ON THE THERMO-MECHANICAL PROPERTIES OF RHEOLOGICAL MEDIA

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I. Preliminaries

Recently the experimental data concerning the absorption and dispersion of ultrasonic waves in polyatomic liquids have been accumulated[1][2][3], and the rheological investigations of solid high-polymeric substances[4][5][6] are also in great progress. The molecular kinetic theories to interpret the phenomena of the elastic relaxation of substances of polyatomic molecules have been tried, and up to the present the quantitative explanation of these phenomena especially in

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liquids from the modern molecular kinetic theories has not yet been quite satisfactory.

On the other hand, the treatment of the rheological characters of the continua has been tried by Oshida[7][8], Frenkel and Obratzov[9][10], Sips[11], Takizawa[12][13], Meixner[14][15], and Kailski[16][17]. Oshida considered the equation of state of visco-elastic body (*i.e.* the relation between stress and strain) in order to explain the high velocity of propagation of hypersonics in liquids, which constitute the main part of the thermal motion in liquids. He also extended his old theory[7] so as to include Frenkel-Obratzov's as a special case. The theory presented by Sips[11] is also included in Oshida's treatment. They all considered merely the stress-strain relation of visco-elastic body and did not take any explicit account of the thermal character of the media. We wonder whether the rheological constants may be called *adiabatic* or *isothermal*, especially under the ultrasonic field of extremely high frequency. In those theories, if we want to take the effects of temperature which is considered as an independent variable, then the effects are merely included implicitly in the statement that the rheological constants are certain functions of temperature. Accordingly, the temperature comes to be only secondarily effective in the final expression of stress, through the change in numerical values of the rheological constants.

While, in the theory of molecular collision presented by Kneser[18][19][20] and Rutgers[21], the equation of state is assumed to be *adiabatic*, and the main part of the theory consists in the final expression of specific heat expressed as a certain function of frequency of external mechanical oscillation. Here the question arises, whether the thermal condition, under which the process takes place, is *adiabatic* or *not*, especially under the region of extremely high frequency, *i.e.* under the hypersonic region. The theories of Frenkel-Obratzov, Oshida, and Sips, result in the decreases of elastic constants and viscosities with increasing temperature, if we fix the frequency of external mechanical oscillation. This, in turn, leads to the decrease of the absorption and velocity of ultrasonics, with increasing temperature. While, following to Kneser's theory, we see that the increase of temperature results in the decrease of specific heat, which, on the contrary to the above case, leads to the increase of the absorption and velocity of ultrasonics. Accordingly, simple liquids such as carbon dioxide and benzene obey to Kneser's collision-theory, while the rôle of the shearing and volume viscosities presented by Frenkel, Oshida, and Sips, rather predominates in the associated liquids such as water and acetic acid. In liquids and solids of high-polymeric substances, the situation is quite complicated, and we should consider the generalized theory of visco-elastic media at the more unified point of view.

The theories presented by Takizawa[12][13] and Sips[11] concluded the theories by Frenkel and Obratzov[9] and Oshida[8] and summarized them in the tensorial formulation of the theory of relaxation. Especially Takizawa[12][13], as Meixner[22] mentioned, formulated the theory of relaxation, apart from the adiabatic or the isothermal condition, and also took explicitly the temperature relaxation into account. Thus he made a first step to the direction of the thermodynamic theory of relaxation[12][13][23]. Meixner[22] extended his theory of elastic relaxation in the framework of the theory of irreversible thermodynamics and generalized the thermodynamic theory of rheology into a more consequent formulation of these theories mentioned above[7][13].

In reference to these theories, the author presents a theory which includes these theories from the rheological point of view. Also, he wishes to generalize the theories of visco-elastic relaxation presented by the above mentioned authors[7)13)], taking explicit account of thermal stress and thermal conduction, with reference to the *temperature wave*. Thus the *sonic* theory may be called *sound*, when we take into explicit account the thermal phenomena.

The macroscopic linear theory of visco-elastic body in the present paper is based on the following assumptions:

(1) the components of stress are linear functions of strain and temperature-deviation,

(2) the media are isotropic,

and

(3) the internal energy *in the macroscopic sense* is expressed as a linear function of temperature and strain.

The theory based on these assumptions is conveniently applied to the absorption and dispersion of supersonics as well as hypersonics in the rheological media. The extension to the theory of anisotropic body[24)25)] is quite easily carried out.

In the following we shall restrict ourselves mainly to the treatment of liquids, because the slight modification of numerical values of rheological constants in the present theory can lead to the theory of the solid visco-elastic body, *mutatis mutandis*. Theory of electric relaxation can be also extended in a similar manner, with slight modification of interpretation of symbols and formulae.

II. Notations

x_i: rectangular coordinates, $(i=1, 2, 3)$

ξ_i: components of displacement, $(i=1, 2, 3)$

$u_i=\dfrac{\partial \xi_i}{\partial t}$: components of velocity, $(i=1, 2, 3)$

$\varepsilon_{ij}=\dfrac{1}{2}\left(\dfrac{\partial \xi_j}{\partial x_i}+\dfrac{\partial \xi_i}{\partial x_j}\right)$: components of strain tensor, $(i, j=1, 2, 3)$

$\tilde{\omega}_{ij}=\dfrac{1}{2}\left(\dfrac{\partial \xi_j}{\partial x_i}-\dfrac{\partial \xi_i}{\partial x_j}\right)$: components of rotation of displacement, $(i, j=1, 2, 3)$

A°_{ij}: components of stress tensor, no temperature effect being taken into account, $(i, j=1, 2, 3)$

$A_{ij}=A^{\circ}_{ij}+A'_{ij}$: components of stress tensor, including explicitly thermal stress, $(i, j=1, 2, 3)$

t: time,

$\rho=\rho_0+\rho'$: density, ρ_0 : density at static state,

$p=p_0+p'$: pressure, p_0 : static pressure,

$T=T_0+\vartheta$: temperature, T_0: initial temperature,

U: internal energy per unit mass *in the macroscopic sense, i.e.* energy of translational and rotational motion of constituent molecules,

ρU: internal energy per unit volume,

q_j: components of heat flux vector, $(j=1, 2, 3)$

κ: thermal conductivity,

k_0: static volume moduls,

λ_r: partial volume moduli, $(r=1, 2, 3, \dots, l)$
$\lambda'_r=\lambda_r\tau_r$: partial volume viscosities, $(r=1, 2, 3, \dots, l)$
μ_r: partial shearing rigidities, $(r=1, 2, 3, \dots, m)$
$\mu'_r=\mu_r\tau_r^{(1)}$: partial shearing viscosities, $(r=1, 2, 3, \dots, m)$
α_r/k_0: coefficients of partial thermal expansion, $(r=1, 2, 3, \dots, n)$
τ_r, $\tau_r^{(1)}$, $\tau_r^{(2)}$, $\tau_r^{(3)}$, $\tau_r^{(4)}$ and $\tau_r^{(5)}$: relaxation times,
C_0: static specific heat at constant volume,
C_r: partial specific heat at constant volume, $(r=1, 2, 3, \dots, p)$
b_0 and $b_{ij}^{(r)}$: material constants, $(i, j=1, 2, 3;\ r=1, 2, 3, \dots, q)$
$\omega=2\pi\nu$: circular frequency, ν: frequency,
v: phase velocity of wave,
a: amplitude absorption of ultrasonics per unit length.

For the sake of abbreviation we shall write the differential operator with respect to time t as follows:

$$D=\frac{d}{dt}=\frac{\partial}{\partial t}+u_j\frac{\partial}{\partial x_j}=\frac{\partial}{\partial t}\,.$$

As usual in the tensorial notations, one should sum up over dummy indices.

The word *thermostatics* will be used for what is usually called thermodynamics. Non-equilibrium thermodynamics should be called simply *thermodynamics* in this paper.

III. Dynamical Equations of State

Stress-Strain Relation

The equations of state of the liquid media, no explicit temperature term being included, *i.e.* the relation between stress and strain, are written as follows[12)13)]:

$$\begin{aligned} A^{\circ}_{ij}= &-p_0\cdot\delta_{ij}+k_0\cdot\varepsilon_{kk}\cdot\delta_{ij}+\Big[\sum_{r=1}^{l}\lambda_r\cdot\Big\{\varepsilon_{kk}(t)-\int_0^{\infty}g_r(t')\cdot\varepsilon_{kk}(t-t')\,dt'\Big\}-\\ &-\frac{2}{3}\sum_{r=1}^{m}\mu_r\cdot\Big\{\varepsilon_{kk}(t)-\int_0^{\infty}h_r(t')\cdot\varepsilon_{kk}(t-t')\,dt'\Big\}\Big]\cdot\delta_{ij}+\\ &+2\sum_{r=1}^{m}\mu_r\cdot\Big\{\varepsilon_{ij}(t)-\int_0^{\infty}h_r(t')\cdot\varepsilon_{ij}(t-t')\,dt'\Big\}, \end{aligned}\tag{3-1}$$

where $g_r(t')$ and $h_r(t')$ are the so-called *relaxation functions* which satisfy the following conditions:

with

$$\left.\begin{aligned} &\int_0^{\infty}g_r(t')\,dt'=1, \qquad (r=1, 2, 3, \dots, l)\\ &\int_0^{\infty}h_r(t')\,dt'=1, \qquad (r=1, 2, 3, \dots, m) \end{aligned}\right\}\tag{3-2}$$

with $\varepsilon_{kk}=\varepsilon_{11}+\varepsilon_{22}+\varepsilon_{33}$, and δ_{ij} Kronecker's delta. In the above equations (3-1), if we put $l=m=1$, the equations reduce to those corresponding to the theory of Sips[11)]. The expression of stress-strain relation presented by Oshida[7)8)] is also obtained, if we put in eqs. (3–1),

$$\left.\begin{aligned} & g_r(t') = \frac{1}{\tau_r}\cdot e^{-t'/\tau_r}, \qquad (\tau_r > 0) \\ \text{and} \qquad & \\ & h_r(t') = \frac{1}{\tau_r^{(1)}}\cdot e^{-t'/\tau_r^{(1)}}, \quad (\tau_r^{(1)} > 0) \end{aligned}\right\} \tag{3-3}$$

and take the oscillatory motion of the system. Further, if we put $l=1$ and $m=2$, eqs. (3–1) are reduced to the equivalent expression as Frenkel-Obratzov's[9].

For the sake of simplicity, we shall take the Maxwellian relaxational process as taken by Oshida[8], eqs. (3–1) reduce to the expression as follows:

$$A^\circ_{ij} = -p_0\cdot\delta_{ij} + \left(k_0 + \sum_{r=1}^{l}\frac{\lambda'_r D}{1+\tau_r D} - \frac{2}{3}\sum_{r=1}^{m}\frac{\mu'_r D}{1+\tau_r^{(1)} D}\right)\varepsilon_{kk}\cdot\delta_{ij} + 2\sum_{r=1}^{m}\frac{\mu'_r D}{1+\tau_r^{(1)} D}\,\varepsilon_{ij}, \quad (i,\ j=1,\ 2,\ 3) \tag{3-4}$$

where $\lambda'_r = \lambda_r\tau_r$ are partial volume viscosities, and $\mu'_r = \mu_r\tau_r^{(1)}$ are partial shearing viscosities.

Eqs. (3–4) are the expression of the stress-strain relation for the visco-elastic media, with the so-called *partial volume viscosities* λ'_r and *partial shearing viscosities* μ'_r, which are subjected to the Maxwellian relaxational processes (3–3) respectively.

Thermal Stress

Now we shall consider the equations of state, taking into account the relaxational thermal-stress. As for the thermodynamical independent variables, we shall take strain ε_{ij} and temperature-deviation $\vartheta(=\delta T)$. If thermal stress is composed of n components, we obtain *thermostatically*:

$$A_{ii}(t) - A^\circ_{ii}(t) \equiv \sum_{r=1}^{n} A'^{(r)}_{ii}(t) = -\sum_{r=1}^{n}\alpha_r\cdot\vartheta, \tag{3-5}$$

with i fixed, where α_r/k_0 are the coefficients of thermal expansion. Accordingly, we obtain:

$$\frac{dA'^{(r)}_{ii}}{dt} = -\alpha_r\frac{d\vartheta}{dt}, \tag{3-6}$$

if the stress $A'^{(r)}_{ii}$ is caused instantaneously by thermal expansion, and the term $(-\alpha_r\vartheta)$ is the *static thermal expansion*. While, in the field of ultrasonics of extremely high frequency, the relaxational process of the media due to the temperature-deviation may be also quite effective. In other words, in such a non-equilibrium state as the supersonic and the hypersonic waves create, the temperature fluctuation or deviation will be caused in liquids. The energy corresponding to the momenta of constituent molecules in an equilibrium state, can be obtained by averaging the translational, rotational, and vibrational momenta over the available configurations of the molecule. In a non-equilibrium state, however, the fluctuation of these momenta may be greater and greater, and sometimes it would be more convenient to consider even the matrix quantity which corresponds to many kinds of momenta of the constituent molecules. Accordingly, sometimes it may be rather useful to take into account the matrix quantity corresponding to many kinds of temperature-deviations in the expression of stress. Here in the present chapter, however, we shall consider merely a scalar quantity of temperature-deviation as an independent variable of *thermodynamical* state. In this case, the thermal stress is not directly proportional to the temperature-deviation itself, but it may be supposed that the stress is also proportional to some averaged value of temperature-deviation in the past, just as in the case of stress-strain relation mentioned above. In this respect, the behaviour of the thermal stress as a function of temperature-deviation greatly differs from the ordinary thermal expansion as treated in the theory of *thermostatics*. Accordingly, as in the case of eqs. (3–1), considering the components for thermal expansion, we see that the normal stress is expressed as[12)13)]:

$$A'_{ii}(t) \equiv A_{ii}(t) - A^{\circ}_{ii}(t) = -\sum_{r=1}^{n}\alpha_r\cdot\left\{\vartheta(t) - \int_0^\infty f_r(t')\cdot\vartheta(t-t')dt'\right\}, \qquad (3\text{-}7)$$

with i fixed, under the condition for the relaxation functions:

$$\int_0^\infty f_r(t')dt' = 1. \qquad (r = 1, 2, 3, \ldots, n) \qquad (3\text{-}8)$$

As for the expressions of the relaxation functions, we shall take:

$$f_r(t') = \frac{1}{\tau_r^{(2)}}\cdot e^{-t'/\tau_r^{(2)}}, \qquad (3\text{-}9)$$

as already mentioned by Takizawa[12)13)].

Considering the relaxation function of Maxwellian type (3–9), and taking the oscillatory motion of the system, we see the following relations hold for the normal stress and temperature-deviation:

$$A'_{ii}(t) \equiv A_{ii}(t) - A^{\circ}_{ii}(t) = -\sum_{r=1}^{n}\frac{\alpha'_r D}{1+\tau_r^{(2)}D}\vartheta, \qquad (i = 1, 2, 3) \qquad (3\text{-}10)$$

with relaxation times $\tau_r^{(2)}$, and partial cubic thermal expansions $\alpha_r/k_0 = \alpha'_r/\{k_0\tau_r^{(2)}\}$.

The first term in the right-hand side of eq. (3-7) is the one analogous to the usual thermal expansion, while the second term represents the rate of dissipation of the stress by plastic flow. In another word, the equation (3–7) means that the temperature does not cause the normal stress instantaneously but there needs finite delay of time to create the normal stress after a sudden increase of temperature. This may be considered also to correspond roughly to the physical picture that after the local temperature has risen, the temperature makes contribution to the normal stress with a small but finite delay of time.

Combining eqs. (3-1) and (3–7), we finally obtain the dynamical equations of state for the rheological bodies with thermal expansion:

$$A_{ij}(t) = A^{\circ}_{ij}(t) - \left[\sum_{r=1}^{n}\alpha_r\cdot\left\{\vartheta(t) - \int_0^\infty f_r(t')\cdot\vartheta(t-t')dt'\right\}\right]\cdot\delta_{ij}, \qquad (i, j = 1, 2, 3) \qquad (3\text{-}11)$$

with $A^{\circ}_{ij}(t)$ as expressed in eq. (3–1).

And, if necessary, the combination of eqs. (3–4) and (3–10) reduces to the expression subjected to the Maxwellian relaxational process:

$$A_{ij}(t) = -p_0\cdot\delta_{ij} + \Big(k_0 + \sum_{r=1}^{l}\frac{\lambda'_r D}{1+\tau_r D} - \frac{2}{3}\sum_{r=1}^{m}\frac{\mu'_r D}{1+\tau_r^{(1)}D}\Big)\varepsilon_{kk}\cdot\delta_{ij} + \\ + 2\sum_{r=1}^{m}\frac{\mu'_r D}{1+\tau_r^{(1)}D}\varepsilon_{ij} - \sum_{r=1}^{n}\frac{\alpha'_r D}{1+\tau_r^{(2)}D}\vartheta\cdot\delta_{ij}. \quad (i,\ j=1,\ 2,\ 3) \quad (3\text{–}12)$$

In case of a continuous distribution of the relaxation time, the summation in eqs. (3–11) and (3–12) can be replaced by Stieltjes integration.

The expression (3–11), including both strain and temperature terms explicitly, can be applicable to describe the rheological behaviours of visco-elastic bodies, *i.e.* internal viscosity effects, structural relaxations, monomer-polymer formation, and temperature relaxation in the system under consideration. The stress-strain relations (3–4) are essentially the same as derived by Oshida[8] in 1950 and include, as special cases, the results obtained by Frenkel-Obratzov[9][10] and Sips[11]. The relation (3–11) or (3–12) is an extension[12][13] of eqs. (3–4), and it is also found to include the equations of state of rheological bodies obtained by Sips[11], Tisza[26], Hall[27], Kneser[28], and others[29][31], respectively as special cases.

Equations of Motion

The equations of motion of the medium under consideration read as follows:

$$\rho\frac{du_i}{dt} = \frac{\partial A_{ij}}{\partial x_j} + \rho X_i, \qquad (i=1,\ 2,\ 3) \qquad (3\text{–}13)$$

where X_i is the components of external body force.

