ON THE THERMAL STRESS IN LIQUIDS UNDER SUPERSONIC AND HYPERSONIC REGIONS

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I. Preliminaries

In recent years, it has been made clear that the liquids[1] under high frequency oscillations undergo the mechanical behaviours different more or less from the one expressed by the classical Navier-Stokes equation, and many experimental evidences have been accumulated[2] concerning the fluids of polyatomic molecules, which actually show remarkable absorption and dispersion of high frequency sound wave.

In some highly viscous solutions of high polymers, which do not obey the ordinary Newton's viscosity law, stating that the shearing stress is proportional to the deformation of velocity (often called gradient of velocity), it has been presumed that such *non-Newtonian liquids* actually have the *rigidity of fugitive nature*. The pure liquids or crystalloïdal solutions, also, may be considered to have some *rigidity* under sufficiently high frequency oscillations.

Some solids such as metals, glasses, or asphalts, undergo plastic deformation by a force acting sufficiently long time. Recently the mechanical and elastic properties of solids of high polymer have been investigated[3] and they also show the anomalous dispersion and absorption of high frequency sound wave and the dielectric losses. These effects are interpreted by the delay of the finite time of cutting off loose bindings or closs-linkages of the constituent molecules.

The molecular kinetic theories to interpret these phenomena in liquids[4][2] and solids[5][6] as well as gases[7][8][16] of polyatomic molecule, have been tried, and up to the present the quantitative explanation of these phenomena especially in liquids from the modern molecular kinetic theories has not yet been quite satisfactory.

On the other hand, the treatment of the oscillatory charactors of the continua for such a high frequency mechanical motion, has been tried by Oshida[10] (Osida[9]) and Frenkel and Obratzov,[11][12] being based on the phenomenological model of the stress-strain relations. Osida[9] developed a theory to explain the high velocity of the waves of thermal motion in liquids, which, often called *hypersonic waves*,[42] found by Raman and Venkateswaran[13] in 1939. His theory, was soon found to be a special case of Frenkel-Obratzov's. Recently, however, taking into account the finite number of relaxation times and rheological constants, he extended his theory[10] so as to include Frenkel-Obratzov's as a special case.

It is the absorption and dispersion of sound wave in liquids with which the present author intends to mainly concern under high frequency regions of mechanical oscillation. In this paper, considering the thermal expansion in liquids under such a high frequency of mechanical oscillation, the author presents a theory by postu-

lating finite number of relaxation times for the stress occuring in liquids, which originates both from the displacements of materials and from the thermal expansion in liquids. Considering the Maxwellian relaxational process occuring in liquids, a generalized thermodynamical equation of state is presented. The *thermal expansion coefficients* and *rheological constants* are all considered as operators of Maxwellian type accompanied by relaxation times. The generalized stress-strain-temperature relation, thus obtained by the present author, is conveniently applied for plasto-elastic bodies, and this relation includs both Oshida's and Frenkel-Obratov's as special cases.

The internal energy (in the macroscopic sense) *not in a thermal equilibrium,* is attempted to be expressed by temperature and strain (or temperature and stress) as two kinds of independent variable of state. The dependence of the internal energy on the two independent variables (i.e. temperature and strain) is assumed to be subjected to the *Maxwellian relaxational process.*[14] And it is noteworthy that the results obtained are formally very similar to the expression obtained by Kneser[4][7][15] and Rutgers[7] from the bases of the molecular collision between the normal and the excited molecules.

Considering that the equation of state is a generalization of the one obtained by Oshida and Frenkel, and further the expression of the internal energy used here is very similar to that of Kneser's, the present theory has the favourable characters of both Frenkel's and Kneser's. Accordingly, the temperature dependence of the absorption of the supersonic waves, for example, shows the collective features of Frenkel's and Kneser's. In another words, in some normal liquids such as benzene and carbon dioxide, the absorption of the sound wave rises with increasing temperature, showing that the mechanism considered by Kneser plays rather an important rôle. On the contrary, in some anomalous liquids (in most cases the constituent molecules having hydrogen bonds and being called *associative liquids*) such as water and acetic acid, the absorption decreases with increasing temperature, showing that the effects of the internal viscosities including the compressional and the shearing ones, are supposed to predominate rather than that of the specific heat terms.

The mechanical behaviour of liquids under the supersonic and the hypersonic regions of frequency can be interpreted by this theory. The possibility of the existence of the transverse wave (shear wave) in liquids is also discussed. In this case, however, owing to the appearance of temperature only in the diagonal terms of the stress tensor, the temperature terms have no influence explicitly on the dynamical equations of the shear wave, except through the expression of the internal energy. The equation of conservation of energy, in this case, plays the rôle of determining the relation between the displacement and temperature. Then the term of specific heat similar to that of Kneser's is also rather important.

The double refraction is supposed really to appear, owing to the compressional and shearing rigidities appearing in liquids under high frequency mechanical oscillations. The compressional ones may appear above the frequencies of the order 10^{10} or 10^{11} cycles per second, which corresponds to the order of the appearance of the compressional rigidities of fugitive nature in most kinds of liquid. On the other hand, however, the flow birefringence due to the shearing rigidities may appear about the 10^8 cycles per second. Thus the one of the experimental methods is offered to determine the existence of the shear wave at these regions of frequency. The experimental evidence of the birefringence due to the compressional

moduli of fugitive nature has not yet been discovered at the present, because of the experimental difficulties of generating the mechanical oscillations of such an extremely high frequency sound wave. The frequency at our hand being under the order 10^6 Herz at present, the possibility of the existence of this kind of refraction is pointed out in most liquids under the supersonic regions of frequency (above 10^{10} Hz.). The experiments in those supersonic regions of frequency are especially of great interest and now are left to the further investigations in future.

The relation of the author's present theory to the molecular kinetic theory is not discussed in the present paper. Later, the discussion about this relation shall be extended along the line similar to the one which we owe mainly to Kneser.

The existence and the high velocity of the hypersonic waves, or the elastic waves of extremely high frequencies caused by thermal agitation in liquids, as found in solids,[17] were also explained from the present theory, which may be comprehensible by the theory of the collision of the constituent molecules in liquids.

In the present paper, the mechanical properties of liquids under the supersonic and the hypersonic regions are mainly focused to describe and are discussed in their general features. The generalized theory proposed here for the expression of the rheological phenomena, however, finds itself not only useful for the liquid states (pure liquids, liquid mixtures, and solutions), but also conveniently applicable, *mutatis mutandis,* to the plasto-elastic bodies in any phase, and the solids of high polymeric substances as well as the gases and their mixtures of polyatomic molecules.

II. Notations

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

ξ_i : components of displacement,

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

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

A_{ij} : components of stress tensor, including explicit temperature terms,

A_{ij}^0 : components of stress tensor, no influence of the thermal stress being considered,

t : time,

$\bar{\rho} = \rho_0 + \rho$: density,　　ρ_0 : density in static state,

$\bar{p} = p_0 + p$: pressure,　　p_0 : pressure in static state,

$\bar{T} = T_0 + T$: temperature,

T : temperature deviation from the original temperature T_0.

U : internal energy per unit mass (in the macroscopic sense), including both translational and vibrational energies of constituent molecules,

q_j : components of heat current vector, possibly put $= -\kappa \dfrac{\partial T}{\partial x_j}$,

κ : thermal conductivity, corresponding to the transfer of the translational energy to the translational energy of molecules,

k_0 : static volume modulus,

λ_r : partial volume modului,　　λ_r' : partial volume viscosities,

μ_r : partial shearing rigidities,　　μ_r' : partial shearing viscosities,

$\dfrac{\alpha_r}{k_0}$: coefficients of partial cubic thermal expansion,

τ_r, $\tau_r^{(1)}$, $\tau_r^{(2)}$, $\tau_r^{(3)}$ and $\tau_r^{(4)}$: relaxation times,

C_0 : specific heat at constant volume, corresponding to the static state,

C_r : partial specific heats at constant volume,

ε_0 and $\varepsilon_{r,ij}$: material constants,

ω : circular frequency $= 2\pi\nu$, $\quad\nu$: frequency,

v : velocity of wave,

a : amplitude absorption of wave per unit length.

For the abbreviation, we shall write the differential operator with respect to time as follows:

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

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

III. Dynamical Equation of State
A. Stress-Strain Relations

Let us derive the general stress-strain relations in a plasto-elastic body by considering the hysteresis function of Volterra,[18],[19] which include Maxwell's relation[14] for plasto-elastic body as a special case. At first we shall confine ourselves in the stress-strain relations accompanied by no explicit temperature effect. Then in the section B of this chapter the effect of temperature shall be taken into account. The stress components, no temperature effect being considered, shall be denoted by the superscript ^{0}. It would be better to consider that the shearing stress A_{ij}^0 $(i \neq j)$, consists of many components $A_{ij}^{(1)}$, $A_{ij}^{(2)}$, $A_{ij}^{(3)}$, ..., each of which is prportional to the shearing strain σ_{ij} $(i \neq j)$ with different coefficients μ_1, μ_2, μ_3, ... Taking m components for the stress, we obtain

$$A_{ij}^0 = \sum_{r=1}^{m} A_{ij}^{(r)}. \qquad (i \neq j) \tag{1}$$

If the deformation obeys the ordinary Hooke's law, we obtain

$$A_{ij}^{(r)} = -2\mu_r \cdot \sigma_{ij}, \qquad (r = 1, 2, 3, \ldots, m) \tag{2}$$

where μ_r's are constants which express, so to speak, the *partial shearing rigidities*. In the plasto-elastic body, however, we suppose that any component $A_{ij}^{(r)}(t)$ of the shearing stress $A_{ij}^0(t)$, being a function of time t, is not directly proportional to the shearing strain $\sigma_{ij}(t)$ itself as in the theory of elesticity, but is proportional to some average value[20] of deformation in the past, accordingly we can write, instead of (2),

$$-A_{ij}^{(r)}(t) = 2\mu_r \cdot \sigma_{ij}(t) - 2\mu_r \int_0^\infty h_r(t') \cdot \sigma_{ij}(t - t')dt', \qquad (i \neq j) \tag{3}$$

where $h_r(t')$ is a weight function, often called the *"fonction héréditaire"* or *hysteresis function*, with the condition:

$$\int_0^\infty h_r(t')dt' = 1.$$

The expression (3) includes the phenomena of the stress decaying with time, owing

to the plasticity of the material under consideration. Although the process of relaxation is incomprehensible in detail in the present state, it is natural to take different hysteresis function for different mechanism.[21] Accordingly we shall denote the hysteresis function of the r-th component of the shearing stress as $h_r(t')$. Thus the collective shearing stress is expressed, from (1), (2), and (3), by

$$A_{ij}^0 = -\sum_{r=1}^{m} 2\,\mu_r \cdot \left\{\sigma_{ij}(t) - \int_0^{\infty} h_r(t') \cdot \sigma_{ij}(t-t')\,dt'\right\}. \qquad (i \neq j) \tag{4}$$

