T_0)}{\partial t} = -ak_T T_0 \frac{\partial \varepsilon}{\partial t} + K \nabla^2 (T - T_0). \quad \dots\dots (62)$$

Similarly (53) should be altered as

$$\frac{\partial}{\partial t} (T' - T_0) = -\frac{ak_T T_0}{\rho c_v'} \frac{d\varepsilon}{dt} - \frac{1}{\tau_K} (T' - T_0) + \frac{1}{\tau_K} (T - T_0) + \frac{K'}{\rho c_v'} \nabla^2 (T - T_0), \quad (63)$$

where K' means the thermal conductivity for the external, i.e. the translational and rotational energy only. Since it is known that for gases the translational energy of molecules propagates more rapidly than the other sorts of energy, the ratio of the velocity being about 5 to 2,³³⁾ K' may be somewhat larger than K , and owing to this fact, the new additive absorption of sound waves can occur. For liquids, however, it seems there is less difference and, for the sake of simplicity, we put K' and K equal.

Substituting (61) to the equations of motion,

$$\begin{aligned} \rho \frac{d^2 u}{dt^2} &= -\frac{dX_x}{dx} - \frac{\partial X_y}{\partial y} - \frac{\partial X_z}{\partial z}, \\ \rho \frac{d^2 v}{dt^2} &= -\frac{\partial Y_x}{\partial x} - \frac{\partial Y_y}{\partial y} - \frac{\partial Y_z}{\partial z}, \\ \rho \frac{d^2 w}{dt^2} &= -\frac{\partial Z_x}{\partial x} - \frac{\partial Z_y}{\partial y} - \frac{\partial Z_z}{\partial z}, \end{aligned}$$

differentiating these equations with respect to x , y , and z respectively, and adding them, we have

$$\rho \frac{\partial^2 \varepsilon}{\partial t^2} = \left(k_T + \frac{4}{3} \cdot \frac{\mu_1 \tau_1 D}{1 + \tau_1 D} \right) \nabla^2 \varepsilon - k_T a \nabla^2 (T' - T_0). \quad \dots\dots (64)$$

We can find ε , T and T' from the equations (62), (63) and (64).

Putting

$$\begin{aligned} \varepsilon &= A \exp(i\omega t - \beta x), \\ \frac{T - T_0}{T_0} &= B \exp(i\omega t - \beta x), \\ \frac{T' - T_0}{T_0} &= C \exp(i\omega t - \beta x), \end{aligned}$$

and introducing them to (64), (62) and (63), we get

$$\left. \begin{aligned} \left\{ \rho \omega^2 + \left(k_T + \frac{4}{3} \frac{\mu i \omega \tau_1}{1 + i \omega \tau_1} \right) \beta^2 \right\} A - k_T a T_0 \beta^2 C &= 0, \\ \frac{k_T a T_0 i \omega}{\rho c_v'} A - \frac{1}{\tau_K} T_0 B + \left(i \omega + \frac{1}{\tau_K} - \frac{K}{\rho c_v} \beta^2 \right) T_0 C &= 0, \\ \frac{k_T a T_0 i \omega}{\rho c_v} A + \left(i \omega - \frac{K}{\rho c_v} \beta^2 \right) T_0 B &= 0. \end{aligned} \right\} \dots\dots (65)$$

To have the simultaneous equations (65) the solution other than the trivial one, $A = B = C = 0$, β must satisfy the following equation.

$$\left| \begin{array}{ccc} \rho\omega^2 + \left(k_T + \frac{4}{3} \frac{\mu i\omega\tau_1}{1 + i\omega\tau_1}\right)\beta^2 & 0 & -k_T a T_0 \beta^2 \\ \frac{ak_T T_0 i\omega}{\rho c_v'} & -\frac{1}{\tau_K} T_0 & \left(i\omega + \frac{1}{\tau_K} - \frac{K}{\rho c_v'} \beta^2\right) T_0 \\ \frac{ak_T T_0 i\omega}{\rho c_v} & \left(i\omega - \frac{K}{\rho c_v} \beta^2\right) T_0 & 0 \end{array} \right| = 0. \quad (66)$$