By making use of the expressions (3–11) or (3–12), we obtain:

$$\rho\Big(\frac{\partial u_i}{\partial t} + u_j\frac{\partial u_i}{\partial x_j}\Big) = -\frac{\partial p_0}{\partial x_i} + k_0\frac{\partial}{\partial x_i}\varepsilon_{kk} + \sum_{r=1}^{l}\lambda_r\frac{\partial}{\partial x_i}\Big\{\varepsilon_{kk} - \int_0^\infty g_r(t')\varepsilon_{kk}(t-t')\,dt\Big\} + \\ + \frac{1}{3}\sum_{r=1}^{m}\mu_r\frac{\partial}{\partial x_i}\Big\{\varepsilon_{kk} - \int_0^\infty h_r(t')\cdot\varepsilon_{kk}(t-t')\,dt\Big\} + \\ + \sum_{r=1}^{m}\mu_r\Delta\Big\{\xi_i(t) - \int_0^\infty h_r(t')\cdot\xi_i(t-t')\,dt'\Big\} - \\ - \sum_{r=1}^{n}\alpha_r\frac{\partial}{\partial x_i}\Big\{\vartheta(t) - \int_0^\infty f_r(t')\cdot\vartheta(t-t')\,dt'\Big\} + \rho X_i, \qquad (i=1,\ 2,\ 3) \\ (3\text{–}14)$$

or

$$\rho\Big(\frac{\partial u_i}{\partial t} + u_j\frac{\partial u_i}{\partial x_j}\Big) = -\frac{\partial p_0}{\partial x_i} + \Big(k_0 + \sum_{r=1}^{l}\frac{\lambda'_r D}{1+\tau_r D} + \frac{1}{3}\sum_{r=1}^{m}\frac{\mu'_r D}{1+\tau_r^{(1)}D}\Big)\frac{\partial}{\partial x_i}\varepsilon_{kk} + \\ + \sum_{r=1}^{m}\frac{\mu'_r D}{1+\tau_r^{(1)}D}\Delta\xi_i - \sum_{r=1}^{n}\frac{\alpha'_r D}{1+\tau_r^{(2)}D}\frac{\partial\vartheta}{\partial x_i} + \rho X_i. \qquad (i=1,\ 2,\ 3) \\ (3\text{–}15)$$

IV. Equation of Conservation of Energy

Energy Equation

The increase of internal energy *in the macroscopic sense* which is consisted of the translational, vibrational, and rotational energies of the molecules, is equal to the work done by the external force plus the energy inflowed by the thermal conduction into the system considered. We shall follow the method of derivation of energy equation presented by Sakadi[32][33].

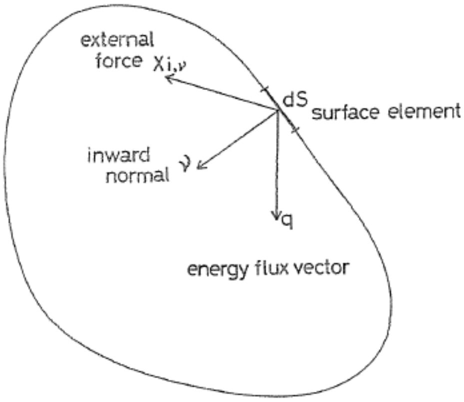

FIG. 4–1. Energy Flux and Inward Normal at the Boundary Surface.

Let us take a part of the medium, in which the kinetic and internal energies are expressed respectively as:

$$L = \frac{1}{2}\int \rho u_i^2\, dx, \tag{4-1}$$

and

$$E = \int \rho U dx, \tag{4-2}$$

where dx is volume element, ρ density of the medium, $u_i = \partial \xi_i / \partial t$ $(i = 1, 2, 3)$ components of velocity, and U internal energy per unit mass. The increments dL and dU in a small interval of time dt, are:

$$\begin{aligned} dL &= dt \cdot \int \rho u_i \frac{du_i}{dt} dx \\ &= dt \cdot \int u_i \frac{\partial A_{ij}}{\partial x_j} dx + dt \cdot \int \rho u_i X_i\, dx, \end{aligned} \tag{4-3}$$

and

$$dE = dt \cdot \int \rho \frac{dU}{dt} dx. \tag{4-4}$$

The equations of motion (3–13) are referred to derive the final expression of eq. (4–3).

The work W_1 done by the surface force at the surface of the medium is expressed as follows:

$$W_1 = dt \cdot \int X_{i,\nu} u_i dS = -dt \cdot \int A_{ij} \cos(\nu, x_j) u_i dS, \tag{4-5}$$

where ν is the inward normal, and $X_{i,\nu}$ the components of external force normal to the surface element dS. The work W_2 done by the body force X_i is

$$W_2 = dt \cdot \int \rho u_i X_i\, dx. \tag{4-6}$$

Accordingly, the work W done by the external force is equal to the sum of W_1 and W_2:

$$
\begin{aligned}
W = W_1 + W_2 &= -dt \cdot \int A_{ij} \cos(\nu, x_j) u_i \, dS + dt \cdot \int \rho u_i X_i \, d\boldsymbol{x} = \\
&= dt \cdot \int \frac{\partial}{\partial x_j} (A_{ij} u_i) \cdot d\boldsymbol{x} + dt \cdot \int \rho u_i X_i \, d\boldsymbol{x} = \\
&= dL + dt \cdot \int A_{ij} \frac{\partial u_i}{\partial x_j} \, d\boldsymbol{x} = \\
&= dL + dt \cdot \int A_{ij} \frac{\partial \varepsilon_{ij}}{\partial t} \, d\boldsymbol{x}, \qquad (4\text{-}7)
\end{aligned}
$$

where the reference is also made of eq. (4-3) and equations of motion (3-13).

The thermal energy obtained Q is expressed as:

$$
Q = dt \cdot \int \boldsymbol{q}_\nu \, dS = -dt \cdot \int \frac{\partial q_j}{\partial x_j} \, d\boldsymbol{x}, \qquad (4\text{-}8)
$$

with q_j ($j=1, 2, 3$) components of heat flux vector, and $\boldsymbol{q}_\nu$ its component normal to the surface dS (cf. Fig. 4-1).

The equation of conservation of energy states:

$$
dL + dE = W + Q. \qquad (4\text{-}9)
$$

From eqs. (4-3), (4-4), (4-7), (4-8) and (4-9), we finally obtain:

$$
\rho \frac{dU}{dt} = A_{ij} \frac{\partial \varepsilon_{ij}}{\partial t} - \frac{\partial q_j}{\partial x_j}. \qquad (4\text{-}10)
$$

Expression of Internal Energy

As for the expression of internal energy, we already took temperature and strain as independent variables, so it is natural to take

$$
\delta U = \delta U_\varepsilon + \delta U_T, \qquad (4\text{-}11)
$$

where δU_ε means the increment of internal energy at iso-strained state, and δU_T is the one at isothermal state. Corresponding to the first term: (specific heat at constant volume C_0) × (the increment of temperature δT), it is considered that the averaged effect of the temperature in the past plays also an important rôle. So we can write:

$$
\delta U_\varepsilon(t) = C_0 \cdot \delta T(t) + \sum_{r=1}^{s} C_r \cdot \left\{ \delta T(t) - \int_0^\infty \bar{f}_r(t') \cdot \delta T(t-t') \cdot dt' \right\}, \qquad (4\text{-}12)
$$

where $\bar{f}_r(t')$ are hysteresis functions satisfying the conditions:

$$
\int_0^\infty \bar{f}_r(t') \, dt' = 1. \qquad (r = 1, 2, 3, \ldots, s) \qquad (4\text{-}13)
$$

In the similar manner, we have

$$
\delta U_T(t) = b_0 \cdot \delta \varepsilon_{kk}(t) + \sum_{r=1}^{q} b_{ij}^{(r)} \left\{ \delta \varepsilon_{ij}(t) - \int_0^\infty \bar{\bar{f}}_r(t') \cdot \delta \varepsilon_{ij}(t-t') \cdot dt' \right\}, \qquad (4\text{-}14)
$$

where

$$\int_0^\infty \overline{\overline{f}}_r(t')\,dt' = 1. \qquad (r = 1, 2, 3, \ldots, q) \tag{4-15}$$

From eqs. (4-11), (4-12) and (4-14), we finally obtain the expression of the increment of internal energy in the rheological media:

$$\begin{aligned}\delta U(t) = C_0\cdot\delta T + \sum_{r=1}^{s} C_r\cdot\left\{\delta T(t) - \int_0^\infty \overline{f_r}(t')\cdot\delta T(t-t')\,dt'\right\} + \\ + b_0\cdot\delta\varepsilon_{kk}(t) + \sum_{r=1}^{q} b_{ij}^{(r)}\left\{\delta\varepsilon_{ij}(t) - \int_0^\infty \overline{\overline{f_r}}(t')\cdot\delta\varepsilon_{ij}(t-t')\,dt'\right\}.\end{aligned} \tag{4-16}$$

Taking the Maxwellian relaxational processes for the hysteresis functions as in eq. (3-3):

$$\overline{f_r}(t') = \frac{1}{\tau_r^{(3)}}\cdot e^{-t'/\tau_r^{(3)}}, \qquad (\tau_r^{(3)} > 0) \tag{4-17}$$

$$\overline{\overline{f_r}}(t') = \frac{1}{\tau_r^{(4)}}\cdot e^{-t'/\tau_r^{(4)}}, \qquad (\tau_r^{(4)} > 0) \tag{4-18}$$

we have, for the oscillatory motion of the system,

$$\delta U = \left\{C_0 + \sum_{r=1}^{s} \frac{C_r \tau_r^{(3)} D}{1 + \tau_r^{(3)} D}\right\}\cdot\delta T + \left\{b_0\cdot\delta_{ij} + \sum_{r=1}^{q} \frac{b_{ij}^{(r)} \tau_r^{(4)} D}{1 + \tau_r^{(4)} D}\right\}\cdot\delta\varepsilon_{ij}, \tag{4-19}$$

where C_0 is *static specific heat* at constant volume, and C_r the so-called *partial specific heats* at constant volume. The summations in the right-hand side of eqs. (4-16) and (4-19), may be replaced by the Stieltjes integrals, if we need more relaxation times or even the continuous distribution of relaxation time.

The relaxational processes in eqs. (3-3), (3-9), (4-17), and (4-18), are Maxwellian, while in some time the relaxation of resonator type:

$$\text{relaxation function} \propto \frac{1 + \tau^2\omega_0^2}{\tau}\cdot\cos(\omega_0 t')\cdot e^{-t'/\tau}, \tag{4-20}$$

is also useful[34)35)]. If such a selective absorption (4-20) takes place in liquids, there should be an eigen-oscillator in the constituting molecules of the liquids. In reality, however, atomic oscillators have extremely high eigen-frequency, for example in the inversion spectrum of ammonium its eigen-frequency is about 10^{10} cycles per second. This is one of the reason why we take the Maxwellian relaxation and not the relaxation of resonator type.

The coefficient (*i.e.* an operator) of δT is the specific heat in a non-equilibrium state, and this operator is seen to be reduced to the formally equivalent term of the specific heat due to Kneser[1)18)19)]. Let C_∞ be the specific heat corresponding to the translational motion of the molecules, then C_∞ is the limiting value of $\delta U_\varepsilon/\delta T$ when the frequency becomes infinite. Thus we obtain:

$$C_\infty = C_0 + \sum_{r=1}^{s} C_r. \tag{4-21}$$

Introducing eq. (4-21), we obtain for the operator corresponding to the specific heat in eq. (4–19):

$$C_0+\sum_{r=1}^{s}\frac{C_r\tau_r^{(3)}D}{1+\tau_r^{(3)}D}=C_\infty-\sum_{r=1}^{s}\frac{C_r}{1+\tau_r^{(3)}D}. \tag{4-22}$$

As a special case, if we take further $s=1$, and $C_r=C_\infty-C_0'$, where C_0' is *static specific heat*, eq. (4–22) reduces to the expression of specific heat obtained by Kneser. Thus the equation (4–19) includes, as a special case, the expression of the term of the *dynamic specific heat* presented by Kneser[1)18)19)].

The expression (4–14) is not so familiar in the usual *thermostatics*. The expression (4–14), however, may be very interesting to consider the thermal stress in a medium under the ultrasonic field, when the disturbances caused by thermal expansion propagate *with finite velocity*. The internal energy is a scalar quantity, which depends *thermostatically* on the state variables ε and T. Accordingly the general expression for the internal energy, which includes the infinitesimal quantities of first order with regard to strain ε and temperature-deviation ϑ, can be given as the expression in the first terms of (4–12) and (4–14). The second terms in eqs. (4–12) and (4–14) come from the thermal and the visco-elastic relaxations, respectively. The scalar property of internal energy leads to the tensor $b_{ij}^{(r)}$. Thus the expressions (4–16) and (4–19) are the more general expression for the internal energy.

Now, we shall consider the physical meaning of the quantities C and b in eq. (4–16). For the sake of simplicity, we shall take and explain merely the first terms of (4–12) and (4–14).

If the *liquids* ($p_0\fallingdotseq 0$ in eq. (3–12)) undergo the infinitesimal deformation *adiabatically*, then the expression:

$$\delta U_{\mathrm{adiab}}=C_0\cdot\vartheta+b_0\cdot\varepsilon_{kk}, \tag{4-23}$$

is the work done by the surface force and is equal to:

$$\frac{1}{\rho_0}\cdot\frac{\partial}{\partial x_j}(A_{ij}\xi_i)\fallingdotseq-\frac{p_0}{\rho_0}\varepsilon_{kk}, \tag{4-24}$$

as we see from the equation of conservation of energy (4–9) or (4–10). The right hand side of eq. (4–24) is a small infinitesimal quantity of first order. In this case, we put:

$$\delta U_{\mathrm{adiab}}=-\frac{p_0}{\rho_0}\varepsilon_{kk}, \tag{4-25}$$

and the change in temperature ϑ is obtained as follows:

$$\vartheta=-\frac{1}{C_0}\Big(b_0+\frac{p_0}{\rho_0}\Big)\varepsilon_{kk}. \tag{4-26}$$

On the other hand, if the *liquids* change *isothermally* always under the *quasi-static process*, the change in free energy δF can be expressed as mechanical work, and is equal to:

$$\delta F=\delta U_T-T\cdot\delta S, \tag{4-27}$$

where δU_T stands for the increment of internal energy in the isothermal process, and S the entropy of the system. The quantity δF is of first order, because p_0 is finite. While, the increment of internal energy in the isothermal process is given by (4-16):

$$\delta U_T = b_0 \cdot \varepsilon_{kk},$$

which is also a quantity of first order. Accordingly, the "Gebundene Energie" $T\delta S$ is of first order, in general case.

The value of b_0 can be estimated, for example, by the experimental value of the velocity of longitudinal hypersonics:

$$v_{\text{hyper}} = \sqrt{\frac{k_0 + \sum_{r=1}^{l} \lambda_r + \frac{4}{3} \sum_{r=1}^{m} \mu_r + \left(b_0 + \frac{p_0}{\rho_0}\right) \cdot \frac{1}{C_0} \sum_{r=1}^{n} \alpha_r}{\rho_0}},$$

as expressed in eq. (6-2), where $\lambda_r/k_0 \ll 1$, $\mu_r/k_0 \ll 1$ and $\alpha_r/k_0 \ll 1$. If we consider that the volume expansion ($\varepsilon_{kk} > 0$) results in the decrease of temperature in most kinds of liquids under the adiabatic process, we see at once $b_0 > -p_0/\rho_0$.

If we take a *solid visco-elastic body* (we can put $p_0 = 0$ in the stress-strain relation (3-12)) instead of liquids, and consider the infinitesimal deformation *adiabatically*, then the internal energy is expressed by the work done by the surface force:

$$\delta U_{\text{adiab}} = C_0 \cdot \vartheta + b_0 \cdot \varepsilon_{kk}, \tag{4-28}$$

and is equal to (cf. eq. (4-9)):

$$\frac{1}{\rho_0} \cdot \frac{\partial}{\partial x_j} (A_{ij} \xi_i) \fallingdotseq \frac{k_0}{\rho_0} \cdot \varepsilon_{kk}^2,$$

the right-hand side of which is a small infinitesimal quantity of second order.

If we put:

$$\delta U_{\text{adiab}} = (\text{terms of second order}), \tag{4-29}$$

then the change in temperature ϑ is obtained as follows:

$$\vartheta = -\frac{1}{C_0} b_0 \cdot \varepsilon_{kk} + (\text{terms of second order}). \tag{4-30}$$

On the other hand, a *solid visco-elastic body* (*i.e.* $p_0 = 0$) changes its state *isothermally* under the quasi-static process, the change δF in free energy is expressed as mechanical work:

$$\delta F = \delta U_T - T\delta S. \tag{4-31}$$

This quantity is obviously of second order, because of $p_0 = 0$. While, from eq. (4-19) the internal energy $\delta U_T \fallingdotseq b_0 \cdot \varepsilon_{kk}$ is of first order. Accordingly, the "Gebundene Energie" $T\delta S$ is of first order. In general, in a solid body, it is easily seen that the quantity b_0 is positive. This comes from the fact that in an adiabatic change the volume expansion ($\varepsilon_{kk} > 0$) leads to the decrease in temperature ($\vartheta < 0$), as is expected from the above equation:

$$\vartheta = -\frac{1}{C_0} \cdot b_0 \cdot \varepsilon_{kk}. \qquad (C_0 > 0) \tag{4-32}$$

Writing the differential form of eq. (4–16), under consideration of the Maxwellian relaxational processes (4–17) and (4–18), we obtain the expression for the increment of internal energy:

$$\begin{aligned} dU(t) = C_0 \cdot dT(t) + \sum_{r=1}^{s} C_r \cdot \left\{ dT(t) - \int_0^\infty \bar{f}_r(t')\, dT(t-t')\, dt' \right\} + \\ + b_0 \cdot d\varepsilon_{kk} + \sum_{r=1}^{q} b_{ij}^{(r)} \cdot \left\{ d\varepsilon_{ij}(t) - \int_0^\infty \bar{\bar{f}}_r(t')\, d\varepsilon_{ij}(t-t')\, dt' \right\}, \end{aligned} \tag{4-33}$$

or

$$dU(t) = \left\{ C_0 + \sum_{r=1}^{s} \frac{C_r \tau_r^{(3)} D}{1 + \tau_r^{(3)} D} \right\} \cdot dT + \left\{ b_0 \cdot \delta_{ij} + \sum_{r=1}^{q} \frac{b_{ij}^{(r)} \tau_r^{(4)} D}{1 + \tau_r^{(4)} D} \right\} \cdot d\varepsilon_{ij}(t). \tag{4-34}$$

The second term of eq. (4–34) expresses that the internal energy is also subjected to the relaxational process due to the normal and shearing strains. In general, it happens that the values of $b_{ij}^{(r)}$ are very small compared with b_0. However, as the frequency ω of the normal and shearing waves in liquids increases greater and greater, and finally approaches to $\tau_r^{(4)} \omega \approx 1$, then the second terms may be comparatively effective. On the other hand, when $\tau_r^{(4)} \omega \ll 1$, we may neglect these terms comparing with the one involving b_0.

Heat Flux—*Generalized Fourier Law*

Now we shall consider the expression of heat flux vector q_j. Kneser[19)20)], Rutgers[21)] and others[1)2)] considered that the dispersion and absorption of supersonic waves occur as a result of the delay of energy exchange between the excited and the normal states of molecules. Accordingly, the medium, through which the wave propagates, is considered as a mixture of two kinds of molecules, between which the reaction analogous to the chemical one can take place. This idea succeeded in the interpretation of the dispersion and absorption of the ultrasonic waves in gases of polyatomic molecules. Later, this treatment was extended to the consideration of the supersonic phenomena in non-associated liquids[18)], Kneser took the assumptions that

(1) one of the excited states is taken into consideration, and the number rate of molecules per unit time in the excited state is a function of volume, temperature, and the number itself,
(2) pressure is also a function of these three variables,
and (3) the thermal process caused in the medium by the disturbance of the elastic waves is adiabatic.

Such a consideration was taken into account by Sakadi, in order to discuss the dispersion of sound wave in gases accompanied by heat conduction and viscosity. Sakadi[32)33)] assumed that the expression of the increment of internal energy in the macroscopic sense dU is expressed by:

$$dU = CdT + E'dn', \tag{4-35}$$

where C is the specific heat of the gas, when the gas is entirely degenerated in the sense of Kneser and Rutgers, dT the increment of temperature, E' energy of excited state of molecules, and n' the number of excited molecules in 1 gramme.