As for the normal stress A_{ii}^0, we can also consider l components, i.e.

$$A_{ii}^0 = \sum_{r=1}^{l} A_{ii}^{(r)}, \qquad (i \text{ fixed}) \tag{5}$$

and

$$A_{kk}^0 = A_{11}^0 + A_{22}^0 + A_{33}^0 = \sum_{r=1}^{l} A_{kk}^{(r)}. \tag{6}$$

Debye in his early paper[22] suggested that the volume dilatation has a finite relaxation time, and Frenkel-Obratzov,[11] Oshida,[10] Kneser,[23] and others[24][25] have also considered this phenomenon. Taking into account the finite number of relaxation times, as Oshida interpreted, for the volume dilatation, the relation between the pressure deviation p and the dilatation $\sigma_{kk} = \sigma_{11} + \sigma_{22} + \sigma_{33}$ takes the form similar to the relation (4). In this case, however, the situation is somewhat different from the one as expressed in the case of the shearing stress. If the volume dilatation is produced suddenly and kept constant (i.e. kept in a state of iso-strain), the pressure decays after sufficiently long time, and does not vanish but really approaches to a constant value, still remaining finite (cf. Fig. 1). This constant thermostatical value, being related to the equation of state of the substance considered, is proportional to the volume dilatation. Taking this equal to $-k_0 \cdot \sigma_{kk}$, where k_0 is static volume modulus, accordingly we obtain for the residual pressure $p - (-k_0 \cdot \sigma_{kk})$, and not for the pressure itself,

$$-p - k_0 \cdot \sigma_{kk} = \frac{1}{3} \sum_{r=1}^{l} A_{kk}^{(r)}, \tag{7}$$

and

$$\frac{1}{3} A_{kk}^{(r)} = \lambda_r \cdot \sigma_{kk} - \lambda_r \int_0^{\infty} g_r(t') \cdot \sigma_{kk}(t-t')\,dt', \tag{8}$$

where λ_r's express, so to speak, the *partial moduli of compression (partial bulk moduli)*, and $g_r(t')$ are hysteresis functions. From equations (4)~(8), and considering that the pressure is defined by the following expression:

$$\bar{p} = p_0 + p = \frac{1}{3} A_{kk}^0 = p_0 - \left(k_0 \cdot \sigma_{kk} + \frac{1}{3} \sum_{r=1}^{l} A_{kk}^{(r)}\right), \tag{9}$$

with the initial pressure p_0, we shall completely set up the stress-strain relations for the isotropic medium, in the symmetric tensorial form so that the relation (9) should hold. Hence, the resultant stress-strain relations are obtained as follows:

$$A_{ij}^{0} = p_0 \cdot \delta_{ij} - k_0 \cdot \sigma_{kk} \cdot \delta_{ij} - \Big[\sum_{r=1}^{l} \lambda_r \cdot \Big\{ \sigma_{kk}(t) - \int_0^{\infty} g_r(t') \cdot \sigma_{kk}(t-t') dt' \Big\}$$

$$- \frac{2}{3} \sum_{r=1}^{m} \mu_r \cdot \Big\{ \sigma_{kk}(t) - \int_0^{\infty} h_r(t') \cdot \sigma_{kk}(t-t') dt' \Big\} \Big] \delta_{ij}$$

$$- 2 \sum_{r=1}^{m} \mu_r \cdot \Big\{ \sigma_{ij}(t) - \int_0^{\infty} h_r(t') \cdot \sigma_{ij}(t-t') dt' \Big\}, \qquad (10)$$

with

$$\int_0^{\infty} g_r(t') dt' = 1,$$

and

$$\int_0^{\infty} h_r(t') dt' = 1.$$

For the continuous distributions of relaxation times, we may replace the summations over r by the integrations.

As a special case, putting the hysteresis functions in the form:

$$g_r(t') = \frac{1}{\tau_r} \cdot e^{-\frac{t'}{\tau_r}}, \qquad (\tau_r > 0)$$

$$h_r(t') = \frac{1}{\tau_r^{(1)}} \cdot e^{-\frac{t'}{\tau_r^{(1)}}}, \qquad (\tau_r^{(1)} > 0) \qquad (11)$$
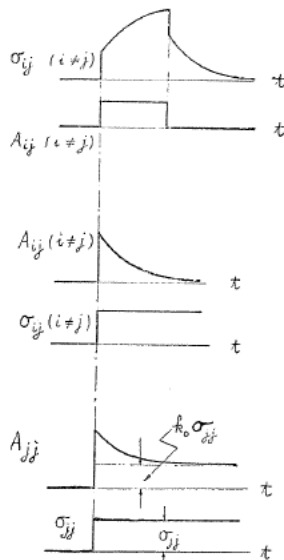
and taking the oscillatory motion, we obtain the extension of the Maxwell's relation for the plasto-elastic body, i.e.

$$A_{ij}^{0} = p_0 \cdot \delta_{ij} - \Big(k_0 + \sum_{r=1}^{l} \frac{\lambda_r' D}{1+\tau_r D} - \frac{2}{3} \sum_{r=1}^{m} \frac{\mu_r' D}{1+\tau_r^{(1)} D} \Big) \sigma_{kk} \cdot \delta_{ij} - 2 \sum_{r=1}^{m} \frac{\mu_r' D}{1+\tau_r^{(1)} D} \sigma_{ij}, \quad (12)$$
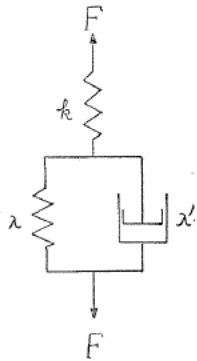
FIG. 1a. Mechanical model of Maxwellian relaxational process. (after Frenkel)

F: Force,
σ : Strain,
k and λ: Spring,
λ': Dashpot.

Timal change corresponding to FIG. 1a.

$$A_{ij} = -2 \frac{\mu' D}{1+\tau^{(1)} D} \sigma_{ij}, \qquad (i \neq j)$$

$$D \equiv \frac{d}{dt} = \frac{\partial}{\partial t}.$$

$$A_{jj} = -\Big(k_0 + \frac{\lambda' D}{1+\tau D} \Big) \sigma_{jj}$$

$$+ \frac{\alpha \tau^{(2)} D}{1+\tau^{(2)} D} T.$$

$$(j \text{ fixed})$$

FIG. 1b. Timal change (absolute value) of stress-strain-temperature.

FIG. 1. Stress-strain-temperature relation.

where

$$D = \frac{d}{dt} = \frac{\partial}{\partial t},$$

and $\lambda_r' = \lambda_r \tau_r$ and $\mu_r' = \mu_r \tau_r^{(1)}$ are, so to speak, the *compressional* and the *shearing viscosities*, respectively. $\tau_r^{(s)}$'s have a dimension of time, and are the measures of the relaxational process. They are often called *relaxation times*.

If we take the functional forms for the hysteresis functions as:

$$\left. \begin{array}{ll} g_r(t') = \dfrac{1 + \tau_r^2 \omega_{0r}^2}{\tau_r} \cdot e^{-\frac{t'}{\tau_r}} \cdot \cos \omega_{0r} t', & (\tau_r > 0) \\[3mm] h_r(t') = \dfrac{1 + \tau_r^{(1)2} \omega_{0r}^{(1)2}}{\tau_r^{(1)}} \cdot e^{-\frac{t'}{\tau_r^{(1)}}} \cdot \cos \omega_{0r}^{(1)} t', & (\tau_r^{(1)} > 0) \end{array} \right\} \tag{13}$$

and further take the oscillatory motion of the material points, we can also obtain a generalization of the equation of state given by Richardson,[26][52] who considered the mechanism of the absorption and dispersion of sound wave as originated from the existence of resonators in molecules, which may be considered as rotators or oscillators with eigen-frequencies ω_{0r} and $\omega_{0r}^{(1)}$. Sometimes at certain region of time, $e^{-\frac{t'}{\tau_r^{(s)}}} \cdot \cos \omega_{0r}^{(s)} t$ become negative, while, in the course of time, at some other region they take positive values.