Using the thermal diffusivities;

$$\frac{K}{\rho c_v} = \kappa, \quad \frac{K}{\rho c_v'} = \kappa',$$

in the place of the thermal conductivities, and the kinematic viscosity

$$\nu' = \mu'/\rho = \mu\tau_1/\rho$$

in the place of the coefficient of viscosity, with (46) and (47), (66) becomes

$$\left| \begin{array}{ccc} 1 + \left(v_N^2 + \frac{4}{3} \frac{\nu' i\omega}{1 + i\omega\tau_1}\right)\frac{\beta^2}{\omega^2} & 0 & -\frac{v_N^2 a T_0 \beta^2}{\omega^2} \\ \frac{v_L^2 - v_N^2}{v_N^2} \cdot \frac{c_v}{c_v'} \cdot \frac{i\omega\tau_K}{a T_0} & -1 & 1 + i\omega\tau_K - \kappa' \tau_K \beta^2 \\ \frac{v_L^2 - v_N^2}{v_N^2} \cdot \frac{i\omega\tau_K}{a T_0} & i\omega\tau_K - \kappa\tau_K \beta^2 & 0 \end{array} \right| = 0.$$

This leads to

$$\left\{1 + \left(v_N^2 + \frac{4}{3} \cdot \frac{\nu' i\omega}{1 + i\omega\tau_1}\right)\frac{\beta^2}{\omega^2}\right\} (1 + i\omega\tau_K - \kappa' \tau_K \beta^2) (i\omega\tau_K - \kappa\tau_K \beta^2) + \frac{i\tau_K \beta^2}{\omega} (v_L^2 - v_N^2) \left\{1 + \frac{c_v}{c_v'} (i\omega\tau_K - \kappa\tau_K \beta^2)\right\} = 0, \quad \dots (67)$$

which is a cubic equation for β^2 .

If τ_K vanishes, and moreover $\omega\tau_1 \ll 1$, the classical result must be obtained. In this case, (67) becomes

$$\left\{1 + \left(v_N^2 + \frac{4}{3} \nu' i\omega\right)\frac{\beta^2}{\omega^2}\right\} (i\omega - \kappa\beta^2) + \frac{i\beta^2}{\omega} (v_L^2 - v_N^2) = 0.$$

β , being a complex number, lies near $i\omega/v_L$ at least for low frequencies. Noting that ν' and κ are of the same order of magnitude and neglecting the square of the small quantities $\nu'\omega/v_N^2$ and $\kappa\omega/v_N^2$, we have

$$\beta^2 \doteq -\frac{\omega^2}{v_L^2} \left(1 + \frac{4}{3} \frac{\nu' \omega}{v_L^2} + \frac{i\kappa\omega}{v_L^2} \cdot \frac{v_L^2 - v_N^2}{v_L^2}\right)$$

and

$$\beta \doteq -\frac{i\omega}{v_L} \left\{1 + \frac{2}{3} \cdot \frac{\nu' \omega}{v_L^2} + \frac{i\kappa\omega(v_L^2 - v_N^2)}{2v_L^4}\right\}.$$

The absorption coefficient is, therefore, given by

$$\alpha = \Re(\beta) = \frac{2}{3} \frac{\nu' \omega^2}{v_L^3} + \frac{\kappa\omega^2(v_L^2 - v_N^2)}{2v_L^5}.$$

The first term corresponds to the classical absorption being originated from viscosity, and the second, that from the conduction of heat, both coincide with the results of

Stokes and Kirchoff respectively ¹⁴⁾.

In reality, τ_K is not zero but has a finite value, and is sometimes called the period of adjustment. For gases, its order of magnitude is known as $10^{-6} \sim 10^{-5}$ sec. Since the mean period between two succeeding collisions for a molecule in gas at 1 atm. and room temperature is about 10^{-10} sec., it is concluded that among 10^4 to 10^5 collisions only one is effective for the transfer of energy from the external to the internal one, or vice versa.

For liquids, owing to their quasi-crystalline structure, a molecule oscillates about its point of equilibrium, which also moves about gradually in the liquid. The quantity, corresponding to the collision frequency for a gas molecule, is twice the intermolecular frequency, and therefore estimated as approximately 10^{12} sec.⁻¹ If the fraction of the effective collisions were unaltered, the period of adjustment for liquids becomes $10^{-12} \times (10^4 \sim 10^5) = 10^{-6} \sim 10^{-5}$ sec.