He also took, after Kneser[36], the equation of reaction between the normal state and the excited state of molecules:

$$\frac{dn'}{dt} = \rho n\{k_1(n-n') - k_2 n'\}, \tag{4-36}$$

where n is the total number of molecules in 1 gramme, ρ the density of the gas, and k_1 and k_2 constants of reaction, whose ratio is expressed as:

$$\frac{k_1}{k_2} = \exp\left[-\frac{E'}{kT}\right], \tag{4-37}$$

with the Boltzmann constant k.

Sakadi also assumed that the heat flux vector q_j is expressed as:

$$q_j = -\kappa_1 \frac{\partial T}{\partial x_j} - \kappa_2 \frac{\partial n'}{\partial x_j}, \qquad (j=1,\ 2,\ 3) \tag{4-38}$$

with constants κ_1 and κ_2. The expression (4–38) is quite different from the classical expression of heat flux vector due to Stokes and Kirchhoff:

$$q_j = -\kappa \frac{\partial T}{\partial x_j}, \qquad (j=1,\ 2,\ 3) \tag{4-39}$$

with κ the ordinary thermal conductivity.

In an early paper, Herzfeld and Rice[37], and Bourgin[39] took into account many sorts of temperature, which correspond to the energies of the vibrational and the translational, as well as the rotational motions of the molecules. They set up two kinds of equations of conservation of energy: *i.e.* first, for the degree of freedom of translation, expressing the fact that this energy can be changed by the external work (work done by the stress), thermal conduction (a molecule's translational motion changes into another's translational one), and the exchange with the internal (in the microscopic sense) degrees of freedom with a finite delay of time of energy transfer (relaxation time); and secondly, for the equation of conservation of energy of the internal vibrational degrees of freedom, stating that there exists the inflow from the external degrees of freedom and the exchange of energy between the internal degrees of freedom themselves. The latter equation includes a rather uncertain idea of the flow of vibrational heat to the vibrational one. Accordingly there might exist three sorts of temperature at any point of coordinate space, having the following relation with initial temperature T_0:

$$C'(T'-T_0) + C''(T''-T_0) = C'''(T'''-T_0), \tag{4-40}$$

where T', T'' and T''' are the translational, internal (vibrational), and thermostatical temperatures, respectively. C', C'' and C''' are the corresponding specific heats. For sufficiently slow motion, the following relations hold:

$$T' = T'' = T'''. \tag{4-41}$$

and

$$C' + C'' = C'''. \tag{4-42}$$

In such a line of consideration, the macroscopic pressure p may be defined as the one which is proportional to the total energy subtracted by the internal vibrational energies, and accordingly p is proportional to the translational energy alone.

The method of dividing the total system into a number of subsystems[40)41)], in each of which the *thermostatical equilibrium* is maintained, is of frequent use, and may contribute to extend the theory of thermodynamics of irreversible processes[42)43)44)]. Such a treatment may be useful for the thermodynamical state not so much deviated from the *thermostatical equilibrium*. The elastic relaxation, structural relaxation, and temperature relaxation etc. can be also treated by dividing the system into many numbers of subsystems.

As Takizawa[12)] already mentioned the assumption of the heat flux vector (4–39), stating that the heat current vector is proportional to the negative gradient of temperature, is sometimes uncertain within such subsystems as disturbed by the mechanical oscillations of extremely high frequency. Accordingly, the expression of the conservation of the internal energy (in the macroscopic sense) is rather ambiguous, in the sense whether the expression (4–39) is valid or not.

Moreover, the classical equation of heat conduction:

$$\frac{\partial T}{\partial t} = \kappa_1 \Delta T, \qquad (\kappa_1 = \text{const.}) \tag{4-43}$$

is based on the assumption (4–39), and gives the solution which expresses the instantaneous propagation of temperature, *i.e.* the velocity of propagation of temperature is infinite. In this respect, it may be also considered that the expressions in both side of eq. (4–43) should be replaced by others, under the sudden change of temperature field, or under the rapid process such as under the ultrasonic field of extremely high frequency.

The modification of the left-hand side of eq. (4–43) has been already made in our eq. (4–33) and (4–34). If we deal with the problems of the so-called *thermal shock* in an elastic solid body, the term containing b_0 in eqs. (4–33) and (4–34) plays an important rôle. The finite values of b_0 and $b_{ij}^{(r)}$ result in the finite velocity of propagation of temperature wave in the solid body. And, as Sakadi[32)33)] mentioned, the numerical value of b_0 is positive, and can be estimated by measuring the velocity of propagation of the temperature wave in the adiabatic process in an solid elastic body. Under the assumption of adiabatic process, the temperature-change δT is expressed[33)] by eq. (4–30), *i.e.*

$$\delta T = -\frac{b_0}{C_0} \cdot \varepsilon_{kk}. \tag{4-44}$$

We put the expression (4–44) into the expression of thermal stress (3–10) ~ (3–12), and calculate the velocity of the longitudinal wave which propagates through the medium. The comparison between the theoretical and the experimental results will give the numerical value of b_0.

The right-hand side of eq. (4–43) can be also modified by introducing the work done by the external force, as was already expressed in eq. (4–9) or (4–10). There, the term $\frac{\partial}{\partial x_j}(A_{ij}u_i)$ was introduced, and in the equation of conservation of energy (4–10), the term $A_{ij}\frac{\partial \varepsilon_{ij}}{\partial t}$ appeared explicitly.

The assumption (4–39) can be interpreted in such a way that the heat transfer takes place by the collision between the same sort of energy, *i.e.* the translational energy to the translational energy of the molecules and the rotational to the rotational one. While, the assumption presented by Kneser[36], Rutgers[21] and Sakadi[32], corresponds to the energy transfer by collision between the same kinds of energies, *i.e.* the translational to translational, and the excited to the excited energies, respectively. In such an assumption of energy transfer by collision in the microscopic point of view, the present author inclines to consider many kinds of excited states and to pursue the transfer process of energies among the excited states. Thus the expression such as in eq. (4–38) may be quite useful. We shall take many numbers of excited states and the number of molecules at each excited state shall be denoted by n_i $(i=0, 1, 2, \dots, s)$, n_0 being the number of molecules at the normal state. We shall consider the equation of first order reaction between these states, and assume:

$$\frac{dn_i}{dt} = \sum_{j\neq i} k_{ji}n_j - k_i n_i, \qquad (i = 0,\ 1,\ 2,\ \dots,\ s) \tag{4–45}$$

under the conditions:

$$\sum_{i=0}^{s} n_i = N = \text{const.}, \tag{4–46}$$

and

$$\sum_{i=0}^{s} e_i n_i = E_0 = \text{const.}, \tag{4–47}$$

where e_i is the energy of a particle at the i-th state, and k_{ji} and k_i are the reaction constants, k_{ji} corresponding to the transition probabilities of particles from the j-th to the i-th energy levels, and $1/k_i$ being relaxation times of the i-th state. This idea corresponds essentially to the generalization of eq. (4–40), taking into account the reaction kinetics among the different energy states.

On the other hand, phenomenological equations of heat conduction of hyperbolic form were presented by Kaliski[16][17][45][46], Nowacki[47] and others[48]~[52]. The classical heat equation (4–43) is parabolic, an essential consequence of which is that the thermal disturbance propagates with infinite velocity. In the physical reality, however, this result is quite inadmissible, and the equation should be modified to describe the real physical phenomena of energy transfer, especially in the non-stationary field or in a rapidly changing field such as ultrasonic field of extremely high frequency. The authors cited above have proposed hyperbolic wave equations of heat conduction, and especially Kaliski has generalized the classical Fourier law and proposed the expression of heat flux vector q_j as follows:

$$\tau\frac{dq_j}{dt} + q_j = -\kappa\frac{\partial T}{\partial x_j}, \tag{4–48}$$

where τ is a constant, which may be called *relaxation time of heat flow.* κ is the thermal conductivity and is reduced to the ordinary thermal conductivity when τ is sufficiently small. The expression (4–48) can be written in linear form:

$$q_j = -\frac{\kappa}{1+\tau D}\cdot\frac{\partial T}{\partial x_j}, \tag{4-49}$$

with $D=\partial/\partial t$.

With reference to the expressions (4–35), (4–38) and (4–49), the present author proposes the generalized Fourier law for the generalized velocity q_j (heat flux) and the generalized force $\partial T/\partial x_j$:

$$q_j(t) = -\sum_{r=1}^{p}\kappa_r\frac{\partial}{\partial x_j}\left\{\int_0^\infty \varphi_r(t')\,\vartheta(t-t')\,dt'\right\}, \tag{4-50}$$

where κ_r $(r=1, 2, 3, \ldots, p)$ are the so-called *partial thermal conductivities.* ϑ is temperature-deviation, and $\varphi_r(t')$ the relaxation functions, which satisfy the conditions:

$$\int_0^\infty \varphi_r(t')\,dt' = 1. \qquad (r=1,\ 2,\ 3,\ \ldots,\ p) \tag{4-51}$$

The expression (4–50) is quite similar to the expressions (3–1), (3–7), (4–12), and (4–14), and is obtained from the consideration that (a) heat flux is consisted of a number of fluxes, and (b) in each flux the time-average of temperature-deviation (cf. the derivation of eqs. (3–1), (3–7), (4–12), and (4–14)) is effective.

If we take the relaxation functions of the form:

$$\varphi_r(t') = \frac{1}{\tau_r^{(5)}}\cdot e^{-t'/\tau_r^{(5)}}, \tag{4-52}$$

as taken already in eqs. (3–3), (3–9), (4–17), and (4–18), then the expression (4–50) reduces to:

$$q_j = -\sum_{r=1}^{p}\frac{\kappa_r}{1+\tau_r^{(5)}D}\cdot\frac{\partial\vartheta}{\partial x_j}, \qquad (j=1,\ 2,\ 3) \tag{4-53}$$

for the oscillatory motion of the system.

It is worth-while remarking that the expression (4–53) is very much resemble with eq. (4–45). And, if we take $p=1$, the expression (4–53) reduces to the expression (4–48) or (4–49).

Further, if we take $\tau_r^{(5)}D \ll 1$, then the expression (4–53) reduces to the ordinary Fourier law:

$$q_j = -\kappa\frac{\partial\vartheta}{\partial x_j}. \qquad \left(\kappa = \sum_{r=1}^{p}\kappa_r\right) \tag{4-54}$$

While, if we take $\tau_r^{(5)}D \to +\infty$, then we have the vanishing thermal conductivities in the expression (4–53), and the expression (4–53) reduces to:

$$q_j = 0. \tag{4-55}$$

This means that the thermal process taking place in the system is *adiabatic.*

Accordingly, the expression of heat flux (4–50) or (4–53) is the generalized Fourier law under the rapidly changing thermal field. The expression (4–50) or (4–53) can describe the general thermal conditions under which the real thermal processes take place. Thus, the equation of conservation of energy is expressed in a hyperbolic form and not in a parabolic form, only if we take the expression of heat flux (4–50) or (4–53) into account.

Under the consideration of eqs. (3–12), (4–19), and (4–53), the equation of conservation of energy (4–10) is written as:

$$\begin{aligned}\rho\Big[\Big\{C_0+\sum_{r=1}^{s}\frac{C_r\tau_r^{(3)}D}{1+\tau_r^{(3)}D}\Big\}\frac{d\vartheta}{dt}+\Big\{b_0\delta_{ij}+\sum_{r=1}^{q}\frac{b_{ij}^{(r)}\tau_r^{(4)}D}{1+\tau_r^{(4)}D}\Big\}\frac{d\varepsilon_{ij}}{dt}\Big]=\\ =\Big\{-p_0\cdot\delta_{ij}+\Big(k_0+\sum_{r=1}^{l}\frac{\lambda_r' D}{1+\tau_r D}-\frac{2}{3}\sum_{r=1}^{m}\frac{\mu_r' D}{1+\tau_r^{(1)}D}\Big)\varepsilon_{kk}\cdot\delta_{ij}+\\ +2\sum_{r=1}^{m}\frac{\mu_r' D}{1+\tau_r^{(1)}D}\varepsilon_{ij}-\sum_{r=1}^{n}\frac{\alpha_r' D}{1+\tau_r^{(2)}D}\vartheta\delta_{ij}\Big\}\cdot\frac{\partial\varepsilon_{ij}}{\partial t}+\sum_{r=1}^{p}\frac{\kappa_r}{1+\tau_r^{(5)}D}\cdot\Delta\vartheta.\end{aligned}\tag{4-56}$$

V. Application to Supersonic Waves

The fundamental equations of the supersonic waves under no body force, which state the conservation of momentum (3–13) and of energy (4–10), are expressed respectively, in linear forms,

$$\rho_0\frac{\partial^2\xi_i}{\partial t^2}=\frac{\partial A_{ij}}{\partial x_j},\tag{5-1}$$

$$\rho_0\frac{\partial U}{\partial t}=A_{ij}\frac{\partial\varepsilon_{ij}}{\partial t}+\kappa\Delta\vartheta,\tag{5-2}$$

where the expression (4–39) was used for the heat flux vector. The change of density is related to the strain through the equation of continuity:

$$\frac{\partial\rho}{\partial t}+\rho_0\frac{\partial u_k}{\partial x_k}=0,\tag{5-3}$$

with $u_i=\partial\xi_i/\partial t$ $(i=1, 2, 3)$.

Putting the expressions (3–12) and (4–19) for the stress and the internal energy into eqs. (5–1) and (5–2), we obtain[12)], retaining the small quantities of first order:

$$\begin{aligned}\rho_0\frac{\partial^2\xi_i}{\partial t^2}=\Big\{k_0+\sum_{r=1}^{l}\frac{\lambda_r' D}{1+\tau_r D}-\frac{2}{3}\sum_{r=1}^{m}\frac{\mu_r' D}{1+\tau_r^{(1)}D}\Big\}\frac{\partial\varepsilon_{kk}}{\partial x_i}+\\ +2\sum_{r=1}^{m}\frac{\mu_r' D}{1+\tau_r^{(1)}D}\cdot\frac{\partial\varepsilon_{ij}}{\partial x_j}-\sum_{r=1}^{n}\frac{\alpha_r' D}{1+\tau_r^{(2)}D}\cdot\frac{\partial\vartheta}{\partial x_i},\end{aligned}\tag{5-4}$$

and

$$\rho_0\Big[\Big\{C_0+\sum_{r=1}^{s}\frac{C_r\tau_r^{(3)}D}{1+\tau_r^{(3)}D}\Big\}\frac{\partial\vartheta}{\partial t}+\Big\{b_0\cdot\delta_{ij}+\sum_{r=1}^{q}\frac{b_{ij}^{(r)}\tau_r^{(4)}D}{1+\tau_r^{(4)}D}\Big\}\frac{\partial\varepsilon_{ij}}{\partial t}\Big]=-p_0\frac{\partial\varepsilon_{kk}}{\partial t}+\kappa\Delta\vartheta.\tag{5-5}$$

If we take the wave of volume dilatation, we obtain, from eq. (5–4), the following equation of motion:

$$\rho_0 \frac{\partial^2}{\partial t^2} \varepsilon_{kk} = \Big(k_0 + \sum_{r=1}^{l} \frac{\lambda'_r D}{1+\tau_r D} + \frac{4}{3} \sum_{r=1}^{m} \frac{\mu'_r D}{1+\tau_r^{(1)} D}\Big) \Delta \varepsilon_{kk} - \sum_{r=1}^{n} \frac{\alpha'_r D}{1+\tau_r^{(2)} D} \Delta \vartheta. \quad (5\text{-}6)$$

Owing to the scalar property of the thermal expansion, which appears merely in the diagonal parts of stress tensor, the explicit temperature term plays rather an important rôle in the equation of motion of the longitudinal wave. While, in the shear wave, the temperature term makes no contribution to the equation of motion.

As a special case, we shall take the plane wave, progressing into the $+x_1$-direction with circular frequency ω:

$$\left.\begin{aligned} & x_1 = x, \qquad \frac{\partial}{\partial x_2} = \frac{\partial}{\partial x_3} = 0, \\ & \xi_1 = \mathscr{R}_e\, \xi \cdot \exp\,[i\omega t - \beta x], \qquad \xi_2 = \xi_3 = 0, \\ & \delta T = \vartheta = \mathscr{R}_e\, \vartheta \cdot \exp\,[i\omega t - \beta x], \\ & \varepsilon_{kk} = \varepsilon_{11} = -\beta \xi \cdot \exp\,[i\omega t - \beta x], \qquad \mathscr{I}_m(\beta) > 0 \\ & \varepsilon_{ij} = 0. \qquad (\text{except } i = j = 1) \end{aligned}\right\} \quad (5\text{-}7)$$

The equations of motion (5–4), and of conservation of energy (5–5), are:

$$\rho_0 \frac{\partial^2}{\partial t^2} \varepsilon_{11} = \Big(k_0 + \sum_{r=1}^{l} \frac{\lambda'_r D}{1+\tau_r D} + \frac{4}{3} \sum_{r=1}^{m} \frac{\mu'_r D}{1+\tau_r^{(1)} D}\Big) \Delta \varepsilon_{11} - \sum_{r=1}^{n} \frac{\alpha'_r D}{1+\tau_r^{(2)} D} \Delta \vartheta, \quad (5\text{-}8)$$

and

$$\Big(C_0 + \sum_{r=1}^{s} \frac{C_{ij}^{(r)} \tau_r^{(3)} D}{1+\tau_r^{(3)} D}\Big) \frac{\partial \vartheta}{\partial t} + \Big(b_0 + \sum_{r=1}^{q} \frac{b_{11}^{(r)} \tau_r^{(4)} D}{1+\tau_r^{(4)} D}\Big) \frac{\partial \varepsilon_{11}}{\partial t} = - \frac{p_0}{\rho_0} \cdot \frac{\partial \varepsilon_{11}}{\partial t} + \frac{\kappa}{\rho_0} \Delta \vartheta. \quad (5\text{-}9)$$

Putting eq. (5–7) into eqs. (5–8) and (5–9), and neglecting the terms of higher order, we obtain:

$$\Big\{\rho_0 \omega^2 + \Big(k_0 + \sum_{r=1}^{l} \frac{i\omega \lambda'_r}{1+i\omega\tau_r} + \frac{4}{3} \sum_{r=1}^{m} \frac{i\omega \mu'_r}{1+i\omega\tau_r^{(1)}}\Big)\beta^2\Big\}\xi + \sum_{r=1}^{n} \frac{i\omega \alpha'_r}{1+i\omega\tau_r^{(2)}} \beta\vartheta = 0, \quad (5\text{-}10)$$

and

$$-i\omega\beta\Big(\frac{p_0}{\rho_0} + b_0 + \sum_{r=1}^{q} \frac{i\omega b_{11}^{(r)} \tau_r^{(4)}}{1+i\omega\tau_r^{(4)}}\Big)\xi + \Big\{i\omega\Big(C_0 + \sum_{r=1}^{s} \frac{i\omega C_r \tau_r^{(3)}}{1+i\omega\tau_r^{(3)}}\Big) - \frac{\kappa}{\rho_0}\beta^2\Big\}\vartheta = 0. \quad (5\text{-}11)$$

Considering that the simultaneous equations (5–10) and (5–11) have non-trivial solution, we see that β is to satisfy the following equation:

$$\begin{vmatrix} \rho_0 \omega^2 + A\beta^2, & \displaystyle\sum_{r=1}^{n} \frac{i\omega \alpha'_r}{1+i\omega\tau_r^{(2)}} \beta \\ -i\omega\beta B, & i\omega\Big(C_0 + \displaystyle\sum_{r=1}^{s} \frac{i\omega C_r \tau_r^{(3)}}{1+i\omega\tau_r^{(3)}}\Big) - \frac{\kappa}{\rho_0}\beta^2 \end{vmatrix} = 0, \quad (5\text{-}12)$$

i.e.

$$-\frac{\kappa}{\rho_0}A\beta^4+\Big[\Big\{i\omega C_0-\sum_{r=1}^{s}\frac{\omega^2 C_r\tau_r^{(3)}}{1+i\omega\tau_r^{(3)}}\Big\}A-\kappa\omega^2-\sum_{r=1}^{n}\frac{\omega^2\alpha_r'}{1+i\omega\tau_r^{(2)}}B\Big]\beta^2+$$
$$+i\omega^3\rho_0\Big(C_0+\sum_{r=1}^{s}\frac{i\omega C_r\tau_r^{(3)}}{1+i\omega\tau_r^{(3)}}\Big)=0, \tag{5-13}$$

with

$$A=k_0+\sum_{r=1}^{l}\frac{i\omega\lambda_r'}{1+i\omega\tau_r}+\frac{4}{3}\sum_{r=1}^{m}\frac{i\omega\mu_r'}{1+i\omega\tau_r^{(1)}},$$

and

$$B=\frac{p_0}{\rho_0}+b_0+\sum_{r=1}^{q}\frac{i\omega b_{11}^{(r)}\tau_r^{(4)}}{1+i\omega\tau_r^{(4)}}.$$

In this equation, if we take $\kappa\rightarrow 0$, which approximately holds for non-metalic liquids such as high polymer solutions, then we obtain:

$$\beta^2=-\frac{\omega^2}{v_0^2}\div\Big[1+\sum_{r=1}^{l}\frac{i\omega\lambda_r'}{k_0(1+i\omega\tau_r)}+\frac{4}{3}\sum_{r=1}^{m}\frac{i\omega\mu_r'}{k_0(1+i\omega\tau_r^{(1)})}+\sum_{r=1}^{n}\frac{i\omega\alpha_r' b_0}{k_0C_0(1+i\omega\tau_r^{(2)})}\times$$
$$\times\Big(1+\frac{p_0}{\rho_0 b_0}+\sum_{r=1}^{q}\frac{i\omega b_{11}^{(r)}\tau_r^{(4)}}{b_0(1+i\omega\tau_r^{(4)})}\Big)\cdot\Big(1+\sum_{r=1}^{s}\frac{i\omega C_r\tau_r^{(3)}}{C_0(1+i\omega\tau_r^{(3)})}\Big)^{-1}\Big], \tag{5-14}$$

with $v_0=\sqrt{k_0/\rho_0}$.

