ON THE SPECIFIC HEAT AND THERMAL CONDUCTIVITY OF RHEOLOGICAL BODY

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RÉSUMÉ

Being based on Debye's and Brillouin's theories, the specific heat and thermal conductivity of rheological body with relaxation-phenomena are calculated under the assumption of small relaxation-coefficients in the maxwellian stress-strain relation of the material.

The results obtained include, as a special case, the expression presented by Lucas, who treated liquid body taking into account shearing viscosity and no volume relaxation.

The expression of specific heat obtained here is also conveniently applied to many rheological bodies such as liquids, visco-elastic bodies and plastic bodies, *mutatis mutandis, i.e.* with slight numerical modification of the rheological constants.

I. Preliminaries

It is considered that the thermal characters of rheological body play a rather important rôle in the case of working of plastic bodies and of the behaviour of materials in the combustion chamber of jet engines. These properties of the materials are seemed to be not yet much investigated at present. Especially, the temperature-dependence of the specific heat and thermal conductivity comes into question. This temperature-dependence shows very complicated aspects through the so-called relaxation times.

As is well known in the kinetic theory of gases and in the theory of solid bodies (Debye's theory), the temperature-dependence of many thermodynamical coefficients of gases is quite different from that of elastic solid bodies. For liquid, which is an intermediate state of gasious and solid-phases, these properties will be here investigated, especially taking into account the relaxation-phenomena of the material.

Recently much experimental evidence concerning liquids has been accumulated and the results 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 thermodynamical properties of liquids, in particular, resemble those of the corresponding solid phases. At temperatures near the fusion 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 is, the liquids consist of a very large number of randomly orientated crystals of submicroscopic size, smaller than 10^2 Å in diameter. This can also be interpreted

by a very close similarity in the X-ray diagramms between a liquid 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[1], the thermal energy of solid body is distributed among three thermoelastic waves, *i.e.* one longitudinal and two transverse phonons. The fact that the difference between the specific heat of a liquid and that of the corresponding solid is rather small, may lead us to apply the Debeye theory to liquids.

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 in a way similar to the Debye theory, even in such phases as of high viscosity and of rigidity of fugitive nature. At the starting point of calculating the specific heat, Debye took the stress-strain relation of perfectly elastic solid body. On the other hand, Lucas[2] started from the expression of Stokes, applicable to viscous fluids. Brillouin[3] considered that the compressional wave still remains in liquid but the energy of the two transverse waves dissipates into the rotation of molecules. Oomori[4] treated the equation of motion of plasto-elastic body presented by Frenkel-Obratzov.[5]

For the present treatment of thermodynamical character of liquids, we shall take a generalized stress-strain relation[6][7][8], which is directly proved from the viewpoint of the theory of irreversible thermodynamics.[9] Accordingly, we are now in the position of treating the specific heat of the system with relaxation phenomena, but, for the sake of simplicity, we shall here consider the specific heat and thermal conductivity of liquids.

II. Notations and Fundamental Equations

Notations

x_i : rectangular coordinates, $(i=1, 2, 3)$
ξ_i : components of displacement, $(i=1, 2, 3)$
T : temperature,
p_0 : initial pressure,
ρ : density in static state,
k_0 : static bulk modulus,
λ_r and μ_r: partial compressional and shearing rigidities,
$\lambda_r' = \lambda_r \tau_r$: partial volume viscosities,
$\mu_r' = \mu_r \tau_r^{(1)}$: partial shearing viscosities,
κ : thermal conductivity,
C_v : static specific heat at constant volume,
τ_r, $\tau_r^{(1)}$: relaxation times,
$D=d/dt=\partial/\partial t$: partial differential operator with respect to time,
$\sigma_{ij} = \frac{1}{2}\left(\frac{\partial \xi_j}{\partial x_i} + \frac{\partial \xi_i}{\partial x_j}\right)$: components of strain tensor σ, $(i, j=1, 2, 3)$
$\tilde{\omega}_{ij} = \frac{1}{2}\left(\frac{\partial \xi_j}{\partial x_i} - \frac{\partial \xi_i}{\partial x_j}\right)$: components of rotation, $(i, j=1, 2, 3)$