There exists, however, the condition which reduces this value remarkably. In gases, two molecules interact only when the two are in collision. But, in a condensed phase, solid or liquid, the situation is utterly altered. The neighbouring molecules always exert the intermolecular force each other, so that the molecular rotation and the intramolecular vibration are easily excited by the intermolecular vibration, and the transfer of the different kind of energy is much easier than that in gas phase. The effect is almost perfect for solids, in which the energy of lattice vibration seems to transfer instantly, or, to speak more exactly, within a period of the vibration, to the internal motion of the molecules. Accordingly, for solids τ_K is exceedingly small, and this explains the small absorption of crystalline solids.

Concerning liquids, the interaction of the intermolecular and the intramolecular motion is not so complete, especially for high temperatures. If we consider that the effect reduces the assumed period τ_K above cited to 1/100, which is not unnatural, we can explain the observed absorption of the supersonic waves in liquids, as follows.

Thereupon the period τ_K for liquids comes to $10^{-10} \sim 10^{-9}$ sec. $\omega\tau_K$ is yet far smaller than unity for the ultrasonic waves, for which ω varies from 10^5 to 10^8 sec.⁻¹. This is the reason why the dispersion of velocity does not take place for most liquids. But the absorption suffers large alteration. From (57) we have the volume viscosity,

$$k_1' = \frac{\alpha^2 k_T^2 T_0 c_v''}{\rho c_v c_v'} \tau_K = (k_s - k_T) \frac{c_v''}{c_v'} \tau_K.$$

For ordinary liquids, the difference $k_s - k_T$ between the adiabatic and the isothermal volume modulus is $(2 \sim 5) \times 10^9$ dyne.cm.⁻² Thereupon, considering that c_v''/c_v' is of the order of unity, k_1' becomes 1~10 poises. This value is from 10 to 10,000 times larger than the ordinary coefficient of viscosity, whose value lies mostly between 10^{-3} and 10^{-2} poises, and hereby we can understand the large absorption of the super-sonics, being from several times to thousands times larger than the classical value.

With increasing temperature, the quasicrystalline structure of liquids is broken up gradually and the liquids approach to gaseous state to some extent. Consequently

the period τ_K becomes longer, and the coefficient k_1' of volume viscosity increases, being contrary to the ordinary viscosity. This accords with the fact that for a majority of liquids the absorption increases with increasing temperature.

Accordingly, though exact evaluation is too difficult to put into action, the mechanism considered here gives a general view concerning to the behaviours of the ultrasonic waves in liquids. There are, however, some exceptions, for which the rearrangement of molecules presumably plays an important part.

The Hypersonic and the Transverse Waves

It is difficult to produce artificially the supersonics the frequencies being over 10^8 cycles per second. However, it is believed at present the elastic waves of about 10^{10} cycles per second exist naturally in solids and liquids owing to their thermal motion of the constituent molecules, and are sometimes called the "hypersonics."¹⁵⁾

The existence of the hypersonics is shown indirectly by the appearance of hyperfine structures in scattered monochromatic light, which results from the reflection of the light by the regular spacing of the denser part in the liquid caused by the longitudinal elastic waves.

Such hyperfine structures were observed first by Gross in 1930.¹⁶⁾ Gross found, in the spectrum of the scattered monochromatic light, two satellite lines on either side of the intense, principal line, the differences in frequency of the satellite and the principal line being given by Brillouin,¹⁷⁾ as

$$\Delta\nu = \pm 2\nu \frac{V}{c} \sin \frac{\theta}{2}, \quad \dots\dots\dots (68)$$

where c is the velocity of light and θ the angle between the incident beam and the direction of the observation.

Gross and many other authors has observed the hyperfine structure and verified the Brillouin's formula (68). But in most cases the calculated value of $\Delta\nu$ was somewhat smaller than the observed value. This is comprehensible if we assume that the velocity V of the hypersonics is 5 to 20 per cent larger than that of the audible or the supersonic sound. The experiments are difficult ones, and the results of the different authors do not necessarily agree each other, but it is undeniable that there exists such a tendency.

For glycerine, which is a highly viscous liquid, the effect is large and cannot be overlooked. According to Raman and Venkateswaran,¹⁸⁾ the velocity of the hypersonic wave, whose frequency is thought to be about 5×10^9 cycles per second, is 30 per cent larger than that of the supersonics, the frequency being 1×10^7 cycles per second. They attributed the discrepancy to that the liquid possesses dissipating rigidity, which is effective for the hypersonics, but not for the supersonics.