Accordingly, the wave-velocity v and amplitude absorption coefficient a per unit length are given respectively:

$$v=\frac{\omega}{\mathscr{I}_m(\beta)}, \tag{5-15}$$

and

$$a=\mathscr{R}_e(\beta). \tag{5-16}$$

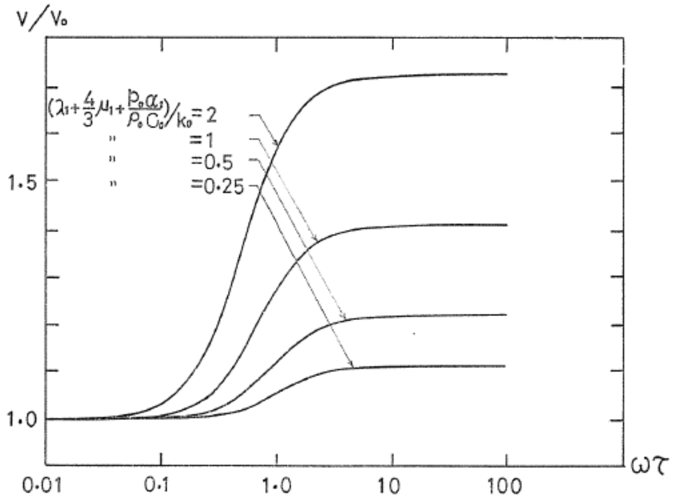

FIG. 5-1. Sound Velocity versus Frequency.

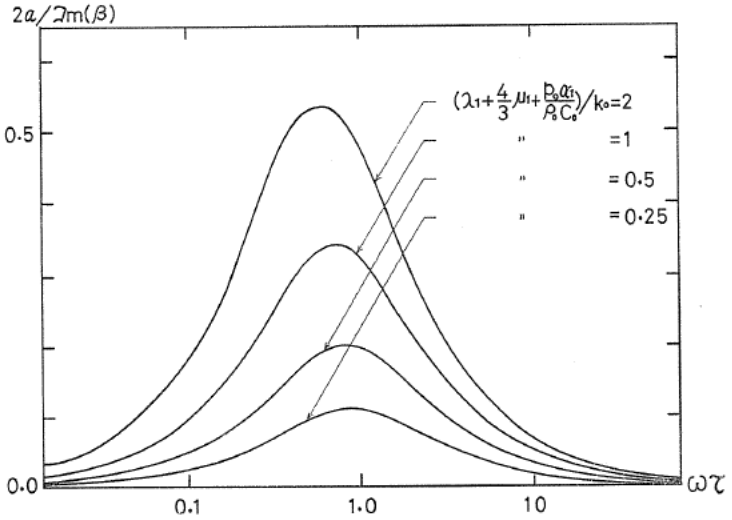

FIG. 5-2. Absorption Coefficient versus Frequency.

In the special case of $\tau=\tau_1=\tau_1^{(1)}=\tau_1^{(2)}$, $b_{11}^{(r)}=C_r=0$, and $b_0/C_0 \ll 1$, the plot of v/v_0 versus ω, and the intensity absorption per unit wave-length $2\,a/\mathcal{T}_m(\beta)$ are shown in Figs. 5-1 and 5-2 for four values of rheological constants. The curve comes essentially from the equations of motion (5-8), and it is interesting to mention that the curves are very similar to those obtained by Kneser on the base of quite different point of view, where Kneser used the so-called *dynamic specific heat*.

In general, the partial elastic moduli, which represent the rheological character of the media, are smaller than the *static modulus* k_0. Accordingly, we can put:

$$\frac{\lambda_r}{k_0} \ll 1, \qquad \frac{\mu_r}{k_0} \ll 1, \qquad \text{and} \qquad \frac{\alpha_r}{k_0} \ll 1. \tag{5-17}$$

In the similar manner, we shall also take:

$$\frac{C_r}{C_0} \ll 1, \qquad \text{and} \qquad \frac{b_{ij}^{(r)}}{b_0} \ll 1, \tag{5-18}$$

which are considered to hold for most kinds of liquids.

By expanding expression (5-13) in powers of λ_r/k_0 etc., and retaining the terms of first order in λ_r/k_0 etc., we obtain:

$$\begin{aligned}\beta = \frac{i\omega}{v_0}\Big\{1 &- \frac{1}{2\,k_0}\sum_{r=1}^{l}\frac{i\omega\lambda_r'}{1+i\omega\tau_r} - \frac{2}{3\,k_0}\sum_{r=1}^{m}\frac{i\omega\mu_r'}{1+i\omega\tau_r^{(1)}} - \frac{1}{2\,k_0 C_0}\sum_{r=1}^{n}\frac{i\omega\alpha_r' b_0}{1+i\omega\tau_r^{(2)}} - \\ &- \frac{1}{2}\,\frac{p_0}{\rho_0 b_0 k_0 C_0}\sum_{r=1}^{n}\frac{i\omega\alpha_r'}{1+i\omega\tau_r^{(2)}} - \frac{1}{2\,k_0 C_0}\sum_{r=1}^{n}\frac{i\omega\alpha_r' b_0}{1+i\omega\tau_r^{(2)}}\cdot\Big(\frac{1}{b_0}\sum_{r=1}^{q}\frac{i\omega b_{11}^{(r)}\tau_r^{(4)}}{1+i\omega\tau_r^{(4)}} - \\ &- \frac{1}{C_0}\sum_{r=1}^{s}\frac{i\omega C_r\tau_r^{(3)}}{1+i\omega\tau_r^{(3)}}\Big)\Big\},\end{aligned} \tag{5-19}$$

where $v_0 = \sqrt{k_0/\rho_0}$ is the velocity of longitudinal wave at low frequency.

From eqs. (5–14), (5–15), (5–16), and (5–19), we have

$$\begin{aligned} a = \frac{\omega^2}{v_0}\cdot\Bigg\{ & \frac{1}{2}\sum_{r=1}^{l}\frac{\lambda_r'}{k_0}\cdot\frac{1}{1+\omega^2\tau_r^2} + \frac{2}{3}\sum_{r=1}^{m}\frac{\mu_r'}{k_0}\cdot\frac{1}{1+\omega^2\tau_r^{(1)2}} + \frac{1}{2}\sum_{r=1}^{n}\frac{p_0}{\rho_0}\cdot\frac{\alpha_r'}{k_0 C_0}\cdot\frac{1}{1+\omega^2\tau_r^{(2)2}} + \\ & + \frac{1}{2}\sum_{r=1}^{n}\frac{\alpha_r' b_0}{k_0 C_0}\cdot\frac{1}{1+\omega^2\tau_r^{(2)2}} + \frac{1}{2}\sum_{r=1}^{n}\frac{\alpha_r'}{k_0}\cdot\frac{1}{1+\omega^2\tau_r^{(2)2}}\cdot\sum_{r=1}^{q}\frac{b_{11}^{(r)}}{C_0}\cdot\frac{\omega^2\tau_r^{(4)2}}{1+\omega^2\tau_r^{(4)2}} - \\ & - \frac{1}{2}\sum_{r=1}^{n}\frac{\alpha_r' b_0}{k_0 C_0}\cdot\frac{1}{1+\omega^2\tau_r^{(2)2}}\cdot\sum_{r=1}^{s}\frac{C_r}{C_0}\cdot\frac{\omega^2\tau_r^{(3)2}}{1+\omega^2\tau_r^{(3)2}}\Bigg\}, \end{aligned} \tag{5-20}$$

and

$$\begin{aligned} v = v_0\cdot\Bigg\{ & 1 + \frac{1}{2}\sum_{r=1}^{l}\frac{\lambda_r'}{k_0}\cdot\frac{\omega^2\tau_r}{1+\omega^2\tau_r^2} + \frac{2}{3}\sum_{r=1}^{m}\frac{\mu_r'}{k_0}\cdot\frac{\omega^2\tau_r^{(1)}}{1+\omega^2\tau_r^{(1)2}} + \frac{1}{2}\sum_{r=1}^{n}\frac{p_0}{\rho_0}\cdot\frac{\alpha_r'}{k_0 C_0}\times \\ & \times\frac{\omega^2\tau_r^{(2)}}{1+\omega^2\tau_r^{(2)2}} + \frac{1}{2}\sum_{r=1}^{n}\frac{\alpha_r' b_0}{k_0 C_0}\cdot\frac{\omega^2\tau_r^{(2)}}{1+\omega^2\tau_r^{(2)2}} - \frac{1}{2}\sum_{r=1}^{n}\frac{\alpha_r'}{k_0}\cdot\frac{\omega}{1+\omega^2\tau_r^{(2)2}}\cdot\sum_{r=1}^{q}\frac{b_{11}^{(r)}}{C_0}\times \\ & \times\frac{\omega\tau_r^{(4)}}{1+\omega^2\tau_r^{(4)2}} + \frac{1}{2}\sum_{r=1}^{n}\frac{\alpha_r' b_0}{k_0 C_0}\cdot\frac{\omega}{1+\omega^2\tau_r^{(2)2}}\cdot\sum_{r=1}^{s}\frac{C_r}{C_0}\cdot\frac{\omega\tau_r^{(3)}}{1+\omega^2\tau_r^{(3)2}}\Bigg\}. \end{aligned} \tag{5-21}$$

The first and second terms of (5–21) are due to the volume and shearing viscosities respectively, and correspond to the terms obtained by Frenkel[9][10], Oshida[7][8], and Sips[11]. The third and fourth terms are mainly due to the work done by thermal expansion by Takizawa[12][13]. The sixth is the one from the relaxation of specific heat, corresponding to the term due to Kneser[18][19][20]. The temperature dependence of wave-dispersion and of the wave-absorption in various kinds of liquids may be also explained by the variation of rheological and thermodynamical constants in the present theory.

At the sufficiently low frequency, expression (5–20) reduces to:

$$a = \frac{2\,\omega^2}{3\,v_0^3\rho_0}\left\{\mu_1' + \frac{3}{4}\lambda_1' + \frac{3}{4}\,\frac{p_0}{\rho_0}\cdot\frac{\alpha_1'}{C_0} + \frac{3}{4}\,\frac{\alpha_1' b_0}{C_0} + \mu_2' + \frac{3}{4}\lambda_2' + \cdots\right\}. \tag{5-22}$$

The quantity μ_1' corresponds to the usual coefficient of viscosity, and the first term gives classical absorption. While λ_1' is the volume viscosity, which vanishes in most kinds of gases under the wave field of very low frequency.

The relaxation time for ordinary viscosity of liquids is very small, being approximately $\tau_1^{(1)} \approx 10^{-11}$ sec. Accordingly, at the frequency of the supersonics region of $\omega = 10^5 \sim 10^8$ cycles per second, we have $\omega\tau_1^{(1)} \ll 1$.

If we take $l = m = 2$ and $n = 1$ in eq. (5–21), we obtain:

$$\frac{a}{\omega^2} = \frac{1}{2\,v_0^3\rho_0}\left\{\lambda_1' + \frac{4}{3}\mu_1' + \frac{\lambda_2'}{1+\omega^2\tau_2^2} + \frac{3}{4}\cdot\frac{\mu_2'}{1+\omega^2\tau_2^{(1)2}} + \frac{p_0}{\rho_0}\cdot\frac{\alpha_1\tau_1^{(2)}}{C_0}\cdot\frac{1}{1+\omega^2\tau_1^{(2)2}}\right\}, \tag{5-23}$$

which are considered to hold for almost all kinds of liquids.

In many kinds of liquids at ordinary temperatures and pressures, however, the quantity a/ω^2 does not change appreciably with increasing frequency up to the supersonic region: $\omega = 10^5 \sim 10^8$ cycles per second. This fact shows that the numerical values of $\omega\tau_2$, $\omega\tau_2^{(1)}$, and $\omega\tau_2^{(2)}$ etc. are comparatively small in most liquids.

VI. Hypersonic and Transverse waves

Elastic waves, the so-called *hypersonics*[53] or *ondes thermiques*[54)55)56)], which have the frequency of $10^{10} \sim 10^{13}$ cycles per second, constitute the main part of thermal motion in solids. It is also believed for the elastic vibration to exist in liquids, whose frequency is of the order 10^{10} cycles per second. Considering the quasi-crystalline structure of liquids, we may consider that the Debye theory[57] of specific heat can also approximately hold in liquids. When the wave-length becomes shorter and shorter and reaches the value comparative with the molecular spacing in liquids, we regard such waves as *waves of thermal motion* or *ondes thermiques*. The critical frequency, under which the *ondes thermiques* exist is about 5×10^{13} cycles per second in usual liquids, and in crystals it can reach 10^{14} cycles per second. Accordingly, the treatment developed here, considering liquids as continua, can be a good approximation even at the high frequency of hypersonics. And, the Debye theory[57] can be considered to hold approximately in liquids as well as in solids. Thus, the waves of thermal motion can be decomposed into three waves, one longitudinal and two transverse.

At sufficiently high frequencies, we may expect that $\omega\tau_r^{(k)} \gg 1$ $(k=0, 1, 2, 3, 4)$ is maintained. In this case, from eqs. (5-13) and (5-23), we have:

$$\beta^2 = -\frac{\omega^2}{v_0^2} \div \left[1+\sum_{r=1}^{l}\frac{\lambda_r}{k_0}+\frac{4}{3}\sum_{r=1}^{m}\frac{\mu_r}{k_0}+\left(1+\frac{p_0}{\rho_0 b_0}\right)\cdot\sum_{r=1}^{n}\frac{\alpha_r b_0}{k_0 C_0}+\cdots\right], \qquad (6\text{-}1)$$

and

$$v = \frac{\omega}{\mathscr{I}_m(\beta)} = v_0\cdot\left[1+\frac{1}{2k_0}\sum_{r=1}^{l}\lambda_r+\frac{2}{3k_0}\sum_{r=1}^{m}\mu_r+\right.$$

$$\left.+\frac{p_0}{2k_0\rho_0 C_0}\sum_{r=1}^{n}\alpha_r+\frac{b_0}{2k_0 C_0}\sum_{r=1}^{n}\alpha_r+\cdots\right]. \qquad (6\text{-}2)$$

Because the value of β is almost purely imaginary for extremely high frequency, the wave of such a high frequency hardly suffers from absorption:

$$a \fallingdotseq 0. \qquad (6\text{-}3)$$

The expression (6-2) also shows that the hypersonics propagate with higher velocity than the velocity v_0 of the ordinary sound wave.

In the frequency region of hypersonics, the transverse wave is also very possible to exist. Because of the fugitive nature of shearing rigidities of Maxwellian relaxational process, as we know from eq. (5-4), we see that the equations of motion for the transverse wave read as follows:

$$\rho_0\frac{\partial^2}{\partial t^2}\tilde{\omega}_{ij} = \sum_{r=1}^{m}\frac{\mu_r\tau_r^{(1)}D}{1+\tau_r^{(1)}D}\Delta\tilde{\omega}_{ij}, \qquad (6\text{-}4)$$

with

$$\tilde{\omega}_{ij} = \frac{1}{2}\left(\frac{\partial\xi_j}{\partial x_i}-\frac{\partial\xi_i}{\partial x_j}\right). \qquad (i,\ j=1,\ 2,\ 3) \qquad (6\text{-}5)$$

Taking the progressing wave into the $+x_1$-direction,

$$\tilde{\omega}_{ij} = \mathscr{R}_e\,\tilde{\omega}_{ij}\cdot\exp\left[i\omega t-\beta x_1\right], \qquad \mathscr{I}_m(\beta)>0 \qquad (6\text{-}6)$$

we have the equation to determine β:

$$-\rho_0\,\omega^2 = \beta^2 \sum_{r=1}^{m} \frac{i\omega\tau_r^{(1)}\mu_r}{1+i\omega\tau_r^{(1)}}. \tag{6-7}$$

Accordingly, the velocity v' and amplitude absorption coefficient a' per unit length of the transverse wave for such high frequency $\omega\tau_r^{(1)} \gg 1$, are given respectively as follows:

$$v' = \frac{\omega}{\mathscr{I}m(\beta)} = \sqrt{\frac{\sum_{r=1}^{m}\mu_r}{\rho_0}}, \tag{6-8}$$

and

$$a' \fallingdotseq 0. \tag{6-9}$$

In this case, the changes in density and in temperature caused in liquids are related to the strain by eqs. (5-3) and (4-26), respectively. Thus, it is considered that the term in eq. (4-14) and especially the terms involving $d\varepsilon_{ij}$ $(i \neq j)$ in eq. (4-14), which appear in the expression of internal energy (4-19) and (4-34), play rather an important rôle at the thermo-mechanical process of extremely high frequency.

