

Irreversible Thermodynamics and Continuum Mechanics*

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Principles of the irreversible thermodynamics are recapitulated. Using the basic conservation principles and the principles of irreversible thermodynamics, the fundamental equations and constitutive relations are obtained for fluids, solids, and visco-elastic media. Equations for the entropy production and heat conduction are derived for various special media and for a general medium having internal constraints. For the latter case, a law generalizing Fourier's law of heat conduction is found.

INTRODUCTION

THE principles of linear irreversible thermodynamics have recently been used to obtain a unified foundation for linear continuum mechanics. The works of Onsager,^{1,2} Onsager and Machlup,^{3,4} Prigogine,^{5,6} DeGroot,⁷ Denbigh,⁸ Greene and Callen,⁹ Staverman,¹⁰ Staverman and Schwarzl,¹¹ Meixner,^{12,13} Biot,^{14,15} and others may be mentioned as being some of the major contributions in this field. The viscous stresses in fluids and in solids are logically brought into the phenomenological relations, and the symmetry of the phenomenological constants are explained. In Biot's work, the Maxwell-type internal friction mechanism is explained in a natural way.

A satisfactory treatment of continuous media undergoing nonlinear reversible changes (such as large static deformations) accompanied by linear irreversible changes does not exist. Moreover, the relation of the viscous fluid to the visco-elastic solid is not clearly explained.¹⁶ Furthermore, basic equations of continuous media are somewhat taken for granted rather than being obtained as a result of the basic principles. For example, either the equations of heat conduction or the stress-strain temperature relations are obtained

from the theory, leaving the other as an untold postulate or as a result of thermostatics, Biot,¹⁵ Lessen.¹⁷ A systematic theory is expected to fulfill all three objectives, and it is with this viewpoint that the present paper is written.

We find a need for a combined use of reversible and irreversible thermodynamics, and rely on thermodynamic functions that are somewhat different from the ones usually used. A logical foundation based on the principles of the linear irreversible thermodynamics soon produces all basic equations of: (a) linear continuum mechanics, (b) deformable bodies undergoing nonlinear reversible changes accompanied by small irreversible changes, and (c) heat conduction; in all of which no additional assumptions need be used.

The present analysis leads to an extended Fourier's Law of Heat Conduction which involves hereditary terms and which is believed to be new. Also, in the special cases of isothermal, isentropic, and adiabatic deformations, the relationships of the phenomenological constants to each other are brought out in a natural fashion.

Below, we first postulate the principles of the irreversible thermodynamics, and then apply these principles to obtain the basic equations of various types of continuous media.

1. PRINCIPLES OF IRREVERSIBLE THERMODYNAMICS

Irreversible forces that cause the irreversible changes in a thermodynamic system may be introduced in a simple way as follows. Consider a thermodynamic system (B) which is imbedded in an adiabatically isolated heat reservoir (R) (Fig. 1). The system (B) may have a variable temperature T , and it is acted upon by external forces p_i . The total entropy change $d\Sigma$ of (R)+(B) is the sum of the entropy change dS of the system (B) and the entropy flow dS_R from the reservoir (R).

$$d\Sigma = dS_R + dS. \quad (1.1)$$

According to the second law of thermodynamics for natural changes, we have

$$d\Sigma \geq 0. \quad (1.2)$$

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⁹ R. F. Greene and H. B. Callen, *Phys. Rev.* **88**, 1387-1391 (1952).

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¹¹ A. J. Staverman and F. Schwarzl, *Proc. Roy. Acad. Sci.* **55**, 474-490 (1952).

¹² J. Meixner, *Kolloid-Z.* **134**, 3-14 (1953).

¹³ J. Meixner, *Z. Naturforsch.* **718a**, 654-655 (1954).

¹⁴ M. A. Biot, *J. Appl. Phys.* **25**, 1385-1391 (1954).

¹⁵ M. A. Biot, *J. Appl. Phys.* **27**, 240-253 (1956).