Now we apply the results of the previous chapter to extremely high frequencies. Hiedemann¹⁹⁾ noted that for sufficiently large frequencies, the wave-lengths become shorter, the transfer of heat from compressed, hot places to extended, cold places

occurs more violently, and finally the process becomes better to say isothermal rather than adiabatic. The transition from the adiabatic to the isothermal condition is determined by the quantity κ/v_0^2 , which has dimension of time. This is shorter than 10^{-13} seconds; for example,

$$\begin{aligned} \kappa/v_0^2 &= 0.63 \times 10^{-13} \text{ sec. for water,} \\ // &= 0.63 \times 10^{-13} \text{ sec. for benzene,} \\ // &= 0.26 \times 10^{-13} \text{ sec. for glycerine.} \end{aligned}$$

Therefore the dimensionless quantity $\kappa\omega/v_0^2$ is yet far smaller than unity even for the hypersonic frequency, that is considered 10^9 to 10^{10} cycles per second. This shows the condition is adiabatic enough even for these high frequencies. Of course, for higher frequencies this is not true, but such waves have so small wave-lengths, being comparable to the molecular spacing in liquids, that they hardly exist when the discrete, molecular structure of matter is taken into account.

Thus we neglect $\kappa\omega/v_N^2$ and also $\kappa'\omega/v_N^2$ which is the same order of magnitude with $\kappa\omega/v_N^2$, in (67), considering β^2 is near $-\omega^2/v_N^2$ and leaving the predominant terms only, we have

$$1 + \left\{ v_N^2 + \frac{4}{3} \frac{\nu' i\omega}{1 + i\omega\tau_1} + \frac{c_v}{c_v'} (v_L^2 - v_N^2) \right\} \frac{\beta^2}{\omega^2} = 0. \quad \dots\dots (68)$$

If $\omega\tau_1 \gg 1$,

$$\beta^2 = - \frac{\omega^2}{v_N^2 + \frac{c_v}{c_v'} (v_L^2 - v_N^2) + \frac{4}{3} \frac{\mu}{\rho}}$$

Herefrom we have the velocity

$$\begin{aligned} v_H &= \frac{\omega}{\Im(\beta)} = \sqrt{v_N^2 + \frac{c_v}{c_v'} (v_L^2 - v_N^2) + \frac{4}{3} \frac{\mu}{\rho}} \\ &= \sqrt{v_L^2 + \frac{c_v''}{c_v'} (v_L^2 - v_N^2) + \frac{4}{3} \frac{\mu}{\rho}}. \quad \dots\dots (69) \end{aligned}$$

Only when $c_v'' = 0$, this agrees with the result of Raman and Venkateswaran:

$$v_H = \sqrt{v_L^2 + \frac{4}{3} \frac{\mu}{\rho}} \quad \dots\dots (70)$$

(69) shows the internal specific heat c_v'' also contributes to the velocity of the hypersonic waves, accordingly the opinion of Raman and Venkateswaran cited above should be modified.

Although τ_1 is not known exactly, it lies near 10^{-11} seconds for ordinary liquids, as stated in the preceding chapter. Hence it follows that $\omega\tau_1 \ll 1$ is more preferable to the reverse. $\frac{\mu}{\rho} = \frac{\mu'}{\rho\tau}$ is considered tolerably smaller than v_L^2 , since $\mu' \sim 10^{-2}$ poises, $\rho \sim 1$ gr.cm.⁻³ and $v_L \sim 10^5$ cm.sec.⁻¹ Therefore the term

$$\frac{4}{3} \frac{\nu' i\omega}{1 + i\omega\tau_1} = \frac{4}{3} \cdot \frac{\mu}{\rho} \cdot \frac{i\omega\tau_1}{1 + i\omega\tau_1}$$

in (68) can be neglected referring to v_N^2 or v_L^2 , and we have, in the place of (70),

$$v_H = \sqrt{v_L^2 + \frac{c_v''}{c_v'}(v_L^2 - v_N^2)}. \quad \dots\dots\dots (71)$$

Taking benzene as an example, we introduce the numerical values

$$c_v'' = 13.8 \text{ cal.mol}^{-1} \text{ }^{20)}$$

$$c_v' = 8.1 \text{ cal.mol}^{-1} \text{ }^{20)}$$

$$\frac{v_N^2}{v_L^2} = \frac{k_T}{k_S} = 0.70 \text{ }^{21)}$$

in (71), and have

$$\frac{v_H}{v_L} = 1.23.$$

On the other hand, the observations of Gross ²²⁾ and Mitra ²³⁾ lead to the corresponding values 1.22 and 1.15 respectively. The agreement is satisfactory, and also for most liquids it is perhaps sure that the 5 to 20 per cent excesses of v_H over v_L are principally caused by the same reason.