Of course, in the equations of state (3-12), we may take the stress tensor corresponding to the thermal expansion, which has non-vanishing off-diagonal elements containing temperature deviation. Here, however, we have taken thermal stress having simply diagonal elements in the stress tensor, so that the explicit temperature term should be vanished in the equations of motion of transverse wave. If the thermal deviation or fluctuation from the state of *thermostatical equilibrium* becomes large enough, so that the tensor quantity corresponding to the averaged momenta of constituent molecules should be taken into account, then the tensor of thermal stress may have some fugitive off-diagonal elements in the expression of stress tensor (3-12).

In crystals, there exist three velocities of component waves, corresponding to one longitudinal and two transverse waves, and three Doppler-doublets[58)59)] appear in the experiment of monochromatic light-scattering[60)61)62)]. Then, following to the Debye theory[57)], the thermal energy in solids is distributed in these three waves. If there were no transverse waves in liquids, the specific heat of liquids should become far smaller than that of corresponding solid bodies[63)64)]. In reality, no such a case occurs. Accordingly, if the Debye theory holds approximately in liquids, the transverse waves of extremely high frequency *do exist* in most liquids. In such a case, the off-diagonal parts in the thermal stress might be comparatively effective.

VII. Thermo-elastic Waves in Liquids, Specific Heat and Thermal Conductivity of Rheological Bodies

As was already stated in Chapter VI, many experimental evidences concerning liquids so far obtained have manifested the fact that liquids are more similar to solid crystalline bodies than to compressed gases at ordinary temperatures and moderate pressures. The *thermostatical* and *thermodynamical* characters of a liquid, for example, resemble themselves especially to those of its corresponding solid phase. At temperatures lying near the crystallization point, a liquid must be more similar to a solid crystalline body with respect to its structure, character of thermal motion, and many kinds of mechanical properties. The application of the method of X-ray structure analysis to liquid bodies has elucidated the vivid image of liquid structure that the liquids consist of a very large number of randomly orientated crystals of submicroscopic size, smaller than 10^2 Å in diameter. And this can be interpreted also by a very close similarity in the X-ray diagrams between a liquid phase and its corresponding solid phase.

The hyperfine structures observed in the spectrum of the scattered monochromatic light have directly proved the existence of the thermal motion or *thermoelastic waves* in liquids. According to the theory of specific heat proposed by Debye 57), the thermal energy of solids is distributed among three thermoelastic waves in liquids, one longitudinal and two transverse. The fact that the difference of the specific heats between a liquid and its corresponding solid is rather small, leads us to apply the Debye theory 57) of specific heat to liquids, which takes into account the thermal vibration of the constituting atoms or molecules of solid (crystalline or amorphous) structure.

In the case of liquids so similar to solids in their structure, it is quite suggestible to estimate the internal energy, which is supposed to be consisted of the thermal waves in liquids. Thus we can calculate the specific heat of liquids according to the method analogous to that of Debye even in such phases as of high viscosity and of rigidity of fugitive nature. At the starting point of calculating the specific heat, Debye 1) took the expression of perfectly elastic body in solid phase. On the other hand, Lucas 55) started from the expression of Stokes, applicable to viscous fluids. Brillouin 64) considered that the compressional wave still remains in liquids but the two transverse waves are degenerated into the rotation of molecules, also having its kinetic energy. Oomori 63) took into account the equation of state for plasto-elastic body presented by Frenkel-Obratzov 9) in his papers of thermoelastic waves in liquids.

In the present treatment of thermodynamical characters of liquids shall be conveniently applied a generalized equation of state, *i.e.* stress-strain-temperature relation, which Takizawa 12) 13) proposed to include Frenkel-Obratzov's 9) and Oshida's 7) 8) treatments as special cases. Moreover, the expression used by Takizawa 12) also includes the terms of dynamic specific heat of Kneser 18) 19) 20) 36) as a special case. Starting from these macroscopic equations of state, one can calculate at once the velocity of the wave-propagation and the absorption coefficient in the medium. The results obtained have a favourite characters 65) both of Frenkel's and of Kneser's theories.

Specific heat of liquids, in which the thermal waves exist, can be calculated merely by counting the number of phonons in liquids. In the liquid hydrogen and liquid hellium, however, the quantum effects predominate. In this chapter we shall be concerned merely with the liquids in which the classical treatment, as Debye mentioned, can be still available. The quantization process is maintained by taking the classical quantum assembly of thermal waves, *i.e.* phonons, into account. In such a treatment, the method applied can describe the thermal and mechanical behaviours of almost all kinds of liquids at moderate pressures and temperatures.

The generalized rheological equations for an isotropic amorphous body, which describe the mechanical behaviour of macroscopically continuous bodies, shall be adopted in the present paper. These equations are already mentioned in the preceding paragraphs as the expression of components of stress tensor (3–11) and that of the increment of internal energy in the macroscopic sense (4–33). In these equations of stress and of internal energy the thermodynamical characters of the media, in which the mechanical and thermal processes actually take place, are all assumed to be subjected to the Maxwellian relaxational process, *i.e.* the rheological constants and thermodynamical coefficients are all considered as operators of Maxwellian type accompanied by relaxation times (3–12) and (4–34). It should be mentioned here that these equations can be also conveniently applied to the solid and gaseous bodies as well as liquids, *mutatis mutandis.* In other words, taking suitable numerical values and their dependence on temperature in the rheological and thermodynamical coefficients in the above equations, we have the expressions of the states of the gaseous, liquid, and solid bodies, respectively.

At first we consider the classical quantum-mechanical assembly of the elementary waves, which can be permitted to exist by the differential equations above cited. Then we shall treat the specific heat according to the theories of Debye, Brillouin, Lucas, and Oomori. The treatment of specific heat of liquids in the manner analogous to that of the corresponding solids, can be considered rigorous, as we take into account the quasi-crystalline structure of liquids, their thermal and mechanical properties and so forth.

The linear equations of motion and of conservation of energy[12][13] in the macroscopic sense, are expressed by (5–1) and (5–2), respectively:

$$\rho_0 \frac{\partial^2 \xi_i}{\partial t^2} = \frac{\partial A_{ij}}{\partial x_j}, \tag{7-1}$$

and

$$\rho_0 \frac{\partial U}{\partial t} = -p_0 \frac{\partial \varepsilon_{kk}}{\partial t} + \kappa \Delta \vartheta, \tag{7-2}$$

where

$$\varepsilon_{kk} = \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}.$$

Inserting the expressions of stress (3–12) with $n=0$, and of internal energy (4–34) into eqs. (7–1) and (7–2), we obtain the equations which govern the dynamical characters of liquids.

Taking sinusoidal motion of plane wave, progressing into $+x_1$-direction, we put:

$$\xi_1 = \mathscr{R}_e\, \xi \cdot e^{i\omega t - \beta_1 x}, \qquad \mathscr{I}_m(\beta_1) > 0, \qquad \mathscr{R}_e(\beta_1) > 0, \tag{7-3}$$

$$x_1 = x, \qquad \frac{\partial}{\partial x_2} = \frac{\partial}{\partial x_3} = 0, \qquad \xi_2 = \xi_3 = 0, \qquad \text{and} \qquad \varepsilon_{kk} = \varepsilon_{11}. \tag{7-4}$$

On the other hand, as for the transverse wave we put in a similar manner:

$$\left.\begin{aligned} &\tilde{\omega}_{ij} \equiv \frac{1}{2}\left(\frac{\partial \xi_j}{\partial x_i} - \frac{\partial \xi_i}{\partial x_j}\right) = \mathscr{R}_e\, \tilde{\omega}_{ij} e^{i\omega t - \beta_2 x}, \qquad (i,\ j = 1,\ 2,\ 3) \\ &\mathscr{I}_m(\beta_2) > 0, \qquad \mathscr{R}_e(\beta_2) > 0. \end{aligned}\right\} \tag{7-5}$$

Taking $l=m=1$, and no thermal expansion in (3-12), and making use of equation of motion (7-1), we obtain the velocities v_l and v_t of longitudinal and transverse waves, and the amplitude absorption coefficient per unit length a_l and a_t of longitudinal and transverse waves, respectively:

$$v_l = \frac{\omega}{\mathscr{I}_m(\beta_1)} = v_0 \cdot \left\{ 1 + \frac{1}{2} \cdot \frac{\lambda_1}{k_0} \cdot \frac{\omega^2 \tau_1^2}{1+\omega^2 \tau_1^2} + \frac{2}{3} \cdot \frac{\mu_1}{k_0} \cdot \frac{\omega^2 \tau_1^{(1)2}}{1+\omega^2 \tau_1^{(1)2}} \right\}, \tag{7-6}$$

$$a_l = \mathscr{R}_e(\beta_1) = \frac{\omega^2}{v_0} \cdot \left\{ \frac{1}{2} \cdot \frac{\lambda_1}{k_0} \cdot \frac{\tau_1}{1+\omega^2 \tau_1^2} + \frac{2}{3} \cdot \frac{\mu_1}{k_0} \cdot \frac{\tau_1^{(1)}}{1+\omega^2 \tau_1^{(1)2}} \right\}, \tag{7-7}$$

$$v_t = \frac{\omega}{\mathscr{I}_m(\beta_2)} = \sqrt{\frac{2\,\mu_1 \tau_1^{(1)} \omega}{\rho_0}} \cdot [\sqrt{1+\omega^2 \tau_1^{(1)2}} + \omega \tau_1^{(1)}]^{-1/2}, \tag{7-8}$$

and

$$a_t = \mathscr{R}_e(\beta_2) = \sqrt{\frac{\rho_0 \omega}{2\,\mu \tau_1^{(1)}}} \cdot [\sqrt{1+\omega^2 \tau_1^{(1)2}} - \omega \tau_1^{(1)}]^{1/2}, \tag{7-9}$$

with
$$v_0 = \sqrt{k_0/\rho_0}\,.$$

The expressions (7-6) ~ (7-9) are derived under the following assumptions:

(I) The thermal conduction corresponding to the external degree of freedom of the constituent molecules is of negligible order.

(II) Among the rheological and thermodynamical coefficients the following relations hold:

$$\frac{\lambda_1}{k_0} \ll 1 \qquad \text{and} \qquad \frac{\mu_1}{k_0} \ll 1.$$

Thus we can neglect small quantities higher than the first order of these terms. In usual liquids, the first assumption was assured by Takizawa[66] with the theoretical calculation even in the extremely high frequency such as over 10^{12} Hz. The second assumption is considered to be usually valid in almost all kinds of liquids.

Combining the theories of specific heat due to Debye, Lucas, and Brillouin, and applying the fundamental equations of state (3-12), we can further proceed in computing the specific heat of liquids, quantizing the longitudinal and transverse waves in the isotropic body. We shall confine ourselves to the consideration of specific heat and viscosity of liquids.

The internal energy E of liquids per unit volume is written by:

$$E = E_l + E_t, \tag{7-10}$$

$$E_l = 4\pi \int_0^{\nu_l^*} \frac{\nu^2}{W_l v_l^2} g(\nu)\,d\nu, \tag{7-11}$$

and

$$E_t = 8\pi \int_0^{\nu_t^*} \frac{\nu^2}{W_t v_t^2} g(\nu)\,d\nu, \tag{7-12}$$

where E_l and E_t are the thermal energies of longitudinal and transverse waves, respectively. v represents phase velocity and W group velocity of the waves.

The suffixes l and t distinguish the quantities corresponding to the longitudinal and transverse waves, respectively. The weight function $g(\nu)$ for the frequency ν comes from Planck's law. ν^* is the cut-off frequency, which originates from the finite number of degrees of freedom in the system considered, and is written by:

$$\left.\begin{aligned} \nu_l^* &= v_l \cdot \left(\frac{3N}{4\pi M} \right)^{1/3}, \\ \text{and} \qquad \nu_t^* &= v_t \cdot \left(\frac{3N}{4\pi M} \right)^{1/3}, \end{aligned}\right\} \tag{7-13}$$

where N is the Loschmidt number, M molecular volume of the liquid. The expressions (7-13) satisfy the following condition for the total degrees of freedom of the molecules, *i.e.* for the total number of the stationary waves:

$$\frac{3N}{M} = \int_0^{\nu_l^*} \frac{4\pi\nu^2}{W_l v_l^2} d\nu + \int_0^{\nu_t^*} \frac{8\pi\nu^2}{W_t v_t^2} d\nu. \tag{7-14}$$

The cut-off frequencies ν_l^* and ν_t^* are determined by use of eqs. (7-13), (7-6), and (7-8), and satisfy the following equations:

$$\frac{\nu_l^*}{v_0 \Lambda} = 1 + \frac{1}{2} \cdot \frac{\lambda_1}{k_0} \cdot \frac{(p\nu_l^*)^2}{1+(p\nu_l^*)^2} + \frac{2}{3} \cdot \frac{\mu_1}{k_0} \cdot \frac{(q\nu_l^*)^2}{1+(q\nu_l^*)^2},$$

and

$$\frac{\nu_t^*}{\Lambda} = \sqrt{\frac{2\mu_1 q\nu_t^*}{\rho}} \cdot [\sqrt{1+(q\nu_t^*)^2} + q\nu_t^*]^{-1/2},$$

i.e.

$$\nu_l^* \fallingdotseq v_0 \Lambda \left\{ 1 + \frac{1}{2} \cdot \frac{\lambda_1}{k_0} \cdot \frac{(pv_0\Lambda)^2}{1+(pv_0\Lambda)^2} + \frac{2}{3} \cdot \frac{\mu_1}{k_0} \cdot \frac{(qv_0\Lambda)^2}{1+(qv_0\Lambda)^2} \right\}, \tag{7-15}$$

$$\nu_t^* = \frac{2\mu_1 q}{\rho} \cdot \Lambda^2 \cdot \left[1 + \frac{4\mu_1 q^2}{\rho} \Lambda^2 \right]^{-1/2}, \tag{7-16}$$

with $p = 2\pi\tau_1$, $q = 2\pi\tau_1^{(1)}$, and $\Lambda = (3N/4\pi M)^{1/3}$.

Thus the limiting frequencies ν_l^* and ν_t^* are determined as functions of τ_1 and $\tau_1^{(1)}$. Accordingly we can also find the temperature-dependence of these frequencies, if we find out the temperature-dependence of τ_1 and $\tau_1^{(1)}$ (cf. eq. (7-25)).

In eqs. (7-11) and (7-12), the group velocity W of waves is defined by:

$$\frac{1}{W} = \frac{d\left(\frac{\nu}{v}\right)}{d\nu} = \frac{d\left(\frac{\omega}{v}\right)}{d\omega}. \qquad (\omega = 2\pi\nu) \tag{7-17}$$

The weight function $g(\nu)$ is expressed as follows:

$$g(\nu) = \frac{h\nu}{\exp\left[\frac{h\nu}{kT}\right] - 1} + \frac{h\nu}{2}, \tag{7-18}$$

where h is the Planck constant, and k the Boltzmann constant. At elevated temperatures we can put $g(\nu) \fallingdotseq kT$.

The expression (7–11) becomes to:

$$E_l = \frac{4\,\pi kT(\nu_l^*)^3}{3\,v_0^3}\left\{1 - \frac{3}{2}\cdot\frac{\lambda_1}{k_0}\cdot\frac{(p\nu_l^*)^2}{1+(p\nu_l^*)^2} - 2\,\frac{\mu_1}{k_0}\cdot\frac{(q\nu_l^*)^2}{1+(q\nu_l^*)^2}\right\}. \tag{7-19}$$

with

and

$$\left.\begin{array}{ll} p = 2\,\pi\tau_1, & q = 2\,\pi\tau_1^{(1)} \\ v_0 = \sqrt{k_0/\rho_0}\,. & \end{array}\right\} \tag{7-20}$$

The equation (7–12) is written by:

$$E_t = \frac{\pi kT}{2}\left(\frac{\mu_1\tau_1^{(1)}\pi}{\rho}\right)^{-3/2}\cdot\int_0^{\nu_t^*}\nu^{1/2}\cdot[\sqrt{1+(q\nu)^2}+q\nu]^{5/2}\cdot[1+(q\nu)^2]^{-1/2}d\nu =$$

$$= \frac{kT(\nu_t^*)^{3/2}}{3\,\pi^{1/2}(\tau_1^{(1)})^{3/2}v_{t\infty}^3}\cdot[\sqrt{1+(q\nu_t^*)^2}+q\nu_t^*]^{3/2}, \tag{7-21}$$

with

$$v_{t\infty} = \sqrt{\mu_1/k_0}\,.$$

The temperature- and pressure-dependence of the material constants appeared in the equation of state and in the expression of macroscopic internal energy, are not known precisely, but at temperatures near the fusion point, liquids being very closely similar to solid bodies in their structure, we can put:

$$\tau \to +\infty,$$

in eq. (7–18), and obtain:

$$E_l \fallingdotseq \frac{4\,\pi kT(\nu_l^*)^3}{3\,v_0^3}\cdot\left[1 - \frac{3}{2}\cdot\frac{\lambda_1}{k_0}\left\{1 - \frac{1}{(2\,\pi\tau_1\nu_l^*)^2}\right\} - \frac{2\,\mu_1}{k_0}\left\{1 - \frac{1}{(2\,\pi\tau_1^{(1)}\nu_l^*)^2}\right\}\right]$$

$$\to \frac{4\,\pi kT(\nu_l^*)^3}{3\,v_0^3}\cdot\left[1 - \frac{3}{2}\cdot\frac{\lambda_1}{k_0} - \frac{2\,\mu_1}{k_0}\right]$$

$$= \frac{N}{M}kT. \tag{7-22}$$

In the expression (7–22), the internal energy appears already in Debye's expression in the first term, and it is clear that eq. (7–22) approaches to the expression of internal energy of a solid body, as $\tau_1^{(1)}$ tends to infinity.

On the other hand, in liquids it is more interesting to consider the effect of transverse waves than that of the longitudinal one.

Considering the approximation:

$$\tau_1^{(1)} \to +\infty,$$

in the expression (7–21), we obtain:

$$E_t \fallingdotseq \frac{8\,\pi kT(\nu_t^*)^3}{3\,v_{t\infty}^3}\cdot\left[1 + \frac{3}{8\,(2\,\pi\tau_1^{(1)}\nu_t^*)^2}\right] \tag{7-23}$$

$$\rightarrow \frac{8\,\pi k T(\nu_t^*)^3}{3\,v_{t\infty}^3}$$
$$= \frac{2\,N}{M} kT. \tag{7-24}$$

The expression (7–23) corresponds to the expression presented by Lucas, and eq. (7–24) is just the contribution to the internal energy due to the transverse waves in a solid body, as Debye mentioned.

The temperature dependence of a relaxation time is expressed, according to Eyring[67], as follows:

$$\tau = \tau^* \cdot \exp\left[\frac{U^*}{kT}\right], \tag{7-25}$$

where U^* is the activation energy corresponding to the transition of a molecule from an equilibrium position to the other adjacent one, and is perhaps of order of magnitude of 0.1 eV. τ represents the mean life of the molecule at an equilibrium position. τ^* is the period of oscillation of the molecule at the equilibrium point.