Because of taking both positive and negative values, these hysteresis functions have no longer the meaning of weight functions in the strict sense. Their physical importance above cited, however, sometimes impelle us to use these types of function. In this case if $\omega_{0r}^{(s)} \to 0$, or if the frequency of the wave with which the wave propagates through the liquids, is very large compared with the eigen-frequencies $\omega_{0r}^{(s)}$ of the resonators, the results obtained reduce to the above mentioned case of no resonators, leading to the types of the Maxellian relaxational process (11). Andrade[27] supposed that there might be such a *resonance absorption* in some cases. But, considering that the molecular eigen-frequencies appear only in higher frequency regions such as over 10^{10} Hz. (for example in the inversion-spectrum of NH_3) Here in the present paper, for the sake of simplicity and in the rheological fashion à la mode, we shall take the hysteresis function of the Maxellian type (11). Then, the most general stress-strain relations for the plasto-elastic bodies subjected to the Maxellian relaxational process, are expressed as (12).

B. Thermal Stress

Now we shall consider the thermal expansion in liquids under high frequency oscillations. In such a non-equilibrium state as the supersonic and the hypersonic waves create, the temperature deviation is 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 sometimes we should treat even the tensor of temperature, corresponding to the momenta of the molecules. Accordingly it may sometimes be rather important to take into account the quantity corresponding to the temperature tensor.[3][23] But here we shall consider merely a scalar

quantity of temperature deviation as an independent variable of 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 average value of temperature in the past, as in the case of the strain already disscussed. In this point the behaviour of the thermal stress as a function of temperature greatly differs from the ordinary thermal expansion as treated in the theory of *thermostatics*. Accordingly, as in the case (8), considering n components for the thermal expansion, normal the stress is expressed by

$$A_{ii}(t) - A_{ii}^0(t) = \sum_{r=1}^{n} \alpha_r \cdot \left\{ T(t) - \int_0^\infty f_r(t') \cdot T(t-t')dt' \right\}, \quad (i \text{ fixed}) \qquad (14)$$

with the condition for the weight functions $f_r(t')$:

$$\int_0^\infty f_r(t')dt' = 1. \quad (i \text{ fixed})$$

As for the forms of the weight function, we may take, for example, either a resonator type (13) or a Maxwellian type for the oscillatory motion of the medium. Considering the Maxwellian type as in (11), we can see that the following relations hold for the normal stress and temperature:

$$A_{ii}(t) - A_{ii}^0(t) = \sum_{r=1}^{n} \frac{\alpha_r' D}{1 + \tau_r^{(2)} D} T, \quad (i \text{ fixed}) \qquad (15)$$

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

The first term in the right-hand side of (14) 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 (14) or (15) means that temperature does not cause the normal stress instantaneously but there exists finite time interval to create the pressure after a sudden uprise of temperature. It may also roughly correspond to the expression that after the local temperature has risen, the temperature takes contribution to pressure with a small but finite delay of time.

Combining (12) and (15), we finally obtain the *dynamical equation of state* for the plasto-elastic bodies subjected to the Maxwellian relaxational process:

$$\left. \begin{aligned} A_{ij} &= A_{ij}^0 + \sum_{r=1}^{n} \frac{\alpha_r' D}{1 + \tau_r^{(2)} D} T \cdot \delta_{ij}, \\ A_{ij}^0 &= p_0 \cdot \delta_{ij} - \left(k_0 + \sum_{r=1}^{l} \frac{\lambda_r' D}{1 + \tau_r D} - \frac{2}{3} \sum_{r=1}^{m} \frac{\mu_r' D}{1 + \tau_r^{(1)} D} \right) \sigma_{kk} \cdot \delta_{ij} \\ &\quad - 2 \sum_{r=1}^{m} \frac{\mu_r' D}{1 + \tau_r^{(1)} D} \sigma_{ij}, \end{aligned} \right\} \qquad (16)$$

with

$$\alpha_r' = \alpha_r \tau_r^{(2)}.$$

The expression (16), including both strain and temperature terms explicitly, can be usefully applicable to describe the rheological behaviours of plsto-elastic bodies, i.e. internal viscosity effects,[10)-12) 23)] structural changes,[30)] and monomerpolymer

formation[31)39)] in the phase under consideration. (cf. Fig. 2.)

The stress-strain relations (12) are the same as derived by Oshida[10)] and include the results obtained by Frenkel-Obratzov,[11)] and by Oshida himself[9)] in 1941, as special cases. The relation (16) is an extension of (12), and also includes the equations of state of liquids obtained by Tisza,[29)] Hall,[30)] and others[23)−25)] as special cases.

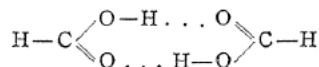$$H-C\diagdown\kern-1.2em\diagup{}^{O-H\ldots O}_{O\ldots H-O}\diagup\kern-1.2em\diagdown C-H$$

FIG. 2. Associative Liquids.

Hydroxyl (OH) and amino (NH₂) units in molecules make sometimes association,[31)] forming *multi-molecular groups*, i.e. *polymers*, because of their *hydrogen bonds* (O . . . H). The actual binding may take the ring- or chain-forms. Formic acid in liquid state shows a vibrational band at 3080 cm⁻¹. In gaseous phase, its characteristic vibration appears at 3570 cm⁻¹, due to the O—H vibration. Hydrogen bond makes also the bridges[57)] as follows: O—H . . . N, O—H . . . S, and N—H . . . N etc.

IV. Conservation of Energy

Kneser[7)15)] and others[1)2)] considered that the dispersion and absorption of supersonic wave originated from the delay of energy exchange between the exited and the normal states of molecules. Accordingly the medium, through which the wave propagates, is considered as a mixture of two kinds of molecule, 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 wave in gases of poly-atomic molecules. Later, this treatment was extended to the consideration of the supersonic phenomena in non-associated liquids.[4)] Kneser took the assumptions that 1) one of 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 change caused by the disturbance of the elastic wave is adiabatic.

In an early paper, Herzfeld and Rice,[32)] and others[33)] 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 the 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 for 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 coodinate space, having the following relation with initial temperature T_0:

$$C'(T'-T_0)+C''(T''-T_0)=C'''(T'''-T_0), \tag{17}$$

where T', T'', and T''' are the translational, internal (vibrational), and thermostatical

temperatures respectively, and C', C'', and C''' are the corresponding specific heats. For sufficiently slow motion, the following relations hold:

$$T' = T'' = T''',$$

and

$$C' + C'' = C'''. \tag{18}$$

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

These methods of dividing the system considered into the subsystems,[34] in which the *thermostatical equilibrium* is maintained, is of frequent use and may offer to some approach to the thermodynamics not in equilibrium. These methods perphaps correspond to the treatment of the small deviation from the thermostatical equilibrium. The assumption of the heat current vector, which we owe to Stokes and Kirchhoff, stating that the heat stream 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. And in the present paper, we shall express the equation of conservation of energy at the macroscopic point of view (i.e. based on the phenomenological model) for the dynamical state including the relaxational process.

The equation of conservation of energy[35] of the system considered states that the increment of the macroscopic internal energy (included both translational and vibrational energies) is caused by the work done due to the stress and the thermal conduction between the molecules in the same sort of energy type. This is written as:

$$\bar{\rho}\frac{\partial U}{\partial t} = -\left(A_{ij}\cdot\frac{\partial \sigma_{ij}}{\partial t} + \frac{\partial q_j}{\partial x_j}\right), \tag{19}$$

where U is the internal energy per unit mass (in the macrocopic sense). And, κ being the thermal conductivity, the heat current vector q_j may be put according to Stokes-Kirchhoff as follows:

$$q_j = -\kappa\frac{\partial T}{\partial x_j}. \tag{20}$$

This means that the heat transfer takes place by the collision between the same sort of energy type, i.e. the translational to the translational, and the rotational to the rotational energy.

While, as for the expression of the macroscopic internal energy, we may consider as follows. Taking two kinds of independent variable as temperature and strain, the energy increment δU_σ in the *iso-strained state*, is proportional to the temperature increase δT, and the proportionality constant is the specific heat at constant volume, as usual in the *thermostatics*. The sudden energy increase, however, is assumed also to proportional to the average value of temperature increment in the past as well as to the temperature uprise itself. Accordingly, considering finite number of mechanisms contributing to the internal energy, we can also state

$$\delta U_\sigma(t) = C_0 \cdot \delta T(t) + \sum_{r=1}^{s} C_r \cdot \left\{ \delta T(t) - \int_0^\infty \bar{f}_r(t') \cdot \delta T(t-t') dt' \right\}, \tag{21}$$

with

$$\int_0^\infty \bar{f}_r(t') dt' = 1,$$

for the hysteresis functions $\bar{f}_r(t')$.

On the other hand, the energy increment δU_T, subjected to the *iso-thermal process*, shall be also expressed as:

$$\delta U_T(t) = \varepsilon_0 \cdot \delta\sigma_{kk}(t) + \sum_{r=1}^{q} \varepsilon_{r,ij} \cdot \left\{ \delta\sigma_{ij}(t) - \int_0^\infty \bar{\bar{f}}_r(t') \cdot \delta\sigma_{ij}(t-t') dt' \right\}, \tag{22}$$

with the condition for the hysteresis functions:

$$\int_0^\infty \bar{\bar{f}}_r(t') dt' = 1.$$

The first term of the right-hand side of (22) is of great importance as to the explanation of thermal stress in a suddenly changing process.[36] The second terms are the ones analogous to the rheological relaxational process.

Combining the two expressions (21) and (22), we shall finally complete the expression of the internal energy δU in the macroscopic sense:

$$\delta U = \delta U_\sigma + \delta U_T. \tag{23}$$

Let us take the Maxwellian relaxational process and presume the oscillatory motion of the liquids, as we have already assumed for the stress-strain relations, (21) and (22) reduce to

$$\delta U_\sigma = \left\{ C_0 + \sum_{r=1}^{s} \frac{C_r \tau_r^{(3)} D}{1 + \tau_r^{(3)} D} \right\} \cdot \delta T, \tag{24}$$

$$\delta U_T = \left\{ \varepsilon_0 \cdot \delta_{ij} + \sum_{r=1}^{q} \frac{\varepsilon_{r,ij} \tau_r^{(4)} D}{1 + \tau_r^{(4)} D} \right\} \cdot \delta\sigma_{ij}, \tag{25}$$

with relaxation times $\tau_r^{(3)}$ and $\tau_r^{(4)}$. C_0 is the so-called *static specific heat* at constant volume, and C_r the so called *partial specific heats* at constant volume.