A_{ij}: components of stress tensor $\mathbf{A}$,
$\mathbf{E}(i\omega, \tau)$: complex elastic compliance,
$\mathbf{E}_0$: elasticity moduli,
v_l : propagation velocity of longitudinal wave,
v_t : propagation velocity of transverse wave,
$\omega = 2\pi\nu$: circular frequency,
ν_l^* : Debye maximum frequency of longitudinal wave,
ν_t^* : Debye maximum frequency of transverse wave,
$g(\nu)$: weight function for frequency ν,
N : Loschmidt number,
M : molar volume of liquid,
F : energy per unit volume,
k : Boltzmann constant,
U^*: activation energy,
$W = d\nu/d(\nu/v)$: group velocity of waves,
α : amplitude absorption coefficient of wave (per unit length),
$v_0 = \sqrt{k_0/\rho}$ and $v_{t\infty} = \sqrt{\mu_1/\rho}$.

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

All the quantities corresponding to the longitudinal and the transverse waves, shall be denoted by the suffixes l and t, respectively.

Fundamental equations

The generalized equations of state (stress-strain relations) are written as

$$\mathbf{A} = \mathbf{E}\,\boldsymbol{\sigma}, \tag{1}$$

where $\mathbf{A}$ is stress tensor, $\boldsymbol{\sigma}$ strain tensor, and $\mathbf{E}$ the so-called complex elastic compliance. The latter is decomposed as

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1(D, \boldsymbol{\tau})$$

$\mathbf{E}_0$ is elastic moduli, and $\boldsymbol{\tau}$ is a parameter which shows the aggregate of the so-called relaxation times. When $\omega\boldsymbol{\tau}$ tends to infinity, $\mathbf{E}_1(\infty)$ represents the extra moduli of elasticity of the material.

For the visco-elastic body, we can express (1) more concretely[8) 9)], for example, by taking into consideration the linear deformation of the substance, which is subjected to the maxwellian relexational process,

$$A_{ij} = p_0\delta_{ij} - \left(k_0 + \sum_{r=1}^{l}\frac{\lambda_r' D}{1+\tau_r D} - \frac{2}{3}\sum_{r=1}^{m}\frac{\mu_r' D}{1+\tau_r^{(1)} D}\right)\sigma_{kk}\,\delta_{ij} - 2\sum_{r=1}^{m}\frac{\mu_r' D}{1+\tau_r^{(1)} D}\,\sigma_{ij}, \tag{1-1}$$

where k_0 is the volume modulus,[8)] or

$$A_{ij} = \left[C_{ijkl} - \sum_{r=1}^{n}\frac{Q_{ijr}Q_{klr}}{1+D\tau_r}\right]\sigma_{kl}, \tag{1-2}$$

where C_{ijkl} and Q's are all material constants.[9)] $(i, j, k, l = 1, 2, 3)$

III. Internal Energy, Specific Heat and Thermal Conductivity of Liquid

Taking a plane progressive wave, we put

$$\xi_1 = \Re_e \xi e^{i\omega t - \beta_1 x_1}, \ \Re_e(\beta_1) > 0, \ \Im_m(\beta_1) > 0,$$
$$\xi_2 = \xi_3 = 0, \ \frac{\partial}{\partial x_2} = \frac{\partial}{\partial x_3} = 0. \tag{2}$$

For the transverse wave, we put, in the analogous manner,

$$\tilde{\omega}_{lj} = \frac{1}{2}\left(\frac{\partial \xi_j}{\partial x_l} - \frac{\partial \xi_l}{\partial x_j}\right) = \Re_e \tilde{\omega}_{lj} e^{i\omega t - \beta_2 x}, \qquad (l, j = 1, 2, 3)$$
$$\Im_m(\beta_2) > 0, \ \Re_e(\beta_2) > 0. \tag{3}$$

Next we obtain the velocities v of waves, longitudinal and transverse; and the absorption coefficients α per unit length with suffixes l and t, respectively:

$$v_l = \frac{\omega}{\Im_m(\beta_1)}, \qquad v_1 = \frac{\omega}{\Im_m(\beta_2)}, \tag{4}$$
$$\alpha_l = \Re_e(\beta_1), \qquad \alpha_t = \Re_e(\beta_2), \tag{5}$$

after solving the equations of motion: $\rho \frac{\partial^2 \xi_i}{\partial t^2} = -\frac{\partial A_{ij}}{\partial x_j}$.