¹⁶ In this respect the excellent work of W. Noll [*J. Rational Mech. and Analysis* **4**, 627 (1955)] represents an exception. Noll, however, does not employ the thermodynamical viewpoint.

The first law of thermodynamics tells us that

$$dS_R = -\delta Q/T_R = -(1/T_R)(dE - \delta W), \quad (1.3)$$

where δQ is the heat flow into (B) , dE is the internal energy change of (B) , and δW is the work done upon the system (B) by the external forces p_i . Suppose system (B) has n degrees of freedom defined by n state variables S, Q_2, Q_3, \dots, Q_n measured from an origin. The state variables Q_i may be coordinates such as volume, concentrations, piezoelectric charges, etc., such that

$$\delta W = p_i dQ_i \quad (i=2, 3, \dots, n), \quad (1.4)$$

where repeated indices indicate summation over the range $(2, \dots, n)$. For example, when dQ_2 is the volume change dV , then $-p_2$ is the pressure p , etc. From (1.3) and (1.4), we will have

$$dS_R = -\delta Q/T_R = -(1/T_R)(dE - p_i dQ_i). \quad (1.5)$$

Prigogine⁶ by use of methods of statistical mechanics has shown that Gibbs' equation, $TdS = dE - pdV$, is valid for a system undergoing irreversible changes not far from equilibrium. This equation in our notation must be interpreted as

$$TdS = dE - p_i^r dQ_i, \quad (1.6)$$

where p_i^r are the reversible parts of the forces p_i . Thus, we write

$$p_i = p_i^r + X_i, \quad (1.7)$$

where X_i are the purely irreversible parts of the forces p_i . They are also called *Onsager forces*. Substituting (1.5), (1.6), and (1.7) into (1.1), we get

$$T_R d\Sigma = (dE - p_i^r dQ_i)[(T_R - T)/T] + X_i dQ_i.$$

Using (1.6), this reads

$$T_R d\Sigma = (T_R - T)dS + X_i dQ_i. \quad (1.8)$$

This equation suggests that $T_R - T$ plays the role of a purely irreversible thermal force while S plays the role of a coordinate conjugate to it. From (1.6), it is clear that T is the reversible part of the thermal force. Thus, if we write

$$p_1 \equiv T_R, \quad Q_1 \equiv S, \quad p_1^r = T, \quad X_1 = T_R - T, \quad (1.9)$$

we find that (1.6) and (1.8) take the form

$$dE = p_i^r dQ_i, \quad (1.10)$$

$$T_R d\Sigma = X_i dQ_i \quad (i=1, 2, \dots, n). \quad (1.11)$$

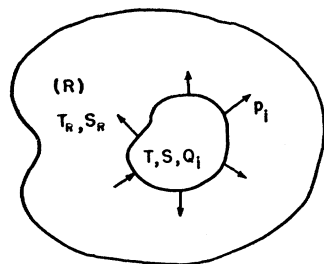


FIG. 1. Thermodynamic system

The first of these indicates that we have an equation of state of the form:

$$E = E(Q_1, Q_2, \dots, Q_n), \quad (1.12)$$

where $Q_1 \equiv S$. Thus, by adding the state variable S to our collection of coordinates Q_i , we have included the thermal forces. The significance of this, as we shall see, is that for $i=1$, Eq. (1.11) leads to the heat conduction equation. From (1.10) and (1.11), we see that

$$p_i^r = \partial E / \partial Q_i, \quad (1.13)$$

$$X_i = T_R \partial \Sigma / \partial Q_i, \quad (1.14)$$

where the partial derivatives are calculated in the usual sense by holding all other $Q_j = \text{const}$, $j \neq i$. These expressions define the purely reversible forces p_i^r and the Onsager forces X_i . From Eq. (1.11), we also have

$$T_R d\Sigma / dt = X_i \dot{Q}_i = X_i J_i. \quad (1.15)$$

Here $J_i \equiv \dot{Q}_i$ are called *fluxes*. Consequently, the sum of products of Onsager forces and fluxes give T_R times the entropy production.