It is of great interest to mention that the expression (24) of the operator corresponds to the specific heat for the oscillatory motion and is formally equivalent to the expression of the specific heat obtained by Kneser.[1][4] If we designate by C_∞ the specific heat for the translation of the molecules, accordingly if C_∞ is the limiting value of $\frac{\delta U_\sigma}{\delta T}$ with infinite frequency, we obtain from (24),

$$C_\infty = C_0 + \sum_{r=1}^{s} C_r. \tag{26}$$

By using (26), we can write the specific heat operator as:

$$C_0 + \sum_{r=1}^{s} \frac{C_r \tau_r^{(3)} D}{1 + \tau_r^{(3)} D} = C_\infty - \sum_{r=1}^{s} \frac{C_r}{1 + \tau_r^{(3)} D}. \tag{27}$$

As a special case, if we take further $s=1$, and put $C_r = C_\infty - C_0'$, where C_0' is static specific heat, (27) reduces to the expression of the specific heat obtained by Kneser. Thus the equation (24) is a generalization of the expression of the specific heat term of Kneser's theory.

The expression (25) is of some interest in the theory of thermal stress when the disturbance caused by the thermal expansion propagates with finite velocity. The second term of (25) 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 $\varepsilon_{r,ij}$ are very small compared with ε_0. As the frequency of the shearing and normal waves in liquids increases greater and greater, and finally becomes $\omega\tau_r^{(4)} \fallingdotseq 1$ (at the hypersonic region), then the second terms may be comparatively effective. On the other hand, when $\omega\tau_r^{(4)} \ll 1$, we may neglect these terms comparing with the one involving ε_0.

Writing the differential form of the internal energy (23), we finally obtain:

$$dU = \left(C_0 + \sum_{r=1}^{s} \frac{C_r \tau_r^{(3)} D}{1 + \tau_r^{(3)} D} \right) \cdot dT + \left(\varepsilon_0 \cdot \delta_{ij} + \sum_{r=1}^{q} \frac{\varepsilon_{r,ij} \tau_r^{(4)} D}{1 + \tau_r^{(4)} D} \right) \cdot d\sigma_{ij}. \tag{28}$$

V. Application to the Supersonic Wave

The fundamental equations for the supersonic waves which state the conservation of momentum and of energy, are expressed respectively, in linear forms,

$$\bar{\rho} \frac{\partial u_i}{\partial t} = - \frac{\partial A_{ij}}{\partial x_j}, \tag{29}$$

$$\bar{\rho} \frac{\partial U}{\partial t} = - A_{ij} \cdot \frac{\partial \sigma_{ij}}{\partial t} + \kappa \Delta T, \tag{30}$$

with $u_j = \dfrac{\partial \xi_j}{\partial t}$.

The density change, if needed, is related to the strain through the equation of continuity:

$$\frac{d\rho}{dt} + \bar{\rho} \frac{\partial u_j}{\partial x_j} = 0. \tag{31}$$

Putting the resultant expression (12) for the stress and the internal energy (28) into (29) and (30), we obtain, neglecting the small quantities of higher order:

$$\rho_0 \frac{\partial^2 \xi_i}{\partial t^2} = \left\{ k_0 + \sum_{r=1}^{l} \frac{\lambda_r' D}{1 + \tau_r D} - \frac{2}{3} \sum_{r=1}^{m} \frac{\mu_r' D}{1 + \tau_r^{(1)} D} \right\} \frac{\partial \sigma_{kk}}{\partial x_i} + 2 \sum_{r=1}^{m} \frac{\mu_r' D}{1 + \tau_r^{(1)} D} \frac{\partial \sigma_{ij}}{\partial x_j}$$
$$- \sum_{r=1}^{n} \frac{\alpha_r' D}{1 + \tau_r^{(2)} D} \frac{\partial T}{\partial x_i}, \tag{32}$$

$$\rho_0 \left[\left\{ C_0 + \sum_{r=1}^{s} \frac{C_r \tau_r^{(3)} D}{1 + \tau_r^{(3)} D} \right\} \frac{\partial T}{\partial t} + \left\{ \varepsilon_0 \cdot \delta_{ij} + \sum_{r=1}^{q} \frac{\varepsilon_{r,ij} \tau_r^{(4)} D}{1 + \tau_r^{(4)} D} \right\} \frac{\partial \sigma_{ij}}{\partial t} \right]$$
$$= - p_0 \frac{\partial \sigma_{kk}}{\partial t} + \kappa \Delta T. \tag{33}$$

If we take the wave of volume dilatation (longitudinal wave), we obtain from (32) for the equations of motion,

$$\rho_0 \frac{\partial^2}{\partial t^2} \sigma_{kk} = \left(k_0 + \sum_{r=1}^{l} \frac{\lambda_r' D}{1 + \tau_r D} + \frac{4}{3} \sum_{r=1}^{m} \frac{\mu_r' D}{1 + \tau_r^{(1)} D} \right) \varDelta \sigma_{kk}$$

$$- \sum_{r=1}^{n} \frac{\alpha_r' D}{1 + \tau_r^{(2)} D} \varDelta T. \tag{34}$$

Owing to the scalar property of temperature term, which appears merely in the diagonal parts of the stress tensor, the explicit temperature term plays rather an important rôle in the equation of motion of the longitudinal wave.

As a special case of (34), we shall take the plane sound wave, progressing into the $+x_1$-direction with circular frequency ω:

$$\left.\begin{aligned}
&x_1 = x, \qquad \frac{\partial}{\partial x_2} = \frac{\partial}{\partial x_3} = 0, \\
&\xi_2 = \xi_3 = 0, \\
&\xi_1 = \mathfrak{R} \xi \cdot e^{i\omega t - \beta x}, \\
&T = \mathfrak{R} T \cdot e^{i\omega t - \beta x}, \qquad \mathfrak{Im}(\beta) > 0, \\
&\sigma_{kk} = \sigma_{11} = -\beta \xi \cdot e^{i\omega t - \beta x}, \\
&\sigma_{ij} = 0. \qquad (\text{except } i = j = 1)
\end{aligned}\right\} \tag{35}$$

The equations of motion (32) or (34), and of conservation of energy (30), are:

$$\rho_0 \frac{\partial^2}{\partial t^2} \sigma_{11} = \left(k_0 + \sum^{l} {}'' + \frac{4}{3} \sum^{m} {}'' \right) \varDelta \sigma_{11} - \sum^{n} {}'' \cdot \varDelta T, \tag{36}$$

$$\rho_0 \left[\left(C_0 + \sum^{s} {}'' \right) \frac{\partial T}{\partial t} + \left(\varepsilon_0 + \sum^{q} \frac{\varepsilon_{r,11} \tau_r^{(4)} D}{1 + \tau_r^{(4)} D} \right) \frac{\partial \sigma_{11}}{\partial t} \right]$$

$$= - p_0 \frac{\partial \sigma_{11}}{\partial t} + \kappa \varDelta T. \tag{37}$$

Putting (35) into (36) and (37), and neglecting the second and higher order small quantities, we obtain:

$$\left\{ \rho_0 \omega^2 + \left(k_0 + \sum^{l} \frac{i\omega \lambda_r'}{1 + i\omega \tau_r} + \frac{4}{3} \sum^{m} \frac{i\omega \mu_r'}{1 + i\omega \tau_r^{(1)}} \right) \beta^2 \right\} \xi + \sum^{n} \frac{i\omega \alpha_r'}{1 + i\omega \tau_r^{(2)}} \beta T = 0, \tag{38}$$

$$- i\omega \beta \left(\frac{p_0}{\rho_0} + \varepsilon_0 + \sum^{q} \frac{i\omega \varepsilon_{r,11} \tau_r^{(4)}}{1 + i\omega \tau_r^{(4)}} \right) \xi + \left\{ i\omega \left(C_0 + \sum^{s} \frac{i\omega C_r \tau_r^{(3)}}{1 + i\omega \tau_r^{(3)}} \right) - \frac{\kappa}{\rho_0} \beta^2 \right\} T = 0. \tag{39}$$

Considering that the simultaneous equations (38) and (39) have the non-trivial solution, we can see that β is to satisfy the following equation:

$$\begin{vmatrix}
\rho_0 \omega^2 + \left(k_0 + \sum^{l} {}'' + \frac{4}{3} \sum^{m} {}'' \right) \beta^2, & \sum^{n} \frac{i\omega \alpha_r'}{1 + i\omega \tau_r^{(2)}} \beta \\
-i\omega \beta \left(\frac{p_0}{\rho_0} + \varepsilon_0 + \sum^{q} \frac{i\omega \varepsilon_{r,11} \tau_r^{(4)}}{1 + i\omega \tau_r^{(4)}} \right), & i\omega \left(C_0 + \sum^{s} \frac{i\omega C_r \tau_r^{(3)}}{1 + i\omega \tau_r^{(3)}} \right) - \frac{\kappa}{\rho_0} \beta^2
\end{vmatrix} = 0,$$

i.e.

$$-\frac{\kappa}{\rho_0} A \beta^4 + \left[\left\{ i\omega C_0 - \sum^{s} \frac{\omega^2 C_r \tau_r^{(3)}}{1 + i\omega \tau_r^{(3)}} \right\} A - \kappa \omega^2 - \sum^{n} \frac{\omega^2 \alpha_r'}{1 + i\omega \tau_r^{(2)}} \cdot \left\{ \frac{p_0}{\rho_0} + \varepsilon_0 + \right. \right.$$

$$\left. \left. + \sum^{q} \frac{i\omega \varepsilon_{r,11} \tau_r^{(4)}}{1 + i\omega \tau_r^{(4)}} \right\} \right] \beta^2 + i\omega^3 \rho_0 \left(C_0 + \sum^{s} \frac{i\omega C_r \tau_r^{(3)}}{1 + i\omega \tau_r^{(3)}} \right) = 0, \tag{40}$$

with $A = k_0 + \sum\limits^{l} '' + \dfrac{4}{3} \sum\limits^{m} ''$.