For example, if we take (1−1) with $l = 1$ and $m = 1$, *i.e.* one relaxation time for shear and one for compression we obtain

$$\left.\begin{aligned}
v_l &= v_0 \cdot \left\{1 + \frac{1}{2}\frac{\lambda_1}{k_0}\frac{\omega^2\tau_1^2}{1+\omega^2\tau_1^2} + \frac{2}{3}\frac{\mu_1}{k_0}\frac{\omega^2\tau_1^{(1)^2}}{1+\omega^2\tau_1^{(1)^2}}\right\}, \\
v_t &= \sqrt{\frac{2\mu_1\tau_1^{(1)}\omega}{\rho}} \cdot \{\sqrt{1+(\omega\tau_1^{(1)})^2} + \omega\tau_1^{(1)}\}^{-1/2}, \\
\alpha_l &= \frac{\omega^2}{v_0}\left\{\frac{1}{2}\frac{\lambda_1}{k_0}\frac{\tau_1}{1+\omega^2\tau_1^2} + \frac{2}{3}\frac{\mu_1}{k_0}\frac{\tau_1^{(1)}}{1+\omega^2\tau_1^{(1)^2}}\right\}, \\
\alpha_t &= \sqrt{\frac{\rho\omega}{2\mu\tau_1^{(1)}}} \cdot \{\sqrt{1+(\omega\tau_1^{(1)})^2} - \omega\tau_1^{(1)}\}^{1/2},
\end{aligned}\right\} \tag{5-1}$$

with $v_0 = \sqrt{k_0/\rho}$,
under the assumption:

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

From the velocities of wave, we have the internal energy of liquid per unit volume:

$$F = F_l + F_t, \tag{6}$$
$$F_l = 4\pi \int_0^{\nu_l^*} \frac{\nu^2}{W_l v_l^2} g(\nu)\, d\nu, \tag{7}$$
$$F_t = 8\pi \int_0^{\nu_t^*} \frac{\nu^2}{W_t v_t^2} g(\nu)\, d\nu, \tag{8}$$

where F_l and F_t are the thermal energies of longitudinal and transverse waves, respectively. v represents phase velocity and W group velocity. The frequency distribution function $g(\nu)$ for ν comes from Planck's law. ν^* are the cut-off frequencies,[1) 2)] which come from the finite number of degrees of freedom in the system considered, and are written as:

$$\nu_l^* = v_l \Lambda, \tag{9}$$

$$\nu_t^* = v_t \Lambda, \tag{10}$$

$$\Lambda = \left(\frac{3N}{4\pi M}\right)^{1/3},$$

with the Loschmidt number N and molar volume M.

The expressions (9) and (10) satisfy the following condition for the total degrees of freedom of constituent molecules, *i.e.* for the total number of the stationary waves:

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

The cut-off frequencies ν_l^* and ν_t^* are determined by use of (9), (10) and (5-1), and satisfy the following equations:

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

and

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

i.e.

$$\nu_l^* \fallingdotseq v_0\Lambda\left\{1 + \frac{1}{2}\frac{\lambda_1}{k_0}\frac{(pv_0\Lambda)^2}{1+(pv_0\Lambda)^2} + \frac{2}{3}\frac{\mu_1}{k_0}\frac{(qv_0\Lambda)^2}{1+(qv_0\Lambda)^2}\right\}, \tag{9-1}$$

$$\nu_t^* = \frac{2\mu_1 q}{\rho} \cdot \Lambda^2\left\{1 + \frac{4\mu_1 q^2}{\rho}\Lambda^2\right\}^{-1/2}, \tag{9-2}$$

with $p = 2\pi\tau_1$ and $q = 2\pi\tau_1^{(1)}$.

Thus the limitting 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. the expression (19)).

The group velocities W are defined by:

$$\frac{1}{W_{l,t}} = \frac{d(\nu/v_{l,t})}{d\nu} = \frac{d(\omega/v_{l,t})}{d\omega}, \tag{11}$$

and

$$g(\nu) = \frac{h\nu}{e^{h\nu/kT}-1} + \frac{h\nu}{2} \fallingdotseq kT, \tag{12}$$

with Planck's constant h. At elevated temperatures we can put $g(\nu) \fallingdotseq kT$, and we shall use this hereafter.