From eqs. (7–10), (7–19), and (7–21), we obtain the molar specific heat at constant volume C_v:

$$C_v = M\frac{\partial E}{\partial T} = \frac{4\,\pi k M}{3\,v_0^2} \cdot \frac{\partial}{\partial T}\left[T(\nu_l^*)^3 \cdot \left\{ 1 - \frac{3}{2} \cdot \frac{\lambda_1}{k_0} \cdot \frac{(2\,\pi\tau_1 \nu_l^*)^2}{1 + (2\,\pi\tau_1 \nu_l^*)^2} - \frac{2\,\mu_1}{k_0} \times \right.\right.$$
$$\left.\left. \times \frac{(2\,\pi\tau_1^{(1)} \nu_l^*)^2}{1 + (2\,\pi\tau_1^{(1)} \nu_l^*)^2} \right\}\right] + \frac{kM}{3\,\pi^{1/3} v_{t\infty}^3} \cdot \frac{\partial}{\partial T}\left[\frac{T(\nu_t^*)^{3/2}}{\tau_1^{(1)3/2}} \left\{ \sqrt{1 + (2\,\pi\tau_1^{(1)} \nu_t^*)^2} + 2\,\pi\tau_1^{(1)} \nu_t^* \right\}^{3/2} \right]. \tag{7-26}$$

In the irreversible process, in which we are interested, the absorption coefficient a plays rather an important rôle. This quantity is directly measured by the experiments of supersonics and hypersonics.

By applying the formula of thermal conduction in solids, which we owe to Brillouin[64], to liquids, we obtain the thermal conductivity in liquids,

$$\kappa = \kappa_l + \kappa_t, \tag{7-27}$$

$$\kappa_l = \frac{4\,\pi}{3} \int_0^{\nu_l^*} \frac{1}{2\,\alpha_l} \cdot \frac{\partial}{\partial T}\left[\frac{\nu^2}{W_l v_l} \cdot g(\nu) \right] d\nu, \tag{7-28}$$

$$\kappa_t = \frac{8\,\pi}{3} \int_0^{\nu_t^*} \frac{1}{2\,\alpha_t} \cdot \frac{\partial}{\partial T}\left[\frac{\nu^2}{W_t v_t} \cdot g(\nu) \right] d\nu, \tag{7-29}$$

where κ_l and κ_t represent thermal conductivities due to the longitudinal and the transverse waves, respectively. From eqs. (7–28) and (7–29) we have:

$$\kappa_l = \frac{k}{3\,v_0} \cdot Q(\nu_l^*,\ 2\,\pi\tau_1,\ 2\,\pi\tau_1^{(1)}), \tag{7-30}$$

$$Q(\nu_l^*,\ p,\ q) =$$
$$= \int_0^{\nu_l^*} \frac{\frac{\partial}{\partial T}\left[T\left\{ 1 - \frac{2\,\lambda_1}{k_0} \cdot \frac{p^2 \nu^2}{G} - \frac{8\,\mu_1}{3\,k_0} \cdot \frac{q^2 \nu^2}{H} + \frac{\lambda_1}{k_0} \cdot \frac{p^4 \nu^4}{G^2} + \frac{4\,\mu_1}{3\,k_0} \cdot \frac{q^4 \nu^4}{H^2} \right\} \right]}{\frac{\lambda_1}{2\,k_0} \cdot \frac{p}{G} + \frac{2\,\mu_1}{3\,k_0} \cdot \frac{q}{H}}\, d\nu, \tag{7-31}$$

with $G=1+p^2\nu^2$ and $H=1+q^2\nu^2$, and

$$\kappa_t=\frac{k\sqrt{\pi\tau_1^{(1)}}}{3\,v_{t\infty}}\int_0^{\nu_t{}^*}\nu^{1/2}\cdot[\sqrt{1+(2\pi\tau_1^{(1)}\nu)^2}+2\pi\tau_1^{(1)}\nu]^{1/2}\times$$
$$\times\frac{\partial}{\partial T}\Big[\frac{T\{\sqrt{1+(2\pi\tau_1^{(1)}\nu)^2}+2\pi\tau_1^{(1)}\nu\}^2}{2\pi\tau_1^{(1)}\sqrt{1+(2\pi\tau_1^{(1)}\nu)^2}}\Big]d\nu, \tag{7-32}$$

with $v_{t\infty}=\sqrt{\mu_1/\rho_0}$.

If we consider the limiting case:

$$\tau_1^{(1)}\nu\ll 1,$$

which means that the effect of shearing viscosity predominates in the medium, the expression (7-32) reduces to:

$$\kappa_t=\frac{k}{9\sqrt{\pi}}\sqrt{\rho\mu_1'}\,\frac{\partial}{\partial T}\Big(\frac{T}{\mu_1'}\Big)\cdot(\nu_t^*)^{3/2}, \tag{7-33}$$

with shearing viscosity $\mu_1'=\mu_1\tau_1^{(1)}$. The expression (7-33) corresponds to the expression of thermal conductivity at elevated temperatures presented by Lucas[55].

In addition, we can see that, as an approximation for small $(\tau_1^{(1)}\nu_t^*)$, the quantity κ_t is roughly equal to (7-33) times $\{1+O(\tau_1^{(1)}\nu_t^*)\}$. Thus the term $O(\tau_1^{(1)}\nu_t^*)$, shows the order of magnitude of the effect of shearing relaxation on κ_t for liquids, when $(\tau_1^{(1)}\nu_t^*)$ is small.

For many kinds of liquids at ordinary temperatures, we can take:

$\mu'=10^{-2}$ poises, $\tau_l=10^{-8}\sim10^{-10}$ sec., $\tau_1^{(1)}=10^{-10}\sim10^{-11}$ sec.,
$\nu_l^*=10^{13}$ sec.$^{-1}$, and $\nu_t^*=10^{13}$ sec.$^{-1}$

Accordingly, we obtain $\tau\nu^*=10^2\sim10^5$. This figure shows that the terms $(\tau\nu^*)$ hardly contribute to the curled brackets in the expressions of internal energy, (7-22) and (7-22′). And the numerical value of (7-22) is almost equal to (7-22′), which includes partial elastic moduli λ_1 and μ_1. For some solutions of high-polymeric substance, it happens sometimes that $\tau_1^{(1)}$ is of order of magnitude $10^{-7}\sim10^{-8}$ sec., and the value of $(\tau_1^{(1)}\nu_t^*)$ reaches to $10^5\sim10^6$. In this case, the expression (7-23) does not differ numerically from (7-24). Thus we can see that calculations of specific heats by the methods of Debye, or of Lucas, are valid for many kinds of liquids exhibiting relaxational properties.

VIII. Theory of Anisotropic Rheological Body

The extension of our theory to the anisotropic rheological body is quite obvious[25]. The visco-elastic constants and coefficients of thermal expansion in the relation of stress-strain-temperature are tensor quantities in an anisotropic body. Accordingly, one can take into account the rheological operators discussed in the preceding chapters and make all of them to be the operators of tensorial character. The operators corresponding to the so-called *dynamic specific heat*, the quantities b's in the expression of the macroscopic internal energy, and the operators corresponding to the thermal conductivity, are taken to be the operators of tensorial character.

In rheological media such as visco-elastic bodies, if the volume dilatation is produced suddenly and kept constant (*i.e.* kept in an isostrained state), normal stress decays after a sufficiently long time and finally vanishes. While, in liquids, pressure also decays after a sufficiently long time, and does not vanish but finally approaches to a constant value, still remaining finite. This is the main difference between solid-like (visco-elastic) and liquid-like materials. In the following we shall be mainly concerned with the equations of state for liquid-like and solid-like bodies, respectively.

Equations of state for Stress, Strain, and Temperature

The equations of state for an anisotropic liquid-like body are written, in linear approximations[25)], as follows:

$$A_{ij}(t) = -p_0\cdot\delta_{ij} + k_0\,\varepsilon_{kk}(t)\cdot\delta_{ij} + \sum_{r=1}^{R} a_{ijkl}^{(r)*}\cdot\varepsilon_{kl}(t) - \sum_{r=1}^{N}\alpha_{ij}^{(r)*}\cdot\vartheta(t), \tag{8-1}$$

$$a_{ijkl}^{(r)*}\cdot\varepsilon_{kl}(t) = a_{ijkl}^{(r)}\cdot\left\{\varepsilon_{kl}(t) - \int_0^\infty f^{(r)}(t')\cdot\varepsilon_{kl}(t-t')\,dt'\right\}, \tag{8-2}$$

$$\alpha_{ij}^{(r)*}\cdot\vartheta(t) = \alpha_{ij}^{(r)}\cdot\left\{\vartheta(t) - \int_0^\infty g^{(r)}(t')\cdot\vartheta(t-t')\,dt'\right\}, \tag{8-3}$$

$$a_{ijkl}^{(r)} = a_{klij}^{(r)} = a_{ikjl}^{(r)}, \qquad (r = 1, 2, 3, \ldots, R) \tag{8-4}$$

$$\alpha_{ij}^{(r)} = \alpha_{ji}^{(r)}, \qquad (i, j, k, l = 1, 2, 3) \tag{8-5}$$

with initial pressure p_0.

The third term in (8–1) accompanied by relaxation functions comes from the elastic relaxation of the media, while the last term expresses the relaxation of thermal expansion.

While, we can write, in an analogous form, the equations of state for solid-like body with a slight modification of the rheological coefficients $a_{ijkl}^{(r)}$ and $\alpha_{ij}^{(r)}$:

$$A_{ij}(t) = \sum_{r=1}^{R} a_{ijkl}^{(r)*}\cdot\varepsilon_{kl}(t) - \sum_{r=1}^{N}\alpha_{ij}^{(r)*}\cdot\vartheta(t). \tag{8-6}$$

The summations in (8–1) and (8–6) can be replaced by Stieltjes integrations when the distribution of relaxation functions is discrete in some region and continuous in the other.

Equations (8–1) are reduced to eqs. (3–1) for an isotropic body:

$$\begin{aligned} A_{ij}(t) = {} & -p_0\cdot\delta_{ij} + k_0\cdot\varepsilon_{kk}\cdot\delta_{ij} + \left\{\sum_{r=1}^{l}\lambda^{(r)*} - \frac{2}{3}\sum_{r=1}^{m}\mu^{(r)*}\right\}\cdot\varepsilon_{kk}(t)\cdot\delta_{ij} + \\ & + 2\sum_{r=1}^{m}\mu^{(r)*}\cdot\varepsilon_{ij}(t) - \sum_{r=1}^{n}\alpha^{(r)*}\cdot\vartheta(t)\cdot\delta_{ij}, \end{aligned} \tag{8-7}$$

$$\left.\begin{aligned} \lambda^{(r)*}\cdot\varepsilon_{kk}(t) &= \lambda^{(r)}\cdot\left\{\varepsilon_{kk}(t) - \int_0^\infty h^{(r)}(t')\cdot\varepsilon_{kk}(t-t')\,dt'\right\}, \\ \mu^{(r)*}\cdot\varepsilon_{ij}(t) &= \mu^{(r)}\cdot\left\{\varepsilon_{ij}(t) - \int_0^\infty \phi^{(r)}(t')\cdot\varepsilon_{ij}(t-t')\,dt'\right\}, \\ \alpha^{(r)*}\cdot\vartheta(t) &= \alpha^{(r)}\cdot\left\{\vartheta(t) - \int_0^\infty g^{(r)}(t')\cdot\vartheta(t-t')\,dt'\right\}, \end{aligned}\right\} \tag{8-8}$$

$$\alpha_{ij}^{(r)} = \alpha^{(r)} \cdot \delta_{ij}, \tag{8-9}$$

with partial coefficients corresponding to Lamé's constants $\lambda^{(r)}$ and $\mu^{(r)}$, and partial coefficients corresponding to the isotropic thermal expansion $\alpha^{(r)}$.

In a solid-like body, eqs. (8–6) are reduced to eqs. (8–10) for the isotropic case,

$$A_{ij}(t) = \left\{ \sum_{r=1}^{l} \lambda^{(r)*} - \frac{2}{3} \sum_{r=1}^{m} \mu^{(r)*} \right\} \cdot \varepsilon_{kk}(t) \cdot \delta_{ij} + 2 \sum_{r=1}^{m} \mu^{(r)*} \cdot \varepsilon_{ij}(t) - \sum_{r=1}^{n} \alpha^{(r)*} \cdot \vartheta(t) \cdot \delta_{ij}, \tag{8-10}$$

with a slight modification of λ^*, μ^*, and α^*.

For the sake of simplicity we shall consider in (8–1), (8–6), (8–7), and (8–10) the Maxwellian relaxations:

$$\left.\begin{aligned} f^{(r)}(t') &= \frac{1}{\tau_1^{(r)}} \cdot e^{-t'/\tau_1^{(r)}}, \\ g^{(r)}(t') &= \frac{1}{\tau_2^{(r)}} \cdot e^{-t'/\tau_2^{(r)}}, \\ h^{(r)}(t') &= \frac{1}{\tau_3^{(r)}} \cdot e^{-t'/\tau_3^{(r)}}, \\ \psi^{(r)}(t') &= \frac{1}{\tau_4^{(r)}} \cdot e^{-t'/\tau_4^{(r)}}, \end{aligned}\right\} \tag{8-11}$$

with τ's all positive.

Then, considering the oscillatory motion of the system, all the operators with superscript $*$, can be written symbolically by the integro-differential operators:

$$\left.\begin{aligned} a_{ijkl}^{(r)*} &= \frac{a_{ijkl}^{(r)} \tau_1^{(r)} D}{1+\tau_1^{(r)} D} = \frac{a_{ijkl}^{(r)\prime} D}{1+\tau_1^{(r)} D}, \\ \alpha_{ij}^{(r)*} &= \frac{\alpha_{ij}^{(r)} \tau_2^{(r)} D}{1+\tau_2^{(r)} D}, \\ \lambda^{(r)*} &= \frac{\lambda^{(r)} \tau_3^{(r)} D}{1+\tau_3^{(r)} D} = \frac{\lambda^{(r)\prime} D}{1+\tau_3^{(r)} D}, \\ \mu^{(r)*} &= \frac{\mu^{(r)} \tau_4^{(r)} D}{1+\tau_4^{(r)} D} = \frac{\mu^{(r)\prime} D}{1+\tau_4^{(r)} D}, \end{aligned}\right\} \tag{8-12}$$

with $D = \partial/\partial t$, where $a_{ijkl}^{(r)\prime}$, $\lambda^{(r)\prime}$ and $\mu^{(r)\prime}$, correspond to the partial coefficients of viscosity.

Expression of Internal Energy

If we take, as usual in the thermostatics, components of strain ε_{ij} and temperature deviation ϑ as independent variables in the expression of internal energy U per unit mass, we have:

$$dU = \left(\frac{\partial U}{\partial T}\right)_{\varepsilon} \cdot dT + \left(\frac{\partial U}{\partial \varepsilon_{ij}}\right)_{T} \cdot d\varepsilon_{ij}, \tag{8-13}$$

where suffixes ε and T outside the blackets mean the iso-strained and the isothermal state, respectively.

In the present theory of an anisotropic rheological body, we can interpret that the term $(\partial U/\partial T)_\varepsilon$ is the operator C^* corresponding to the specific heat at iso-strained state, while the term $(\partial U/\partial \varepsilon_{ij})_T$ is the operator b^*_{ij} corresponding to the term which measures the effect of deformation of the body at isothermal state. These are written as:

$$C^* = C^\circ + \sum_{r=1}^{s} C^{(r)*}, \tag{8-14}$$

$$C^{(r)*} \cdot \vartheta(t) = C^{(r)} \cdot \left\{ \vartheta(t) - \int_0^\infty \bar{f}^{(r)}(t') \cdot \vartheta(t-t')\,dt' \right\}, \tag{8-15}$$

and

$$b^*_{ij} = b^\circ_{ij} + \sum_{r=1}^{q} b^{(r)*}_{ij}, \tag{8-16}$$

$$b^{(r)*}_{ij} \cdot \varepsilon_{ij}(t) = b^{(r)}_{ij} \cdot \left\{ \varepsilon_{ij}(t) - \int_0^\infty \bar{\bar{f}}^{(r)}(t') \cdot \varepsilon_{ij}(t-t')\,dt' \right\}, \tag{8-17}$$

as mentioned by Takizawa[25].

The operators in (8–14) and (8–17) can be reduced to the following expressions:

$$C^{(r)*} = \frac{C^{(r)}\tau_5^{(r)} D}{1+\tau_5^{(r)} D}, \tag{8-18}$$

and

$$b^{(r)*}_{ij} = \frac{b^{(r)}_{ij}\tau_6^{(r)} D}{1+\tau_6^{(r)} D}, \tag{8-19}$$

if we take the Maxwellian relaxation functions:

$$\bar{f}^{(r)}(t') = \frac{1}{\tau_5^{(r)}} \cdot e^{-t'/\tau_5^{(r)}}, \tag{8-20}$$

and

$$\bar{\bar{f}}^{(r)}(t') = \frac{1}{\tau_6^{(r)}} \cdot e^{-t'/\tau_6^{(r)}}, \tag{8-21}$$

and consider the oscillatory motion of the system.

Heat Flux

The expression (4–49) of heat flux for an isotropic material will be generalized to the anisotropic case, and is written as follows:

$$q_j = -\sum_{r=1}^{p} \kappa^{(r)}_{jk} \cdot \frac{\partial}{\partial x_k} \left\{ \int_0^\infty \varphi^{(r)}(t') \cdot \vartheta(t-t')\,dt' \right\}, \tag{8-22}$$

with heat flux vector q_j $(j=1, 2, 3)$, the tensors of thermal conductivities $\kappa^{(r)}_{jk}$ $(j, k=1, 2, 3;\ r=1, 2, 3, \ldots, p)$ and the relaxation functions $\varphi^{(r)}(t')$ which satisfy the conditions:

$$\int_0^\infty \varphi^{(r)}(t')\,dt' = 1 \tag{8-23}$$

Taking Maxwellian relaxational processes:

$$\varphi^{(r)}(t') = \frac{1}{\tau_7^{(r)}} \cdot e^{-t'/\tau_7^{(r)}}, \qquad (r=1, 2, 3, \ldots, p) \tag{8-24}$$

and considering the oscillatory motion of the system, we obtain, from (8–22), the following expressions:

$$q_j = -\sum_{r=1}^{p} \frac{\kappa_{jk}^{(r)}}{1+\tau_7^{(r)} D} \cdot \frac{\partial \vartheta}{\partial x_k}. \tag{8-25}$$

The expression (8–25) is a generalization of eq. (4–48) or (4–49) for the anisotropic materials. If we put $p=1$ in eq. (8–25), we have the expression for the anisotropic body proposed by Kaliski 16) 17).