In this equation, if we take $\kappa \to 0$, which may approximately hold for nonmetalic liquids, then we obtain:

$$
\begin{aligned}
\beta^2 = -\omega^2 \frac{\rho_0}{k_0} \div \Bigg[& 1 + \sum^{l} \frac{i\omega\lambda_r'/k_0}{1 + i\omega\tau_r} + \frac{4}{3}\sum^{m} \frac{i\omega\mu_r'/k_0}{1 + i\omega\tau_r^{(1)}} + \\
& + \sum^{n} \frac{i\omega\alpha_r'\varepsilon_0/(k_0 C_0)}{1 + i\omega\tau_r^{(2)}} \cdot \Big(1 + \frac{p_0}{\rho_0\varepsilon_0} + \sum^{q} \frac{i\omega\varepsilon_{r,11}\tau_r^{(4)}/\varepsilon_0}{1 + i\omega\tau_r^{(4)}} \Big) \times \\
& \times \Big(1 + \sum^{s} \frac{i\omega C_r\tau_r^{(3)}/C_0}{1 + i\omega\tau_r^{(3)}} \Big)^{-1} \Bigg].
\end{aligned}
\tag{41}
$$

The sound velocity v and the amplitude absorption a per unit length are obtained as follows:

$$
v = \frac{\omega}{\Im\mathrm{m}(\beta)},
\tag{42}
$$

$$
a = \Re(\beta).
\tag{43}
$$

For the limiting case $l = m = n = 1$, the curves of v/v_0 versus ω and of $2a/\Im\mathrm{m}(\beta)$ versus ω, are shown in Fig. 3, where $v_0 = \sqrt{k_0/\rho_0}$.

In general, it may be often considered that the partial elastic moduli, expressing the rheological behaviours of liquids, are small, compared with the *static* elastic modulus. We shall treat this case. Then, putting

$$
\frac{\lambda_r}{k_0}, \quad \frac{\mu_r}{k_0}, \quad \text{and} \quad \frac{\alpha_r}{k_0} \ll 1,
$$

and taking

$$
\frac{C_r}{C_0} \ll 1, \quad \frac{\varepsilon_{r,ij}}{\varepsilon_0} \ll 1,
$$

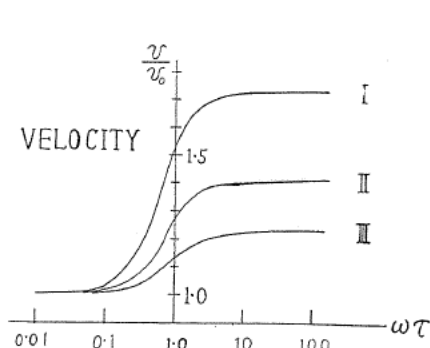and expanding the quantities in the power series of $\dfrac{\lambda_r}{k_0}$ etc., and retaining the terms
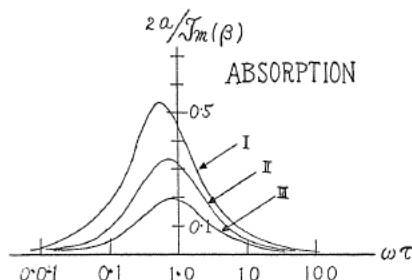

FIG. 3a. Velocity versus frequency.

FIG. 3b. Absorption versus frequency.

Curve I : $\Big(\lambda_1 + \dfrac{4}{3}\mu_1 + \dfrac{p_0}{\rho_0}\dfrac{\alpha_1}{C_0} \Big) \Big/ k_0 = 2$

　　 II :　　　 $''$　　　 $''$　　 $= 1$

　　 III :　　　 $''$　　　 $''$　　 $= 0.5$

up to the order $\frac{\lambda_r}{k_0}$ etc., we obtain:

$$\beta = \frac{i\omega}{v_0}\Big\{1 - \frac{1}{2}\sum^l \frac{i\omega\lambda_r'/k_0}{1+i\omega\tau_r} - \frac{2}{3}\sum^m \frac{i\omega\mu_r'/k_0}{1+i\omega\tau_r^{(1)}}$$

$$- \frac{1}{2}\sum^n \frac{i\omega\alpha_r'\varepsilon_0/(k_0 C_0)}{1+i\omega\tau_r^{(2)}} - \frac{1}{2}\frac{p_0}{\rho_0\varepsilon_0}\sum^n \frac{i\omega\alpha_r'/(k_0 C_0)}{1+i\omega\tau_r^{(2)}}$$

$$- \frac{1}{2}\sum^n \frac{i\omega\alpha_r'\varepsilon_0/(k_0 C_0)}{1+i\omega\tau_r^{(2)}}\cdot\Big(\sum^q \frac{i\omega\varepsilon_{r,11}\tau_r^{(4)}/\varepsilon_0}{1+i\omega\tau_r^{(4)}} -$$

$$- \sum^s \frac{i\omega C_r\tau_r^{(3)}/C_0}{1+i\omega\tau_r^{(3)}}\Big)\Big\}, \tag{44}$$

with

$$v_0 = \sqrt{\frac{k_0}{\rho_0}}, \tag{45}$$

which corresponds to the sound velocity at low frequency.

From (42) and (43), we obtain:

$$v = v_0\cdot\Big\{1 + \frac{1}{2}\sum^l \frac{\lambda_r'}{k_0}\frac{\omega^2\tau_r}{1+\omega^2\tau_r^2} + \frac{2}{3}\sum^m \frac{\mu_r'}{k_0}\frac{\omega^2\tau_r^{(1)}}{1+\omega^2\tau_r^{(1)2}}$$

$$+ \frac{1}{2}\sum^n \frac{p_0}{\rho_0}\frac{\alpha_r'}{k_0 C_0}\frac{\omega^2\tau_r^{(2)}}{1+\omega^2\tau_r^{(2)2}} + \frac{1}{2}\sum^n \frac{\alpha_r'\varepsilon_0}{k_0 C_0}\frac{\omega^2\tau_r^{(2)}}{1+\omega^2\tau_r^{(2)2}}$$

$$- \frac{1}{2}\sum^n \frac{\alpha_r'}{k_0}\frac{\omega}{1+\omega^2\tau_r^{(2)2}}\cdot\sum^q \frac{\varepsilon_{r,11}}{C_0}\frac{\omega\tau_r^{(4)}}{1+\omega^2\tau_r^{(4)2}}$$

$$+ \frac{1}{2}\sum^n \frac{\alpha_r'\varepsilon}{k_0 C_0}\frac{\omega}{1+\omega^2\tau_r^{(2)2}}\cdot\sum^s \frac{C_r}{C_0}\frac{\omega\tau_r^{(3)}}{1+\omega^2\tau_r^{(3)2}}\Big\}, \tag{46}$$

$$a = \frac{\omega^2}{v_0}\cdot\Big\{\frac{1}{2}\sum^l \frac{\lambda_r'}{k_0}\frac{1}{1+\omega^2\tau_r^2} + \frac{2}{3}\sum^m \frac{\mu_r'}{k_0}\frac{1}{1+\omega^2\tau_r^{(1)2}}$$

$$+ \frac{1}{2}\sum^n \frac{p_0}{\rho_0}\frac{\alpha_r'}{k_0 C_0}\frac{1}{1+\omega^2\tau_r^{(2)2}}$$

$$+ \frac{1}{2}\sum^n \frac{\alpha_r'\varepsilon_0}{k_0 C_0}\frac{1}{1+\omega^2\tau_r^{(2)2}}$$

$$+ \frac{1}{2}\sum^n \frac{\alpha_r'}{k_0}\frac{1}{1+\omega^2\tau_r^{(2)2}}\cdot\sum^q \frac{\varepsilon_{r,11}}{C_0}\frac{\omega^2\tau_r^{(4)2}}{1+\omega^2\tau_r^{(4)2}}$$

$$- \frac{1}{2}\sum^n \frac{\alpha_r'\varepsilon_0}{k_0 C_0}\frac{1}{1+\omega^2\tau_r^{(2)2}}\cdot\sum^s \frac{C_r}{C_0}\frac{\omega^2\tau_r^{(3)2}}{1+\omega^2\tau_r^{(3)2}}\Big\}. \tag{47}$$

About the dependence of the absorption on frequency, from (47) we can see that the first and second terms take the somewhat different features to the fifth and sixth terms. The formers are the ones obtained by Frenkel and Oshida, and are corresponding to the compressional and shearing viscosities; while the sixth corresponds to the term obtained by Kneser. Thus, taking adaptable values for either the formers or the latter, we can see that the frequency dependence of the absorption takes the same feature each other. Thus one of their theories, treating the mechanical behaviour of liquids, can interprete the relaxation phenomena. Owing to the nature of the specific heat terms and viscosity terms (both compressional and shearing ones included), the temperature dependence of these two

terms is quite different. And one of these theories can not explain the mutually different temperature dependences of the normal liquids and the associated liquids. In the present theory, however, we can successfully take into consideration these complicated temperature dependence of the absorption, because of the inclusion of both the specific heat terms and the viscosity terms. It may be considered that the specific heat terms can predominate in the normal liquids, and on the other hand the viscosity terms play rather an important rôle in the associated liquids. Naturally the liquids such as acetates, and acids, especially formic acids, in which the chemical reaction of forming monomers and dimers takes place, are accompanied with the relaxation of establishing the equilibrium between these two phases. (cf. Fig. 2.)