When we take (5-1) for liquids, we obtain from (7):

$$F_l \doteqdot \frac{4\pi kT\nu_l^{*3}}{3v_0^3}\left\{1-\frac{3}{2}\frac{\lambda_1}{k_0}\frac{(p\nu_l^*)^2}{1+(p\nu_l^*)^2}-2\frac{\mu_1}{k_0}\frac{(q\nu_l^*)^2}{1+(q\nu_l^*)^2}\right\}. \tag{13}$$

As for the equation (8) with $m=1$, it is written by:

$$\begin{aligned} F_t &= \frac{\pi kT}{2}\left(\frac{\mu_1\tau_1^{(1)}\pi}{\rho}\right)^{-3/2}\int_0^{\nu_t^*}\nu^{1/2}\{\sqrt{1+(q\nu)^2}+q\nu\}^{5/2}\cdot\{1+(q\nu)^2\}^{-1/2}d\nu \\ &= \frac{kT\nu_t^{*3/2}}{3\pi^{1/2}\tau_1^{(1)3/2}v_{t\infty}^3}\{\sqrt{1+(q\nu_t^*)^2}+q\nu_t^*\}^{3/2}, \end{aligned} \tag{14}$$

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

At temperatures near the fusion point, where liquids are very similar to solids in their structure, we can put $\tau\to\infty$ in the expression (13),

$$F_l \doteqdot \frac{4\pi kT\nu_l^{*3}}{3v_0^3}\left[1-\frac{3}{2}\frac{\lambda_1}{k_0}\left\{1-\frac{1}{(2\pi\tau_1\nu_l^*)^2}\right\}-2\frac{\mu_1}{k_0}\left\{1-\frac{1}{(2\pi\tau_1^{(1)}\nu_l^*)^2}\right\}\right] \tag{15}$$

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

$$= \frac{N}{M}kT. \tag{16}$$

Thus the expression (13) approaches that for the internal energy of the corresponding solid body, and it is clear that the final expression (16) is just the expression presented by Debye.

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 (14), we can easily obtain

$$F_t \doteqdot \frac{8\pi kT\nu_t^{*3}}{3v_{t\infty}^3}\left\{1+\frac{3}{8(2\pi\tau_1^{(1)}\nu_t^*)^2}\right\} \tag{17}$$

$$\to \frac{8\pi kT\nu_t^{*3}}{3v_{t\infty}^3}$$

$$= \frac{2N}{M}kT. \tag{18}$$

The expression (17) corresponds to that of Lucas and (18) is just the contribution to the internal energy from the transverse waves in a solid body.

We may also consider that the temperature dependence of the relaxation time is expressed, according to Eyring[10], as follows:

$$\tau=\tau^*\cdot\exp[U^*/kT] \tag{19}$$

where U^* is the the so-called 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 time of oscillation of the molecule. τ^* is the period of oscillation of the molecule at that point.

From (6), (13) und (14), we obtain the molar specific heat at constant volume C_v,

$$C_v = M\frac{\partial F}{\partial T} = \frac{4\pi kM}{3v_0^3}\frac{\partial}{\partial T}\Big[T\nu_l^{*3}\Big\{1-\frac{3}{2}\frac{\lambda_1}{k_0}\frac{(2\pi\tau_1\nu_l^*)^2}{1+(2\pi\tau_1\nu_l^*)^2} - 2\frac{\mu_1}{k_0}\frac{(2\pi\tau_1^{(1)}\nu_l^*)^2}{1+(2\pi\tau_1^{(1)}\nu_l^*)^2}\Big\}\Big] + \frac{kM}{3\pi^{1/2}v_{t\infty}^3}\frac{\partial}{\partial T}\Big[\frac{T\nu_t^{*3/2}}{\tau_1^{(1)3/2}}\{\sqrt{1+(2\pi\tau_1^{(1)}\nu_t^*)^2}+2\pi\tau_1^{(1)}\nu_t^*\}^{3/2}\Big]. \tag{20}$$

In the irreversible process, in which we are now interested, the damping coefficient plays a rather important rôle. This quantity is directly measured by the ultrasonic experiments.