Water is not the case. Since c_v'' is very small for water, v_H/v_L calculated from (71) is undistinguishable practically from unity. On the other hand, the observed value $\Delta v = 0.24 \pm 0.02$ for $\theta = 90^\circ$ by Gross ²²⁾ leads to $v_H/v_L = 1.15 \pm 0.10$. The discrepancy is hard to explain even if we take the rigidity term $\frac{4}{3} \frac{\mu}{\rho}$ into account because $\omega\tau_1 \ll 1$ is also probable for the hypersonic waves in water.

It is believed, as already referred to, that some liquids, including water, have different origin of absorption for sound wave from that stated somewhat long in the preceding chapter. Hall ²⁴⁾ thought a structural change, namely a transformation of the type of molecular lattice, accompanied by the change of pressure change, and this cause the absorption. Such process, if it exists, has presumably much longer time of relaxation than τ_1 , has influence upon the normal tractions rather than upon the shearing stress, and this perhaps gives the explanation of the behaviour of water in the supersonic and hypersonic frequencies, though the reliable numerical calculation is hard to do.

The fact, that β , has very nearly a purely imaginary value for the hypersonic waves, shows that these waves propagates in liquids without much absorption.

For the hypersonic frequency, there is also possibility of the existence of the transverse elastic waves in liquids. On elimination of ϵ from (25), we have

$$\rho \frac{\partial^2}{\partial t^2} \tilde{\omega}_s = \left(\sum_i \frac{\mu_i \tau_i D}{1 + i\tau_i D} \right) \nabla^2 \tilde{\omega}_s, \quad (s = 1, 2, 3). \quad \dots\dots\dots (72)$$

Assuming

$$\tilde{\omega}_s = \exp(i\omega t - \beta x),$$

(72) becomes

$$-\rho\omega^2 = \beta^2 \sum_i \frac{i\mu_i \omega \tau_i}{1 + i\omega \tau_i},$$

or,

$$\beta^2 = -\rho\omega^2 \left/ \left(i \sum_i \frac{\mu_i \omega \tau_i}{1 + i\omega \tau_i} \right) \right.$$

The velocity and the coefficient of absorption can, as well as the longitudinal waves, be obtained from (28) and (29) respectively. If ω is so large that $\omega\tau_i$ is much larger than unity even for the smallest τ_i , β is given approximately by

$$\beta^2 = -\rho\omega^2 / \left(\sum_i \mu_i \right).$$

In this case β is a pure imaginary number, showing the absorption is slight. No experimental evidence has been heretofore obtained, but it is not absurd to consider the transverse wave in liquid. According to the theory of specific heat of Debye the heat energy of solid is distributed on the longitudinal and the transverse elastic waves in it. If there was no transverse wave in liquid, its specific heat should be diminished largely compared with that of solid phase. In general, the difference of the specific heat is rather small, and we must assume the transverse waves in liquids, if Debye's theory holds, even though approximately, for the liquids.

Summary

The general stress-strain relations for plasto-elastic bodies having any number of time of relaxation were obtained. The author's previous theory and Frenkel and Obrtatzov's theory are included as special cases.

The elastic waves in such a body were discussed, and the results were compared with that of the molecular theory. It was shown that the mechanism, postulated by Kneser in his theory of the absorption of the supersonic wave in gases, plays important rôle also in liquids. By this mechanism, the behaviour of most liquids for supersonic frequency is comprehensible at least qualitatively. The effects of viscosity and conduction of heat were discussed. The existence and the high velocity of the hypersonic waves, or the elastic waves of extremely high frequencies caused by thermal agitation, were also explained being grounded on the same mechanism.

There are, however, some exceptions, including water, for which the other mechanism, that is perhaps the rearrangement of molecules, predominates.

As the transverse waves have also the possibility of existence, they were discussed briefly at the end.

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