The third term in (47) is also of the same character as the first ones above discussed, and is originated from the relaxation phenomena of thermal expansion. The dependence of the term on frequency is similar to the viscosity terms.

As for the thermal conductivity, however, the thermal conduction in mercury plays very important rôle, whose effect, combined with the classical viscosity effect, is considered to occupy about 80% of the absorption[37] of the wave. (No relaxation phenomena are considered in mercury). On the contrary, in the usual liquids of polyatomic molecule, the relaxation phenomena predominate, and the effect of thermal conduction is rather small.[35][33] Thus the assumption made here that the thermal conduction can be neglected, is not so unrigorous. If we wish to take into account the effect of thermal conductivity κ, as Herzfeld and Rice[32] and others,[33] the exact solution of (40) is to be used, or the conductivity term can be treated as a perturbation, then the meaning of the static bulk modulus suffers modification and is different from the one k_0 for $\kappa \rightarrow 0$.

For sufficiently low frequencies, the equation (47) reduces to

$$a = \frac{2 \omega^2}{3 v_0^3 \rho_0} \left\{ \mu_1' + \frac{3}{4} \lambda_1' + \frac{3}{4} \frac{p_0}{\rho_0} \frac{\alpha_1'}{C_0} + \frac{3}{4} \frac{\alpha_1' \varepsilon_0}{C_0} + \mu_2' + \frac{3}{4} \lambda_2' + \ldots \right\}. \qquad (48)$$

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

$$a = \frac{2 \omega^2 \mu_1'}{3 v_0^3 \rho_0}, \qquad (49)$$

gives the classical dissipation, arising from the ordinary viscosity, which was derived by Stokes. Then λ_1' is what was called by Kirchhoff the second coefficient of viscosity,[56] and is considered to vanish for gases.

The last term in (47) due to the relaxation of specific heat, is the combination of, what is called by Kneser, the translational and vibrational heat terms depending upon the frequency.

The third term is due to the relaxation of thermal expansion, and is considered to express, in some sense, the chemical change of monomer-polymer formation,[31] combining with the viscosity relaxations of the first and second terms.

In general, the values of all relaxation times are different each other, owing to the different mechanisms of the relaxation. But sometimes it may be suggested that the relaxation of a component of the normal traction and that of a component of the tangential traction are to be attributed to a similar causes. In this case, it is natural that we may take almost equal time constants, e.g.

$$\frac{\lambda_r'}{\lambda_r} \fallingdotseq \frac{\mu_{r'}'}{\mu_{r'}} \fallingdotseq \frac{\alpha_{r''}'}{\alpha_{r''}},$$

i.e.

$$\tau_r \fallingdotseq \tau_{r'}^{(1)} \fallingdotseq \tau_{r''}^{(2)}.$$

Then the dynamical equation of state (16), can be a little simplified:

$$A_{ij} = p_0 \cdot \delta_{ij} - \left(k_0 + \sum \frac{\lambda_r - (2/3)\mu_r}{1 + \tau_r D} \cdot \tau_r \cdot D \right) \sigma_{kk} \cdot \delta_{ij}$$

$$- 2 \sum \frac{\mu_r \tau_r D}{1 + \tau_r D} \sigma_{ij} + \sum \frac{\alpha \tau_r D}{1 + \tau_r D} T \cdot \delta_{ij}. \tag{16'}$$

For the continuous distribution of the relaxation times, if necessary, we may replace the summations over r with the integrations. In most liquids of polyatomic molecule of simpler constitution, the distribution of relaxation times is discrete, and it is natural and sufficient to consider only the finite number of relaxation times.

The relaxation time of ordinary viscosity is considered to be very short, being the order 10^{-11} sec. for ordinary liquids. Accordingly we have $\omega\tau_1 \ll 1$ for the supersonic waves, whose frequencies lie between $10^5 \sim 10^8$ Hz. Then, considering only one more extra relaxation, we see that (47) becomes to

$$a = \frac{\omega^2}{2 v_0^3 \rho_0} \left\{ \lambda_1' + \frac{4}{3}\mu_1' + \frac{\lambda_2'}{1 + \omega^2 \tau_2^2} + \frac{(4/3)\mu_2'}{1 + \omega^2 \tau_2^{(1)2}} + \frac{p_0}{\rho_0} \frac{\alpha_1'}{C_0} \frac{1}{1 + \omega^2 \tau_1^{(2)2}} \right\}. \tag{50}$$

According to (50), a/ν^2 decreases with increasing frequency from

$$\frac{2\pi^2}{v_0^3 \rho_0} \left\{ \lambda_1' + \frac{4}{3}\mu_1' + \lambda_2' + \frac{4}{3}\mu_2' + \frac{p_0}{\rho_0} \frac{\alpha_1'}{C_0} \right\} \quad \text{to} \quad \frac{2\pi^2}{v_0^3 \rho_0} \left\{ \lambda_1' + \frac{4}{3}\mu_1' \right\}.$$

The fact that most liquids show no distinguishable change of a/ν^2 with frequency ν, can be interpreted that the second relaxation times are so small that the products $\omega\tau_2$, $\omega\tau_2^{(1)}$, and $\omega\tau_1^{(2)}$, are also fairly smaller than unity.

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

$$\tau_2 = \tau_2^{(1)} = \tau_1^{(2)} = \tau = 2.86 \times 10^{-7} \text{ sec.},$$

$$\frac{2\pi^2}{v_0^3 \rho_0} \left(\lambda_1' + \frac{4}{3}\mu_1' \right) = 1.515 \times 10^{-15} \text{ sec}^2. \text{ cm}^{-1}.,$$

and

$$\frac{2\pi^2}{v_0^3 \rho_0} \left(\lambda_2' + \frac{4}{3}\mu_2' + \frac{p_0}{\rho_0} \frac{\alpha_1'}{C_0} \right) = 1.600 \times 10^{-12} \text{ sec}^2. \text{ cm}^{-1}.,$$

(50) gives good agreement with the experimental data [39] as is shown in Fig. 4.
Considering that

$$\rho_0 = 1.049 \text{ g. cm}^{-3}.,$$

and

$$v_0 = 1.141 \times 10^5 \text{cm. sec}^{-1}. \text{ at } 0.5 \text{ MHz.,}$$

we have from above figures,

$$\lambda_1' + \frac{4}{3}\mu_1' = 0.120 \text{ poises},$$

$$\lambda_2 + \frac{4}{3}\mu_2 + \frac{p_0}{\rho_0}\frac{\alpha_1}{C_0} = 4.42 \times 10^8 \text{ dyne. cm}^{-2}.$$

If we identify μ_1' with ordinary coefficient of viscosity, which is 0.0146 poises for acetic acid at 20°C, the second coefficient of viscosity λ_1' should be equal to 0.100 poises. In this case, the postulation, that

$$\frac{\lambda_1}{k_0} = \frac{\lambda_1'}{k_0\tau} \ll 1, \quad \text{and} \quad \lambda_2 + \frac{4}{3}\mu_2 + \frac{p_0}{\rho_0}\frac{\alpha_1}{C_0} \ll k_0,$$

is sufficiently satisfied, considering that the static bulk modulus $k_0 = \rho_0 v_0^2$ has the figure approximately equal to 1.366×10^{10} dyne. cm^{-2}.

From the expressions obtained above, the dispersion is always accompanied with the absorption.

$$v = v_0 \cdot \left\{ 1 + \frac{1}{2}\left(\frac{\lambda_2}{k_0} + \frac{4}{3}\frac{\mu_2}{k_0} + \frac{p_0}{\rho_0}\frac{\alpha_1}{k_0 C_0} \right)\frac{\omega^2\tau^2}{1+\omega^2\tau^2} \right\}. \tag{51}$$

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

$$v = v_0 \cdot \left\{ 1 + \frac{\lambda_2 + (4/3)\mu_2}{2\,k_0} + \frac{p_0\alpha_1}{2\,k_0\rho_0 C_0} \right\}, \tag{52}$$

and the relative dispersion for the acetic acid becomes approximately 1.62% using the figures cited above.

Spakovskij's experiment[40] gives 0.9% relative dispersion for the frequency range 0.24~2.7 MHz., and from Claeys-Errea-Sack,[41] and Bär,[37] Oshida gave a value about 0.3% for this frequency range. While, by using the data given by Lamb-Pinkerton,[39] (51) gives the relative dispersion to be about 1.62% for the range: 0.5 to 67.5 MHz.; and about 1.60% for the frequency: 0.5 to 5.0 MHz. While, their experiment[39] gives the relative dispersion about 1.2% for this frequency range.

Thus, the possibly impure sample used by Spakovskij and others[41] and the ambiguity of the figures above on which our present calculation based, make the results rather complicated. And at present situation, though no precise decision can
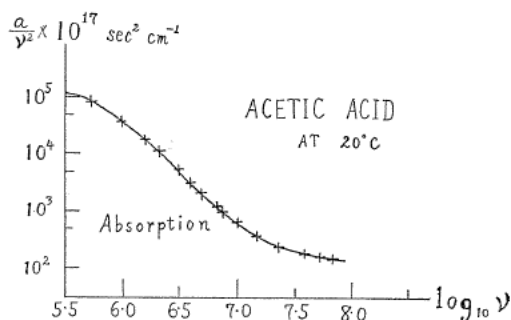

FIG. 4. Absorption versus frequency of acetic acid at 20°C.