Applications and Discussions of the Theory of Anisotropic Rheological Body

The simultaneous equations (3–13) and (4–10) with eqs. (8–6) and (8–13) ~ (8–17); or with (8–12), (8–14), (8–16), (8–18), and (8–19), are generalized fundamental equations of motion and of conservation of energy for anisotropic rheological media. These, when simplified, can be applicable to the theories of surface rheology of mono-molecular layer of macromolecules such as presented by Tachibana-Inokuchi 68), Oka 69), Oka-Satô 70), and Frenkel 10), and also may have some contributions of acoustic (ultrasonic) birefringence in high polymer solutions and highpolymeric substances. The rheology of solid crystal-like materials is also involved in the present theory, *mutatis mutandis.*

When the process occurring in the media is isothermal, *i.e.* $\delta T=0$, eqs. (3–13) with eq. (8–6) can be simplified, and eq. (4–10) shall be omitted. For the sake of simplicity we shall take the Maxwellian relaxational process and consider the progressing sinusoidal wave with circular frequency ω. Then, as is well known, owing to the symmetric property of the matrix $a_{ijkl}^{(r)}$, we see that there exist three waves with different velocities, whose planes of oscillation are perpendicular to each other. Moreover these waves show the dispersion and the dissipation because of the existence of the complex elastic moduli:

$$a_{ijkl}^{(r)*} = \frac{i\omega a_{ijkl}^{(r)\prime}}{1+i\omega\tau_1^{(r)}}. \qquad (i, j, k, l=1, 2, 3)$$

When the initial stress of finite magnitude is distributed in the solid-like media, we have the equations of motion in the isothermal process according to Sakadi's formalism 71):

$$\rho_0 \frac{\partial^2 \xi_i}{\partial t^2} = -\varepsilon_{jk} \frac{\partial A_{ij}^{\circ}}{\partial x_k} + \frac{\partial \tilde{\omega}_{jk}}{\partial x_k} A_{ij}^{\circ} + \frac{\partial \tilde{\omega}_{ji}}{\partial x_k} A_{kj}^{\circ} + \frac{\partial A_{ij}}{\partial x_j} + \rho_0 (X_i - \varepsilon_{kk} X_i^{\circ} + \tilde{\omega}_{ij} X_j^{\circ}), \tag{8-26}$$

where A_{ij} is given by eqs. (8–6), $X_i^{\circ}(x')$ body force per unit mass at initial coordinate point x' and $X_i(x)$ body force at x in a strained state.

At the reference state in equilibrium with initial stress, we have:

$$\rho_0(x) X_i^{\circ}(x) + \frac{\partial A_{ij}^{\circ}(x)}{\partial x_j} = 0. \tag{8-27}$$

Here the initial stress is expressed as $A^{\circ}_{ij}(x')$ at initial coordinate point x', $\rho_0(x')$ being the initial density.

Boundary conditions state:

$$F_i - F^{\circ}_i = -\varepsilon_{kj} n^{\circ}_k A^{\circ}_{ij} + \varepsilon_{kl} n^{\circ}_k n^{\circ}_l F^{\circ}_i + \tilde{\omega}_{ki} F^{\circ}_k + n^{\circ}_j A_{ij}, \quad (i=1,\ 2,\ 3) \qquad (8\text{-}28)$$

with initial conditions at the mechanical equilibrium:

$$F^{\circ}_i = n^{\circ}_j A^{\circ}_{ij}, \qquad (i=1,\ 2,\ 3) \qquad (8\text{-}29)$$

where n°_j are direction cosines of the outward normal to the boundary of the unstrained state; F°_i and F_i surface tractions at initial state and at strained state, respectively.

Due to the existence of the initial stress, the progressing waves such as surface waves actually damp, and moreover the fugitive character of rheological stress A_{ij} makes the damping more rapid. Eqs. (8–26) may be quite useful in practical problems occurring in many engineering fields.

As a special case, with isotropic stress (8–10), we have from eqs. (8–26), by using complex Lamé's moduli $\lambda^{(r)*}$ and $\mu^{(r)*}$, complex velocities of three waves for infinite solid-like media:

$$\left.\begin{aligned} v_1 &= \sqrt{\frac{\mu_1}{\rho_0}}, &&\text{with} && \mu_1 = \sum_{r=1}^{m} \mu^{(r)*} - \frac{1}{2}(B^{\circ}_{11} - B^{\circ}_{33}), \\ v_2 &= \sqrt{\frac{\mu_2}{\rho_0}}, &&\text{with} && \mu_2 = \sum_{r=1}^{m} \mu^{(r)*} - \frac{1}{2}(B^{\circ}_{22} - B^{\circ}_{33}), \\ \text{and}\quad v_3 &= \sqrt{\frac{\lambda_1}{\rho_0}}, &&\text{with} && \lambda_1 = \sum_{r=1}^{l} \lambda^{(r)*} + 2\sum_{r=1}^{m} \mu^{(r)*}, \end{aligned}\right\} \qquad (8\text{-}30)$$

if we take $B^{\circ}_{12}=0$ after suitable coordinate transformation, B°_{ij} being the transformed initial stress, and X°_i and X_i being put equal to zero.

Starting from eqs. (3–13) with eq. (8–12), or with eqs. (8–6), no temperature terms and no body force being taken into account, we can see that the three waves, one purely longitudinal and two purely transverse, are obtained after suitable orthogonal transformation of coordinates. Calculation of the transformed elements of the matrix $a^{(r)*}_{ijkl}$ can be quite analogously carried out as in the case of elastic waves in crystals[71)72)73)]. Once the velocities of these three waves are determined, we can obtain specific heat of anisotropic media, when they are solid-like or liquid-like, according to Debye's theory[57)] and Oomori's treatment[63)] of the dissipative wave, as was mentioned in Chapter VII.

In the analogous line of consideration the surface energy of liquids can be also calculated by using the relaxationally decaying elastic surface waves, following to the method presented by Frenkel (cf. his book[10)] Chap. VI).

When no initial stress exists, the behaviour of the mechanical and thermodynamical system hitherto considered, is completely described by the system of equations (3–13) and (4–10) with eqs. (8–6), and (8–13) ~ (8–17); or with (8–12), (8–14), (8–16), (8–18) and (8–19). This macroscopic system, however, is not itself *closed* in the sense of *thermostaics*. Here arises a question how we can consider the system in itself closed from the viewpoint of the theory of irreversible thermodynamics. Actually, the terms of heat conduction, fugitive specific heat, bulk and shearing viscosities, and thermal expansion and conductivity of fugitive nature, are present in our fundamental equations, so the dissipation of energy and the entropy production do actually occur in our *open system.* But, if we take some subsystems characterised by some extra *inner variables*, including those such as chemical potentials and some measures of excited states of constituent molecules and atoms, we may set up a *closed system* as a whole. Meixner[22)74)] considered affinities in the expression of internal energy and arrived at the relaxation functions in the stress-strain relation after eliminating the linearly decaying inner variables. He, however, did not propose any equation involving thermal conduction. So, the expression of internal energy and that of energy equation in the present paper are different from his expression in these points.

Taking into consideration some subsystems with a sufficient number of inner variables and of energy equations, and those of entropy production in the individual subsystems, we may be in the goal of the *closed system* in the sense of the theory of irreversible thermodynamics, after eliminating a sufficient number of inner variables, which do not fall under our direct observation. Thus, eqs. (3–13) and (4–10) with eqs. (8–6), and (8–13) (8–17), although still remained in the scope of an open system, should be reconsidered, if necessary, from the view-point of a consistent theory of irreversible thermodynamics.

IX. Ultrasonic Birefringence in a Rheological Body under Initial Stress

The Dynamical behaviour of a solid elastic body under initially stressed state has been already discussed by Biot[75)76)] and Sakadi and Takizawa[71)]. In the present chapter, calculations are made on the velocities and absorption coefficients of ultrasonic waves[78)] in a Maxwellian visco-elastic medium[12)25)66)77)], which is initially at rest under certain initial stress. Two differently polarized waves in a medium under initially stressed state have different phase-velocities. Accordingly, one can observe the phase-difference of two differently polarized transverse waves after they have travelled through the medium. The phase-difference is proportional to the product of the wave-frequency and the difference of the principal stresses.

By means of the expression for the phase-difference, one can obtain the difference of principal stresses from the observed data of phase-difference of the waves. Such an experiment for a perfectly elastic medium will be called the *acousto-elastic* method[79)~82)], which is quite analogous to the *photo-elastic* one.

The superiority of this method to the photo-elastic one is as follows. It is unnecessary to make use of the optically transparent models, such as models of high-polymer substances. The method is practically applicable to the optically opaque materials, such as metals, non-metals as well as organic substances. The method enables us to measure the initial residual stress not only in a model but also in any part of mechanical structures of complicated form, such as buildings, bridges, and machines etc. The experimental device for this method is rather simple, and one can make his measurement outdoors, without using a dark room etc., *i.e.* the method is quite convenient for field works.

In order to make more precise measurement in the *acousto-visco-elastic* experiment than the present one[80][81][82], it is convenient to make use of a number of small mosaic crystals as detectors of the ultrasonics, so that one can obtain *acoustical pictures* (or its intensity distribution) on the detector surface. The problem to be solved at present is to improve the precision of such a detecting apparatus of the ultrasonics of high frequency.

Fundamental Equations in a Visco-Elastic Body with Initial Stress

We shall take a solid body under initial stress. Let x_i $(i=1, 2, 3)$ be rectangular coordinates, and the components of the initial stress be A°_{ij} $(i, j=1, 2, 3)$. Let ρ_0 be the density of the body under the initially stressed state. The body undergoes infinitesimally small deformation from the initially stressed state. The small displacement of first order is denoted by ξ, whose rectangular components are ξ_i $(i=1, 2, 3)$. Components of strain ε_{ij} $(i, j=1, 2, 3)$ are:

$$\varepsilon_{ij}=\frac{1}{2}\left(\frac{\partial\xi_j}{\partial x_i}+\frac{\partial\xi_i}{\partial x_j}\right). \qquad (i, j=1, 2, 3) \tag{9-1}$$

Further, we put:

$$\tilde{\omega}_{ij}=\frac{1}{2}\left(\frac{\partial\xi_j}{\partial x_i}-\frac{\partial\xi_i}{\partial x_j}\right). \qquad (i, j=1, 2, 3) \tag{9-2}$$

Let the components of stress be A_{ij} $(i, j=1, 2, 3)$, due to the displacement ξ in the body.

a) If the body is perfectly elastic, we have from Hooke's law:

$$A_{ij}=\lambda_0\varepsilon_{kk}\cdot\delta_{ij}+2\mu_0\varepsilon_{ij}, \qquad (i, j=1, 2, 3) \tag{9-3}$$

with

$$\varepsilon_{kk}=\varepsilon_{11}+\varepsilon_{22}+\varepsilon_{33}=\operatorname{div}\xi, \tag{9-4}$$

where λ_0 and μ_0 are Lamé's constants, and δ_{ij} is Kronecker's delta.

b) If the body is visco-elastic, which is subjected to the Maxwellian relaxational process (3-12) with $\alpha_r=0$ and $l=m=1$, we have:

$$A_{ij}=\left(\lambda_0+\lambda^*-\frac{2}{3}\mu^*\right)\varepsilon_{kk}\cdot\delta_{ij}+2(\mu_0+\mu^*)\varepsilon_{ij}, \qquad (i, j=1, 2, 3) \tag{9-5}$$

where λ_0 and μ_0 are Lamé's constants, and:

$$\left.\begin{aligned}\lambda^*&=\frac{\lambda_1\tau_1 D}{1+\tau_1 D},\\ \mu^*&=\frac{\mu_1\tau_2 D}{1+\tau_2 D},\end{aligned}\right\} \tag{9-6}$$

are the visco-elastic (integro-differential) operators, with $D=d/dt$ (differential operator with respect to time t). λ_1 and μ_1 are extra elastic constants, corresponding to the extra Lamé's constants. τ_1 and τ_2 are the corresponding relaxation times with volume viscosity coefficient $\lambda_1\tau_1$ and shearing viscosity coefficient $\mu_1\tau_2$.

c) If the body is visco-elastic, described by the Voigt model, we have:

$$A_{ij} = \left(\lambda_0 + \eta_1 D - \frac{2}{3}\eta_2 D\right)\varepsilon_{kk}\delta_{ij} + 2\,(\mu_0 + \eta_2 D)\,\varepsilon_{ij}, \qquad (i,\ j=1,\ 2,\ 3) \qquad (9\text{-}7)$$

with volume viscosity coefficient η_1 and shearing viscosity coefficient η_2.

The equations of motion of the system under initial stress are given by Sakadi and Takizawa[71]. The equations of motion read, under no external body force, as follows:

$$\rho_0 \frac{\partial^2 \xi_i}{\partial t^2} = \frac{\partial \widetilde{\omega}_{jk}}{\partial x_k} A^{\circ}_{ij} + \frac{\partial \widetilde{\omega}_{ji}}{\partial x_k} A^{\circ}_{kj} - \varepsilon_{jk} \frac{\partial A^{\circ}_{ij}}{\partial x_k} + \frac{\partial A_{ij}}{\partial x_j}, \qquad (i=1,\ 2,\ 3) \qquad (9\text{-}8)$$

where the summation convention over dummy indices is used, as usual in the tensorial notations.

Here, in the present chapter, the author calculates the velocities, absorption coefficients, and phase-difference of waves in a visco-elastic body, which is subjected to the Maxwellian relaxational process (9-5). For the case (9-7) of the Voigt model, calculations can be carried out in a similar manner.

Elastic Waves in the System with Constant Initial Stress

In general, the components A°_{ij} of initial stress are functions of coordinates. In this paragraph, for the sake of simplicity, we shall take A°_{ij} $(i,\ j=1,\ 2,\ 3)$ to be constants.

By suitable orthogonal transformation (*i.e.* principal axis transformation), we can choose such new rectangular axes that all the components of initial shearing stresses should vanish. In the new rectangular coordinates x_i $(i=1,\ 2,\ 3)$, we shall take the components of the initial stress as follows:

$$\left.\begin{aligned} A^{\circ}_{11} &= \text{const.}, \\ A^{\circ}_{22} &= \text{const.}, \\ A^{\circ}_{33} &= \text{const.}, \\ A^{\circ}_{ij} &= 0. \qquad (i \neq j) \end{aligned}\right\} \qquad (9\text{-}9)$$

Let us take a plane-wave propagating into the $+x_3$-direction, with circular frequency ω:

$$\xi_j = C_j \cdot \exp\left[i\omega t - \beta_j x_3\right], \quad \mathscr{R}_e(\beta_j) > 0, \quad \mathscr{I}_m(\beta_j) > 0, \quad (j=1,\ 2,\ 3) \quad (9\text{-}10)$$

with constants C_j $(j=1,\ 2,\ 3)$.

Putting eqs. (9-10) into eqs. (9-8), we obtain:

$$\left.\begin{aligned} -\omega^2\rho_0 &= \left\{\mu_0 + \mu^* - \frac{1}{2}(A^{\circ}_{11} - A^{\circ}_{33})\right\}\beta_1^2, \\ -\omega^2\rho_0 &= \left\{\mu_0 + \mu^* - \frac{1}{2}(A^{\circ}_{22} - A^{\circ}_{33})\right\}\beta_2^2, \\ -\omega^2\rho_0 &= \left\{\lambda_0 + \lambda^* + 2\,\mu_0 + \frac{4}{3}\mu^*\right\}\beta_3^2, \end{aligned}\right| \qquad (9\text{-}11)$$

with

$$\lambda^* = \frac{i\omega\lambda_1\tau_1}{1+i\omega\tau_1},$$

and

$$\mu^* = \frac{i\omega\mu_1\tau_2}{1+i\omega\tau_2}.$$

From eqs. (9-11) we have:

$$\left.\begin{aligned}
\beta_1^2 &= \frac{-\rho_0\,\omega^2}{\mu_0+\mu^*-\dfrac{1}{2}(A_{11}^\circ-A_{33}^\circ)}, \\
\beta_2^2 &= \frac{-\rho_0\,\omega^2}{\mu_0+\mu^*-\dfrac{1}{2}(A_{22}^\circ-A_{33}^\circ)}, \\
\beta_3^2 &= \frac{-\rho_0\,\omega^2}{\lambda_0+\lambda^*+2\,\mu_0+\dfrac{4}{3}\,\mu^*}.
\end{aligned}\right\} \qquad (9\text{-}12)$$

The wave velocities v_j $(j=1, 2, 3)$ and the amplitude absorption coefficients a_j $(j=1, 2, 3)$ are given by:

$$v_j = \frac{\omega}{\mathscr{I}_m(\beta_j)}, \qquad (j=1, 2, 3) \qquad (9\text{-}13)$$

and

$$a_j = \mathscr{R}_e(\beta_j), \qquad (j=1, 2, 3) \qquad (9\text{-}14)$$

respectively, where β_j $(j=1, 2, 3)$ are the square roots of eqs. (9-12).

While, the phase-difference δ between two transverse waves will be expressed as:

$$\delta = h\cdot\mathscr{I}_m(\beta_1-\beta_2), \qquad (9\text{-}15)$$

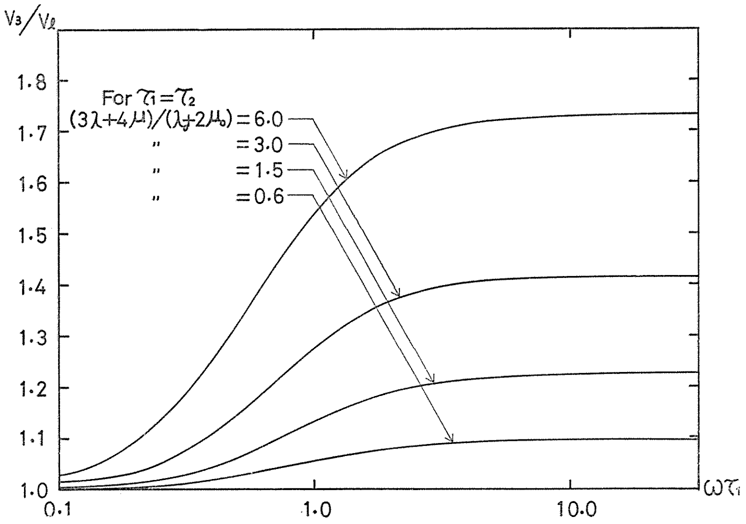

FIG. 9-1. Velocity of Longitudinal Wave, Eq. (9-13).

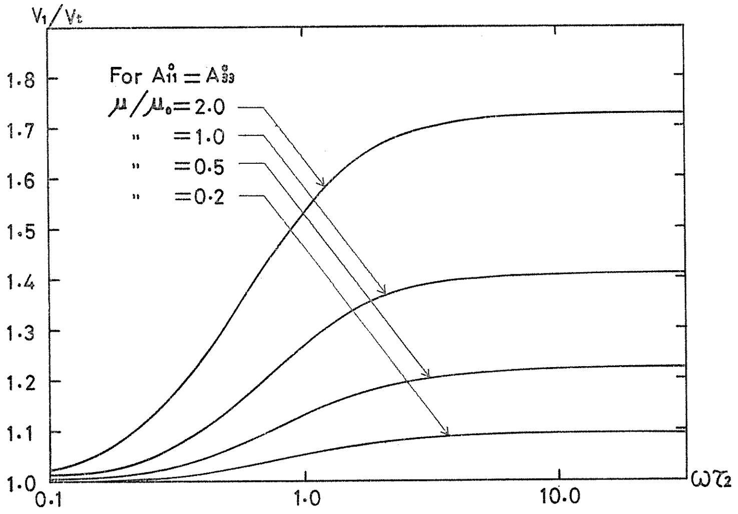

FIG. 9-2. Velocity of Transverse Wave, Eq. (9-13).