By applying the theory of thermal conduction in solids, which we owe to Brillouin, to liquids, we obtain the thermal conductivity of liquid,

$$\kappa = \kappa_l + \kappa_t, \tag{21}$$

$$\kappa_l = \frac{4\pi}{3}\int_0^{\nu_l^*}\frac{1}{2\alpha_l}\frac{\partial}{\partial T}\Big[\frac{\nu^2}{W_l v_l}g(\nu)\Big]d\nu, \tag{22}$$

$$\kappa_t = \frac{8\pi}{3}\int_0^{\nu_t^*}\frac{1}{2\alpha_t}\frac{\partial}{\partial T}\Big[\frac{\nu^2}{W_t v_t}g(\nu)\Big]d\nu, \tag{23}$$

where κ_l and κ_t represent thermal conductivities due to the longitudinal and the transverse waves, respectively.

$$\kappa_l = \frac{k}{3v_0}Q(\nu_l^*, 2\pi\tau_1, 2\pi\tau_1^{(1)}), \tag{22-1}$$

$$Q(\nu_l^*, p, q) = \int_0^{\nu_l^*}\frac{\frac{\partial}{\partial T}\Big[T\Big\{1-2\frac{\lambda_1}{k_0}\frac{p^2\nu^2}{G}-\frac{8}{3}\frac{\mu_1}{k_0}\frac{q^2\nu^2}{H}+\frac{\lambda_1}{k_0}\frac{p^4\nu^4}{G^2}+\frac{4}{3}\frac{\mu_1}{k_0}\frac{q^4\nu^4}{H^2}\Big\}\Big]}{\frac{1}{2}\frac{\lambda_1}{k_0}\frac{p}{G}+\frac{2}{3}\frac{\mu_1}{k_0}\frac{q}{H}}d\nu, \tag{22-1}$$

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

$$\kappa_t = \frac{k\sqrt{\pi\tau_1^{(1)}}}{3v_{t\infty}}\int_0^{\nu_t^*}\nu^{1/2}\{\sqrt{1+(2\pi\tau_1^{(1)}\nu)^2}+2\pi\tau_1^{(1)}\nu\}^{1/2}\times \times\frac{\partial}{\partial T}\Big[\frac{T\{\sqrt{1+(2\pi\tau_1^{(1)}\nu)^2}+2\pi\tau_1^{(1)}\nu\}^2}{2\pi\tau_1^{(1)}\sqrt{1+(2\pi\tau_1^{(1)}\nu)^2}}\Big]d\nu, \tag{23-1}$$

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

If we consider the limitting case:

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

which means that the effect of shearing viscosity predominates in the medium,

the expression (23-1) reduces to

$$\kappa_t = \frac{k}{9\sqrt{\pi}} \sqrt{\rho\mu_1'} \frac{\partial}{\partial T}\left(\frac{T}{\mu_1'}\right) \cdot \nu_t^{*3/2}, \tag{23-2}$$

with shearing viscosity $\mu_1' = \mu_1 \tau_1^{(1)}$. This expression (23-2) corresponds to the expression of thermal conductivity at elevated temperatures presented by Lucas.

In addition, we can see that, as an approximation for small $(\tau_1^{(1)}\nu_t^*)$, κ_t is roughly equal to (23-2) times $\{1+0(\tau_1^{(1)}\nu_t^*)\}$. Thus the term $0(\tau_1^{(1)}\nu_t^*)$, 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 liquids at ordinary temperatures, we can take $\mu_1' = 10^{-2}$ poises,

$$\tau_1 = 10^{-8} \sim 10^{-10} \text{ sec.}, \ \tau_1^{(1)} = 10^{-10} \sim 10^{-11} \text{ sec.},$$
$$\nu_l^* = 10^{13} \text{ sec}^{-1}. \text{ and } \nu_t^* = 10^{13} \text{ sec.}^{-1}$$

Accordingly, we obtain $\tau\nu^* = 10^2 \sim 10^5$. This figure shows that the terms $(\tau\nu^*)$ hardly contribute to the curled brackets in the expressions of internal energy, (15) and (16). And the expression (15) is almost equal to (16), which includes partial elastic moduli λ_1 and μ_1. For some solutions of high-polymeric substance, it happens semetimes that $\tau_1^{(1)}$ is of order of magnitude $10^{-7} \sim 10^{-8}$ sec., and $(\tau_1^{(1)}\nu_t^*)$ reaches $10^5 \sim 10^6$. In this case, the expression (17) does not differ practically from (18). 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 relaxation properties.

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