ν : frequency,

a : absorption per unit length.

For the case : $\tau_2 = \tau_2^{(1)} = \tau_1^{(2)} = 2.86 \times 10^{-7}$ sec.

+ : experiment (Lamb and Pinkerton[39]).

—— : theoretical (formula (50)).

not be drawn, we can say, in any case, that the theoretical and the experimental results are in agreement in the order of magnitude.

As for the anomalous absorption[41] of methyl acetate and ethyl acetate, no satisfactory interpretation is given at present, and it is not so easy to understand the inclination[1][2] of the curves of their absorption versus frequency. According to Byer and Smith,[60] the absorption coefficient a for ethyl acetate is *directly proportional* to frequency at the frequency region 3~40 MHz., i.e. a/ν is approximately constant, being $(10\sim15)\times10^{-9}$ c.g.s. unit. Such a fact can not be explained by (50). A combination of three and more relaxations may reproduce approximately the experimental result of the apparent linearity relation between absorption coefficient and frequency. In this case, the relaxations, which appear both from the thermal expansion and the specific heat terms, may have a great possibility of contributing to the absorption. At present, we can hardly say anything about the precise and firm reality of these individual relaxations. Accordingly, the comprehension of these experimental facts still remains unsolved, and in future this real feature of relaxations must be explored at the point of view of molecular kinetic theory. In this case. the method of consideration as is carried out by de Groot[34] and by Oomori,[58][59] may offer some information about the order and the relation of relaxation times, in the macroscopic and microscopic points of view, respectively.

For sufficiently high frequencies, the expressions (46) and (47) become to

$$v = v_0 \cdot \left\{ 1 + \frac{1}{2\,k_0}\sum_{}^{l}\lambda_r + \frac{2}{3\,k_0}\sum_{}^{m}\mu_r + \frac{p_0}{2\,k_0 C_0 \rho_0}\sum_{}^{n}\alpha_r + \frac{\varepsilon_0}{2\,k_0 C_0}\sum_{}^{n}\alpha_r + \ldots \right\}, \quad (53)$$

$$a \fallingdotseq 0. \quad (54)$$

Thus we obtained the velocity and absorption for extremely high frequencies, which we call the hypersonic frequencies. The interpretation of the high velocity of this kind of wave is obviously accomplished, owing to the large values of the apparent bulk and shear moduli, which appeared in (53). On the other hand, the absorption hardly suffers from damping. This owes mainly to the properties of liquids, whose behaviours at the hypersonic regions of oscillation are very similar to those of solid bodies. On the hypersonic waves, we shall discuss in detail in Chapter VI.

VI. Hypersonic and Transverse Waves

Elastic waves, so called *supersonics*, ranging in the region of frequency $10^5\sim10^8$ Hz., can be generated by the ordinary radio methods, whichever they may be the longitudinal or the transverse. The elastic vibrations of the extremely high frequency, lying in the region $10^{10}\sim10^{13}$ Hz., sometimes called the *hypersonic waves*,[42] are known to exist under the natural condition in solids, constituting the main part of the thermal agitation in such bodies. In liquids it is also believed at present that the elastic waves of the high frequency of the order 10^{10} Hz. or above, do exist owing to the thermal motion of the constituent molecules. If we take into account the quasicrystalline structure of liquids, i.e. a domain, in which the motion of the molecules interacts over wide range with one another in their neighbourhood, then we can see that the thermal waves analogous as in solids exist, and that Debye's theory is also considered to hold approximately. The region of the frequency covers so widely as the wave-length is longer than the mean free

path of the constituent molecules, i.e. the *Schwingungsdauer* is greater than the mean collision time. Thus, in liquids, this ranges lower than 5×10^{13} Hz. (in crystals 10^{14} Hz.). Accordingly the theory developed here, which treats the liquids as continua, is supposed to be a good approximation for describing the mechanical properties of liquids even under such hypersonic regions of frequency. Debye's theory thus can be also applied to the liquid state as well as the monoatomic solids, in which the thermal motion may be described as a superposition of longitudinal and transverse waves.

The existence of the hypersonic waves in liquids is shown directly by the scattering of monochromatic light quite analogous to the Debye-Scherrer method applied to the crystal lattice. In liquids the appearance of hyperfine structures in scattered monochromatic light, was observed by Gross[43] in 1930, as a result of the reflection (Rayleigh scattering) of the light by the regular spacing of the denser part (thermal fluctuation of density) caused by the longitudinal elastic waves in liquids. In this case, the reflected planes, which obey Bragg's condition, moves with the sound velocity v. Thus Doppler's effect is introduced, resulting the appearance of the symmetric satellite lines on the both sides of the principal line. The difference in frequency $\Delta\nu$ is given by Brillouin[44] as

$$\frac{\Delta\nu}{\nu} = \pm 2\frac{v}{c} \sin \frac{\vartheta}{2}, \qquad (55)$$

where c is the light velocity, and ϑ the glancing angle. This formula (55) is verified by the observation of the hyperfine structure by Gross[47] and others[45] with the accuracy of about $\pm 10\%$. Thus from the wave-length of light λ_{light} used, the existence[13] of the elastic waves in liquids with the frequency 5×10^9 Hz. ($\lambda \sim 2 \times 10^{-5}$ cm $\sim \frac{1}{2} \lambda_{light}$) is obviously shown, where λ is the wave-length of hypersonics.

With increasing viscosity, the effect becomes clearer, and we can observe[13][45] this phenomenon in phenol at 25°C and in glycerine, which are rather highly viscous liquids.

According to Hiedemann,[46] it is mentioned that for sufficiently large frequencies, when the wave-lengths become shorter, the transfer of heat from the compressed (heated) places to the extended (cooled) places occurs more violently, and finally the process reaches isothermal rather than adiabatic.[32] Whether the process occuring in liquids is adiabatic or isothermal, is determined by the order of magnitude of the dimensionless quantity: $\dfrac{\kappa\nu}{\rho_0 C_0 v_0^2}$.

If this ratio is smaller than unity, the rôle of heat conduction must be relatively small, i.e. the process is almost adiabatic. In the opposite case, however, the vibrations must take place with the isothermal character.

Considering the values:

$$\kappa/\rho_0 C_0 v_0^2 = 0.63 \times 10^{-13} \text{ sec. for water,}$$
$$\qquad '' \qquad = 0.62 \times 10^{-13} \text{ sec. for acetic acid,}$$
$$\qquad '' \qquad = 0.83 \times 10^{-13} \text{ sec. for benzene,}$$
$$\qquad '' \qquad = 0.26 \times 10^{-13} \text{ sec. for glycerine,}$$

we can see that $\kappa\nu/\rho_0 C_0 v_0^2$ is far smaller than unity even for $\nu = 10^9 \sim 10^{12}$ Hz. which corresponds to the hypersonic frequencies. Thus the process occuring in liquids

under the hypersonic regions of frequency is considered to remain still *adiabatic*.

Certainly, for higher frequencies, this is not the case, but such waves have so small wave-lengths, comparable with the molecular spacing in liquids, that they can hardly exist when the discrete molecular structure is taken into consideration. Thus the neglect of κ in (40) is quite adequate, for the liquids cited above and perphaps other similar organic compounds.

For the waves of sufficiently high frequency $\omega\tau_r^{(s)} \gg 1$, we obtain from (41),

$$\beta^2 = -\frac{\omega^2}{v_0^2} \div \left[1 + \sum_{}^{l}\frac{\lambda_r}{k_0} + \frac{4}{3}\sum_{}^{m}\frac{\mu_r}{k_0} + \left(1 + \frac{p_0}{\rho_0\varepsilon_0}\right) \cdot \sum_{}^{n}\frac{\alpha_r\varepsilon_0}{k_0C_0} + \ldots \right], \qquad (56)$$

or from (53),

$$v = \frac{\omega}{\Im m(\beta)} = v_0 \cdot \left\{ 1 + \frac{1}{2}\frac{1}{k_0}\sum_{}^{l}\lambda_r + \frac{2}{3}\frac{1}{k_0}\sum_{}^{m}\mu_r + \frac{p_0}{2\,k_0\rho_0C_0}\sum_{}^{n}\alpha_r + \frac{\varepsilon_0}{2\,k_0C_0}\sum_{}^{n}\alpha_r + \ldots \right\}. (57)$$

Owing to the almost purely imaginary value of β, the waves of such high frequency suffer no remarkable absorption and thus we have:

$$a \doteqdot 0. \qquad (58)$$

Oshida[10] mentioned that we neglecting the two thermal conductivities within the two subsystem themselves of the translational and the vibrational motions of molecules, the velocity v_H of hypersonic wave is given by:

for $\omega\tau_1^{(1)} \gg 1$;

$$v_H = \sqrt{v_N^2 + \frac{C'''}{C'}(v_L^2 - v_N^2) + \frac{4}{3}\frac{\mu_1}{\rho_0}}$$
$$= \sqrt{v_L^2 + \frac{C''}{C'}(v_L^2 - v_N^2) + \frac{4}{3}\frac{\mu_1}{\rho_0}}, \qquad (59)$$

where v_N is the isothermal velocity, and v_L the adiabatic velocity; and C', C'' and C''' correspond to the translational (rotational included), the vibrational, and the thermostatical specific heats respectively, as is mentioned in (18) of Chapter IV. Accordingly the internal specific heat C'' also contributes to the velocity of the hypersonic wave. His theory as well as the author's present theory fails to explain the marked decrease of the propagation velocity in acetone found by Rao[42][43] near the region of $\nu = 10^{10}$ Hz.