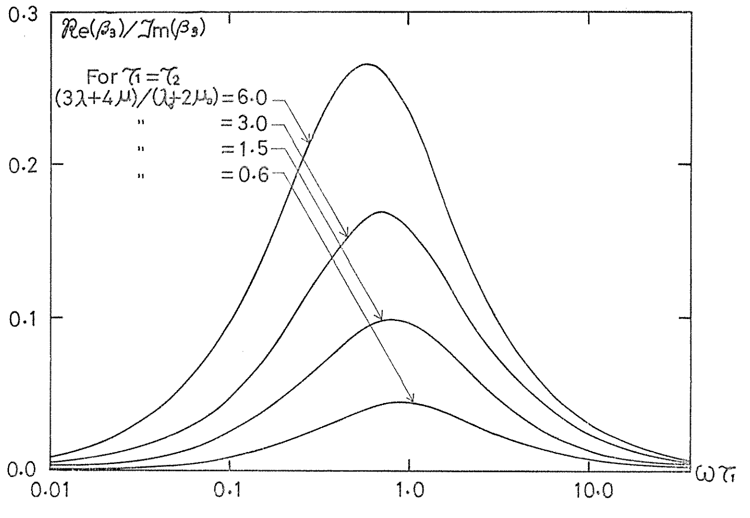

FIG. 9-3. Absorption Coefficient of Longitudinal Wave, Eq. (9-14).

after the waves have travelled through the medium of thickness h.

By means of eqs. (9-13), (9-14), and (9-15), the sound velocities, absorption coefficients, and phase-difference, are plotted as functions of circular frequency ω for four values of extra elastic constants. Fig. 9-1 and Fig. 9-2 show the sound velocities (9-13), and Fig. 9-3 and Fig. 9-4 the absorption coefficients (9-14). While, Fig. 9-5 shows the phase-difference (9-15) versus circular frequency ω.

In practical problems, in which λ_0 and μ_0 are $10^{10} \sim 10^{11}$ dynes/cm^2, and λ_1 and μ_1 are less than $10^8 \sim 10^9$ dynes/cm^2, it is interesting to consider the case:

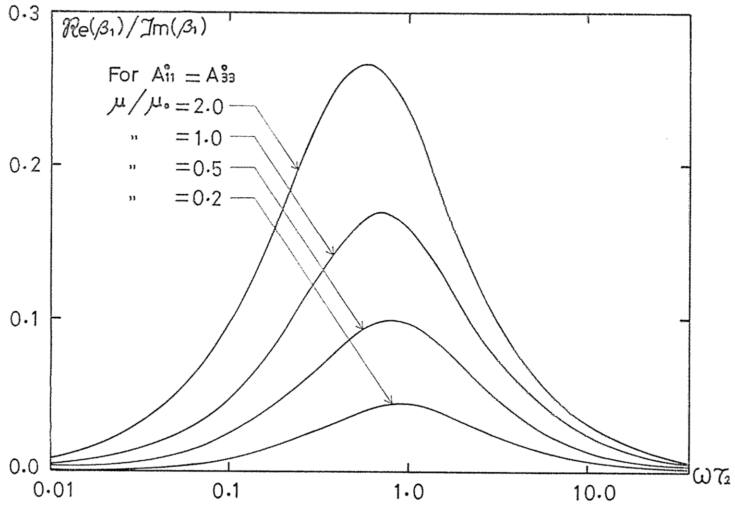

FIG. 9-4. Absorption Coefficient of Transverse Wave, Eq. (9-14).

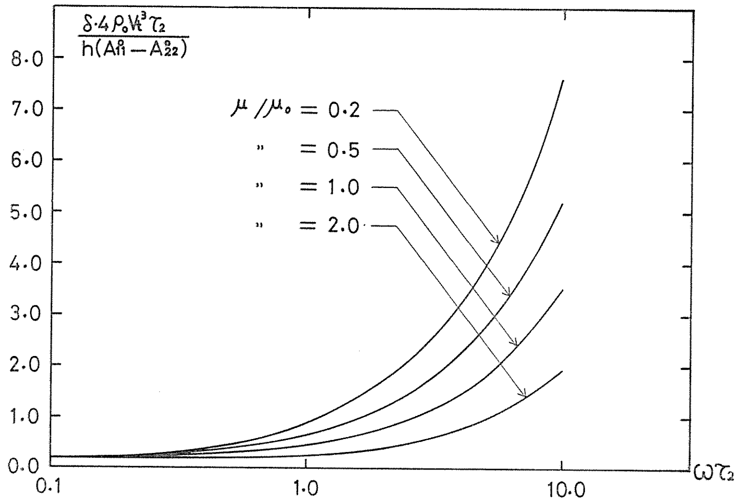

FIG. 9-5. Phase Difference between Two Transverse Waves, Eq. (9-15).

and

$$\left.\begin{array}{ll} \dfrac{\lambda_1}{\lambda_0} \ll 1, & \dfrac{\mu_1}{\mu_0} \ll 1, \\[2ex] \dfrac{A^\circ_{11} - A^\circ_{33}}{\mu_0} \ll 1, & \dfrac{A^\circ_{22} - A^\circ_{33}}{\mu_0} \ll 1, \end{array}\right\} \qquad (9\text{-}16)$$

where A°'s are far smaller than 10^8 dynes/cm^2. Then the expression (9-12) becomes to:

$$\left.\begin{aligned}
\beta_1 &= i\frac{\omega}{v_t}\left[1-\frac{1}{2}\frac{\mu^*}{\mu_0}+\frac{1}{4\,\mu_0}(A^\circ_{11}-A^\circ_{33})+\frac{3}{8}\left\{\frac{\mu^*}{\mu_0}-\frac{1}{2\,\mu_0}(A^\circ_{11}-A^\circ_{33})\right\}\right],\\
\beta_2 &= i\frac{\omega}{v_t}\left[1-\frac{1}{2}\frac{\mu^*}{\mu_0}+\frac{1}{4\,\mu_0}(A^\circ_{22}-A^\circ_{33})+\frac{3}{8}\left\{\frac{\mu^*}{\mu_0}-\frac{1}{2\,\mu_0}(A^\circ_{22}-A^\circ_{33})\right\}\right],\\
\beta_3 &= i\frac{\omega}{v_l}\left[1-\frac{1}{2}\frac{1}{\lambda_0+2\,\mu_0}\left(\lambda^*+\frac{4}{3}\mu^*\right)+\frac{3}{8}\frac{1}{(\lambda_0+2\,\mu_0)^2}\left(\lambda^*+\frac{4}{3}\mu^*\right)^2\right],
\end{aligned}\right\} \tag{9-17}$$

with

$$v_t=\sqrt{\frac{\mu_0}{\rho_0}},$$

and

$$v_l=\sqrt{\frac{\lambda_0+2\,\mu_0}{\rho_0}}. \tag{9-18}$$

Accordingly, the wave-velocities v_j $(j=1, 2, 3)$ are:

$$v_1=\frac{\omega}{\mathscr{I}_m(\beta_1)}=v_t\cdot\left[1+\frac{1}{2}\frac{\mu_1}{\mu_0}\cdot\frac{\omega^2\tau_2^2}{1+\omega^2\tau_2^2}-\frac{1}{4\,\mu_0}(A^\circ_{11}-A^\circ_{33})\right],$$

$$v_2=\frac{\omega}{\mathscr{I}_m(\beta_2)}=v_t\cdot\left[1+\frac{1}{2}\frac{\mu_1}{\mu_0}\cdot\frac{\omega^2\tau_2^2}{1+\omega^2\tau_2^2}-\frac{1}{4\,\mu_0}(A^\circ_{22}-A^\circ_{33})\right],$$

and

$$v_3=\frac{\omega}{\mathscr{I}_m(\beta_3)}=v_l\cdot\left[1+\frac{1}{2}\frac{\lambda_1}{\lambda_0+2\,\mu_0}\cdot\frac{\omega^2\tau_1^2}{1+\omega^2\tau_1^2}+\frac{2}{3}\frac{\mu_1}{\lambda_0+2\,\mu_0}\cdot\frac{\omega^2\tau_2^2}{1+\omega^2\tau_2^2}\right]. \tag{9-19}$$

The amplitude absorption coefficients a_j $(j=1, 2, 3)$ are:

$$a_1=\mathscr{R}_e(\beta_1)=\frac{\omega}{v_t}\frac{\mu_1}{2\,\mu_0}\cdot\frac{\omega\tau_2}{1+\omega^2\tau_2^2},$$

$$a_2=\mathscr{R}_e(\beta_2)=\frac{\omega}{v_t}\frac{\mu_1}{2\,\mu_0}\cdot\frac{\omega\tau_2}{1+\omega^2\tau_2^2},$$

and

$$a_3=\mathscr{R}_e(\beta_3)=\frac{\omega}{v_l}\cdot\left[\frac{1}{2}\frac{\lambda_1}{\lambda_0+2\,\mu_0}\cdot\frac{\omega\tau_1}{1+\omega^2\tau_1^2}+\frac{2}{3}\frac{\mu_1}{\lambda_0+2\,\mu_0}\cdot\frac{\omega\tau_2}{1+\omega^2\tau_2^2}\right]. \tag{9-20}$$

After the two polarized transverse waves have travelled through the medium of thickness h, they will have a phase difference δ as follows:

$$\delta=h\cdot\mathscr{I}_m(\beta_1-\beta_2)=\frac{\omega h}{4\,\rho_0 v_t^3}(A^\circ_{11}-A^\circ_{22})\cdot\left[1-\frac{3}{2}\frac{\mu_1}{\mu_0}\cdot\frac{\omega^2\tau_2^2}{1+\omega^2\tau_2^2}\right]. \tag{9-21}$$

$\mathscr{R}_e(z)$ and $\mathscr{I}_m(z)$ represent real and imaginary parts of z, respectively. The expression (9–21) may be called the *acousto-viscoelastic law*.

If we put $\mu_1\tau_2=0$ in eq. (9–21), we have:

$$\delta=\frac{\omega h}{4\,\rho_0 v_t^3}(A^\circ_{11}-A^\circ_{22}), \tag{9-22}$$

which is essentially the same as is obtained by Tokuoka and Iwashimizu[79] for a perfectly elastic material. The expression (9–22) may be called the *acousto-elastic law.*

The expressions (9–21) and (9–22) are conveniently applied to the practical measurement of the initial residual stress in the medium, when one detects the phase-difference δ and the frequency $\omega/2\pi$ of the ultrasonics.

The velocities (9–13) of ultrasonic waves (one longitudinal and two transverse) and their amplitude absorption coefficients (9–14) in a visco-elastic body under initial stress were obtained in this chapter, where the Maxwellian relaxational process (9–5) is adopted as a mathematical model of the visco-elastic body. For the visco-elastic body of the Voigt type, the similar calculations can be carried out immediately.

Because of the difference between the propagation velocities of two polarized transverse waves travelling through the medium under an initial stress, a phase difference between these waves develops as they progress. The phase difference of the transverse waves, after they have travelled through the medium of thickness h, is given by eq. (9–21) for a Maxwellian visco-elastic body, and by eq. (9–22) for a perfectly elastic body. The phase difference δ is proportional to the product of the circular frequency ω and the difference of the initial principal stresses $(\overset{\circ}{A}_{11}-\overset{\circ}{A}_{22})$.

Being based on eq. (9–21) or (9–22), the so-called *acousto-elasitc* experiment can be carried out, which is very analogous to the *photo-elastic* one. This method of experiment is conveniently applied to the measurement of initial residual stress in any part of real mechanical structures, such as buildings, bridges, machines etc., and also finds some applications in engineering fields.

X. Conclusion and discussions

In the theory of thermo-mechanical properties of rheological media, the thermal stress of fugitive nature and the thermal conductivity corresponding to the dynamical process under high frequency oscillation are taken into account. The generalized stress-strain-temperature relation was introduced after the theory presented by Takizawa(12). The visco-elastic media are considered to have finite numbers of relaxational processes, *i.e.* elastic relaxations, thermal relaxations, and structural relaxations etc. The tensorial formulation of the mathematical theory of rheological bodies is presented by taking explicit account of thermal phenomena. In this formulation, the shearing and volume viscosities and the coefficient of thermal expansion, are expressed as integro-differential operators, which reduce to the usual relaxation operators for the case of Maxwellian relaxational process.

The equation of conservation of energy is also modified by taking explicitly the *relaxational thermal conductivity* into account. Accordingly, the theory presented in this paper can describe the thermo-mechanical relaxational process completely. Especially, the thermo-mechanical process, which takes places under the dynamical field, such as of ultrasonic field of extremely high frequency, can be conveniently interpreted by the equations presented here. Thus, the theory developed here includes, as special cases, the theories presented by Frenkel-Obratzov(9), Oshida(8), Sips(11), Takizawa(12), and Meixner(22), as well as Kneser(18)(19), Tisza(26), Hall(27), and Kaliski(45)(46).

In Chapter I, the theories of elastic and thermal relaxation were briefly reviewed, with the notations (in Chapter II) used in the following chapters. Chapter III treats the dynamical equations of state, especially stress-strain relation, thermal stress, and equations of motion of rheological body. Here the emphasis is laid on the elastic relaxation and relaxating thermal stress which have been discussed by Takizawa[12)] and Meixner[54)], and are found to be useful in the treatment of rheological bodies.

In Chapter IV the equation of conservation of energy was discussed somewhat in detail. The expression of internal energy with relaxating specific heat (4–22) was given, which can be verified to reduce to the *dynamic specific heat* presented by Kneser[1) 18) 19) 20) 36)]. The operator corresponding to the coefficient of internal energy accompanied by volume change at isothermal state[12)] was also introduced. The term corresponding to this operator is useful, if we treat the elastic breakdown due to the thermal stress. This term relates to the existence of finite velocity of propagation of thermal waves. The numerical values of b's in eqs. (4–16) and (4–19) can not be evaluated directly in experiments, but their effect can be observed in the velocity and absorption of hypersonics.

The relaxation times τ's involved in eqs. (3–12) and (4–19) may have some relations one another. In order to find out the relationship, we should treat the theory under the consideration of the theory of irreversible thermodynamics, of microscopic theory of collisions and molecular relaxations.

The expression of heat flux, *i.e.* a generalized Fourier law, in a rapidly changing field, was also given with some discussions of subsystems accompanied by mutual energy flows. Here, the idea of *relaxating partial thermal conductivities*, or the operator corresponding to the thermal conductivity, was introduced. In a special simple case, the expression of relaxating thermal conductivities given here, were reduced to the expression of Kaliski[16) 17) 45) 46)] for the case of Maxwellian relaxational process.

In Chapter V, the application of the theory to supersonic waves was briefly mentioned. The velocity and absorption of supersonics are calculated and the dispersion relation and the absorption curves are plotted against frequency.

The neglect of the term of thermal conduction is not so adequate in metalic liquids, for example, in mercury. In mercury at ordinary temperature, as is well known, about 70% of total absorption is due to the thermal conduction under the region of frequency 10^9 cycles per second, and the effect of relaxation times hardly appears, because of the liquid structure composed of monoatomic molecules. The absorption due to the effect of viscosity is about 20%. Accordingly, the solution of equation with thermal conduction must be considered in most kinds of metalic liquids. In the sonic field near the boundary surface of the media, *i.e.* in the so-called *boundary layer*, the thermal conduction is shown to be comparatively large, and can not be neglected even in usual liquids.

While, in Chapter VI some comments on the hypersonic waves were given, and it was shown that the high velocity of hypersonics in liquids comes from the extra elastic constants of liquid bodies, subjected to the Maxwellian relaxational process. The transverse waves of high frequency were also discussed in this chapter, being based on the fundamental equations given in Chapters III and IV. It was made clear that such waves propagate through the medium with high velocity, because of the presence of extra rigidities subjected to the Maxwellian relaxational process.

In Chapter VII, thermo-elastic waves in liquids and specific heat and thermal conductivity of rheological bodies are calculated after the method developed by Debye[57], Brillouin[53][64], Lucas[54][55][56], and Oomori[63]. The result obtained shows that the relaxational effect hardly contributes to the numerical values of specific heat and thermal conductivity in usual liquids, because of the small values of elastic relaxation times of liquids.

In Chapter VIII, the theory of anisotropic rheological bodies was extended along the line of consideration of the elastic relaxation, whose isotropic case was already shown in Chapter III. Thermal stress and thermal conductivity in anisotropic bodies were also discussed somewhat in detail. Application of the theory is also briefly mentioned. Theory of surface rheology can be also extended by the present theory. Some problems to be solved are stated, without detailed calculations.

Finally, in Chapter IX, calculations are made on the velocities and absorption coefficients of longitudinal and transverse ultrasonic waves in a visco-elastic body under initial stress, being based on Sakadi-Takizawa's formalism[71]. The ultrasonic birefringence in the field of constant initial stress was discussed. The plot of wave-velocities and absorption coefficients versus wave-frequency is given. The phase-difference between two differently polarized transverse waves is also calculated. For small extra shearing rigidity and small initial stresses, the phase-difference of two transverse waves is proportional to the product of wave-frequency and the difference of components of initial stress. Briefly mentioned is the so-called *acousto-viscoelastic* method for measuring stress, which is quite analogous to the *photo-elastic one.*

In the present discussions, the author took implicitly into account the relaxation among different states of energy, for example, the relaxation between translational and vibrational states, the relaxation between many structures of molecular crystals, and the relaxation of monomer-polymer formations etc. Especially, the relaxation due to the thermal stress may correspond roughly to the physical picture that the sudden increase of local temperature causes the stress after a short but finite delay of time. In other words, after the local temperature has risen, it takes a finite interval of time to create the operative stress.

The relaxation appeared in the expression of heat flux, *i.e.* the *generalized Fourier law,* may contribute to the physical phenomena in a rapidly changing field, such as in ultrasonic field of extremely high frequency. The physical background of the thermal conductivity expressed as integral operators has some ambiguity in its relativistic derivation[51]. On the other hand, the phenomenological theory presented in this paper can be easily accepted, taking into consideration that the heat flux in a rapidly changing field may be proportional to the averaged generalized force such as a time-averaged value of temperature-gradient in the past.

The equation of conservation of energy with the *generalized Fourier law* discussed above in Chapter IV, can serve to describe the supersonic and hypersonic field, simultaneously with the equations of motion given in Chapter III. These fundamental equations, expressed in linear form, are quite useful to describe the wave field with relaxational phenomena, especially taking explicitly the elastic relaxations and the thermal relaxations into account.

The phenomena due to the other causes not cited above, however, may sometimes play an important part in the dynamical behaviour of rheological bodies. In such cases, the theory presented here can not be available without keen criticism. For example, the scattering of waves due to the constituent molecules, the cavity formation in liquids, and the absorption due to the non-linear terms etc., may be out of the scope of the present theory of thermo-mechanical relaxation.

Here, in the present paper, the rheological behaviour of the media is mainly focused to describe the dynamical and thermal character of liquids. The discussion can be easily applied to interpret the physical properties in gases and solids, *mutatis mutandis*. In other words, the slight modification of numerical values in the rheological and thermodynamical operators, corresponding to the elastic moduli, coefficients of thermal expansion, specific heats, and thermal conductivity etc., make this theory applicable to various kinds of continuous bodies of gaseous phase, as well as liquid and solid phases, respectively.

The theory presented here can be also extended to the theory of electro-magnetic relaxation, *mutatis mutandis, i.e.* with slight modification and symbolical interpretation of the present theory. Thus the unified phenomenological theory of thermo-electro-magneto-rheology can be easily extended along the line of consideration, as was suggested in the present theory.

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