The relaxation time $\tau_1^{(1)}$ corresponding to the ordinary viscosity, is not known exactly, but considered pherhaps to lie near 10^{-11} sec. for ordinary liquids. Hence it follows that to take $\omega\tau_1^{(1)} \ll 1$ is more preferable instead of $\omega\tau_1^{(1)} \gg 1$. In this case,

the term $\dfrac{\mu_1}{\rho_0} = \dfrac{\mu_1'}{\rho_0\tau_1^{(1)}}$ is considered utterly smaller than v_L^2 or v_N^2, since

$$\mu_1' \sim 10^{-2} \text{ poises}, \quad \rho_0 \sim 1 \text{ gr.cm}^{-3}, \quad v_L \sim 10^5 \text{ cm. sec}^{-1}.$$

And then we obtain:

$$v_H = \sqrt{v_L^2 + \frac{C''}{C'}(v_L^2 - v_N^2)} \cdot \qquad (60)$$

For benzene,[49][50] taking

$$C'' = 13.8 \text{ cal. mol}^{-1}., \quad C' = 8.1 \text{ cal. mol}^{-1}., \quad \text{and} \quad \frac{v_N^2}{v_L^2} = 0.70,$$

Oshida gives the ratio

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

This value fairly agrees with the data based on the observation of Gross[47] and Mitra.[51] Thus he supposed that the excess of 5%~30% of v_H over v_L is realized in most liquids.

Water is not interpreted by this mechanism. Some liquids, including water, however, have different origins of the absorption and the dispersion of sound wave. The structural change between two states of molecular lattice,[30] the monomer-polymer formation[31] as in some organic acids,[39] the hydroxyl or amino units contained in constituent molecules, the acoustical scattering by molecules,[26][52][53] the cavity formation, the non-linear absorption, etc.,[55] may also be other causes of the absorption and the dispersion in liquids.

In the region of the hypersonic frequency, the transverse elastic waves have also a great possibility of existence. Owing to the shearing rigidities of fugitive nature, from (32) we obtain:

$$\rho_0 \frac{\partial^2}{\partial t^2} \widetilde{\omega}_{ij} = \sum_{r=1}^{m} \frac{\mu_r \tau_r^{(1)} D}{1 + \tau_r^{(1)} D} \Delta \widetilde{\omega}_{ij}, \tag{61}$$

with

$$\widetilde{\omega}_{ij} = \frac{1}{2} \left(\frac{\partial \hat{\xi}_j}{\partial x_i} - \frac{\partial \hat{\xi}_i}{\partial x_j} \right). \qquad (i, j = 1, 2, 3)$$

Taking the progressive wave into the $+x_1$-direction:

$$\widetilde{\omega}_{ij} = \Re \widetilde{\omega}_{ij} \cdot e^{i\omega t - \beta x_1}, \quad \Im m (\beta) > 0, \tag{62}$$

we obtain the equation concering β:

$$-\rho_0 \omega^2 = \beta^2 \sum_{r=1}^{m} \frac{i\omega \tau_r^{(1)} \mu_r}{1 + i\omega \tau_r^{(1)}}, \tag{63}$$

i.e.

$$\beta^2 = \frac{-\rho_0 \omega^2}{\sum_{r=1}^{m} \frac{i\mu_r \omega \tau_r^{(1)}}{1 + i\omega \tau_r^{(1)}}}. \tag{64}$$

Accordingly we can compute the velocity v' and the absorption a' per unit length for shear wave:

$$v' = \frac{\omega}{\Im m (\beta)}, \tag{65}$$

$$a' = \Re (\beta). \tag{66}$$

For sufficiently large ω, we put $\omega \tau_r^{(1)} \gg 1$, and obtain,

$$\beta^2 \fallingdotseq \frac{-\rho_0 \omega^2}{\sum_{r=1}^{m} \mu_r}. \tag{67}$$

The almost purely imaginary value of β, leads to the very slight absorption:

$$a' \doteqdot 0, \tag{68}$$

$$v' = \sqrt{\dfrac{\sum\limits_{r=1}^{m} \mu_r}{\rho_0}} . \tag{69}$$

In this case, the temperature deviation caused in liquids is considered to be connected with the strain by the relation (33), which plays also an important rôle for such high frequency transverse waves.

In crystals, it appears three Doppler-doublets,[45] corresponding to the three velocities of the component waves, one longitudinal and two transverse. Thus, according to Debye's theory the thermal energy in solids is distributed among these three waves. In liquids,[53][59] if there were no transverse waves, their specific heats should be diminished greately compared with those of their solid phases. In reality, however, the difference of the specific heats between these two phases, is rather small, and this would support the existence of the transverse waves with sufficiently high frequencies even in liquids, if Debye's theory approximately holds for liquids.

VII.　Discussions and Summary

In dynamics of liquids of polyatomic molecule, the thermal stress of fugitive nature is emphasized to play an important rôle. The general stress-strain-temperature relations (16) for plasto-elastic bodies having finite number of relaxation times and rheological constants, were obtained especially under the consideration of thermal stress. The materials being subjected to the Maxwellian relaxational process, these relations are generalization of the results obtained by Frenkel-Obratzov and Oshida, applicable to the phenomena in liquids for the supersonic and the hypersonic waves. Moreover, the expression obtained includes the ever presented theories both of the compressional and the shearing viscosities, of the structural change, and of collisions, caused in liquids under such high frequency mechanical oscillations.

An attempt was made to formulate the expression of the internal energy (in the macroscopic sense) of liquids not in a thermal equilibrium. The expression of the internal energy used here, is assumed to be subjected to the Maxwellian relaxational process both for the temperature and for the strain. This is also found to include, as a special case, the expression obtained by Kneser for the non-associated liquids.

The combination of these expressions of state and of internal energy, using the equations of motion and of conservation of energy, results in the formulae for the dispersion and the absorption of waves of high frequency mechanical oscillation, giving the preferable characters of both Frenkel-Obratzov's and Kneser's theories. Thus, for example, the temperature dependence of the absorption and of the velocity of the wave, has the better aspects of these two theories. Accordingly the present theory is conveniently applied, regardless of sorts of liquid, to the ultrasonic phenomena.

Moreover, as the description of the present theory is mainly focused to the phenomena in liquids, this is also applicable, *mutatis mutandis*, to the dynamical behaviour of amorphous bodies : solids, liquids, and gases of polyatomic molecules

under the high frequency of mechanical oscillations.

The rheological phenomena in high polymers can be also explained by the present theory with slight modification of rheological constants.

Owing to the presence of the compressional and the shearing rigidities of fugitive nature under the high frequency of mechanical oscillation, the birefringence does appear even in liquids. The order of frequency of their appearance may be 10^8 Hz. for the shearing rigidities ; and above 10^{10} Hz. for the compressional moduli. As the relaxation time for some high polymer solutions is of the order 10^{-s} sec., the birefringence may appear at about the frequency of order 10^8 Hz. As for the compressional moduli, the order of 10^{10} Hz. is the one which corresponds to the hypersonic waves existing in liquids and solid crystals found in nature as Debye mentioned. The hypersonic waves existing in nature are thus of great interest from the point of view of optical observations.

The high frequency elastic waves in the elasto-plastic body were discussed in Capters V and VI. The results obtained were compared with experimental data. The relation of the present theory to the molecular kinetic theories are not yet discussed here. This shall be treated later elsewhere according to the line of consideration developed by Kneser. If we consider some model of the constituent molecules, and treat the matter on the bases of molecular kinetic theory, we may have some relations between the above mentioned $\tau_r^{(s)}$'s. And the temperature relaxation and the internal energy have some more rigorous foundation. On the macroscopic model, however, we can hardly say anything about the relations, which might hold between the thermodynamical dependent variables.

The behaviour of most liquids for supersonic frequency regions, is comprehensible at least qualitatively by the present theory. The temperature dependence of non-associated liquids and the so-called anomalous liquids, the latter being distinguishable for their having hydrogen bonds, can be also interpreted.

The existence and the high velocity of the hypersonic waves, i.e. the elastic waves of extremely high frequency caused by thermal agitation in liquids, were also considered.

The inflected form [37] [41] [54] of the curves of the absorption versus frequency, which appears in the cases of acetic acid, methyl acetate, and ethyl acetate, may be at least qualitatively comprehensible by the present theory, with the ordinary viscosity, and two kinds of extra relaxational viscosity. A precise interpretation, however, can not be sufficiently made by this theory. The thermal expansion terms may contribute to the absorption in this case. So it may be possible to interprete these curves, if we take more relaxation times or the thermal expansion terms.

Richardson [52] and Lucas [53] have considered that the loss of the ultrasonics is also due to the scattering of the wave by density fluctuation. This is another sort of the apparent absorption of quite different nature, and such a possibility may make the phenomena extremely complicated. Some liquids, including water, can be considered to show the structural absorption, some the monomer-polymer reaction, and some non-associated the collision of Kneser's type. All these can be implicitly included in the present theory, but the absorption due to the scattering loss did not said above. Accordingly such a case may sometimes be effective, and the loss can be estimated and interpreted by that mechanism, as well as the non-linear absorptions and the formation of cavities in the acoustical field of liquids.

Even in liquids, the transverse waves have also the possibility of existence, as

Oshida and Frenkel emphasised. The thermal stress does not influence directly on this type of the wave. In this case, however, it may be supposed that the more the fluctuation does appear, the greater the effects of temperature deviation may become. The tensor, corresponding to the momenta of the constituent molecules, may sometimes be of use, but here we merely considered the scalar temperature, relaxating to the internal energy according to the energy expression (28). Thus the strain-temperature relation is considered to be supported by the equation of conservation of energy (30).

The thermal stress terms appear in the logitudinal waves directly, and the structural mechanism, i.e. perhaps owing to the rearrangement of molecules, effectively appears in the dilatational waves, with combination of strain terms, as is shown in (46) and (47).

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