The *Onsager principle* states that the Onsager forces are linear functions of the fluxes with the coefficients being symmetric.

$$X_i = T_R (\partial \Sigma / \partial Q_i) = b_{ij} J_j, \quad J_i = \dot{Q}_i = b_{ij}^{-1} X_j, \quad (1.16)$$

where

$$b_{ij} = b_{ji}, \quad b_{ij} \geq 0, \quad (1.17)$$

and b_{ij}^{-1} is the inverse matrix to b_{ij} . These latter relations are called the *Onsager reciprocal relations*.

We are now in a position to pronounce the principles of the irreversible thermodynamics, with reference to the closed system $(R) + (B)$:

- (i) The total energy is conserved.
- (ii) The entropy production is positive definite (i.e., $d\Sigma/dt \geq 0$).
- (iii) Gibbs' equation, (1.6) or (1.8) is valid for small irreversible changes about a state of equilibrium.
- (iv) In the neighborhood of an equilibrium state, the Onsager forces X_i are linear functions of the fluxes J_i [Eq. (1.16)].¹⁸
- (v) The phenomenological coefficients b_{ij} that relate Onsager forces to fluxes are symmetric tensors [Eq. (1.17)], provided that the forces and fluxes are selected in such a way that the sum of their products gives T_R times the entropy production [Eq. (1.15)].

It has been shown that when a magnetic field \mathbf{B} exists, this symmetry condition is modified as $b_{ij}(\mathbf{B}) = b_{ji}(-\mathbf{B})$.⁷

The first two of the foregoing principles are the same as those of the classical thermodynamics, the last two being new. Let us note that (v) also gives a method of

¹⁸ Some authors regard this as a *restriction* to Onsager's principle. See, for instance, K. G. Denbigh, *The Thermodynamics of the Steady State* (Methuen and Company, Ltd., London, 1951), pp. 30, 31. We include this as a principle to complete the description of linear irreversible phenomena.

calculating the entropy production which, in general, is not possible through the principles of classical thermodynamics. In applying these principles to continuous media, we shall be working with *thermodynamic densities* which are defined as the thermodynamic variables per unit mass of (B), e.g.,

$$\sigma = \Sigma/M, \quad s = S/M, \quad \epsilon = E/M, \\ 1/\rho = V/M, \quad q_i = Q_i/M, \quad (1.18)$$

where M is the mass of our system (B). Substitution of (1.18) into some of the foregoing equations, with the use of the *principle of mass conservation* $dM=0$, leads to

$$\delta Q/M = d\epsilon - p_i dq_i \quad (\text{principle i}), \quad (1.19)$$

$$\dot{\sigma} \geq 0 \quad (\text{principle ii}), \quad (1.20)$$

$$d\epsilon = p_i^r dq_i \quad (\text{principle iii}), \quad (1.21)$$

$$X_i = T_R(\partial\sigma/\partial q_i) = b_{ij}\dot{q}_j \quad (\text{principle iv}), \quad (1.22)$$

$$b_{ij} = b_{ji}, \quad b_{ij} \geq 0 \quad (\text{principle v}). \quad (1.23)$$

By definition, we also have

$$X_i = p_i - p_i^r = p_i - (\partial\epsilon/\partial q_i). \quad (1.24)$$

For principle (v) to be valid, we must also have

$$T_R\dot{\sigma} = X_i\dot{q}_i = b_{ij}\dot{q}_i\dot{q}_j = b_{ij}^{-1}X_iX_j. \quad (1.25)$$

In dealing with continuous media, we must, of course, use the usual conservation principles, such as conservation of mass, momentum, and energy (the first principle) and all other principles enunciated above.

2. DIFFERENTIAL EQUATIONS OF STATE VARIABLES

From Eqs. (1.22) with the use of (1.24), we get

$$T_R(\partial\sigma/\partial q_i) + \partial\epsilon/\partial q_i = p_i. \quad (2.1)$$

Two other versions of this system are

$$b_{ij}\dot{q}_j + \partial\epsilon/\partial q_i = p_i, \quad (2.2)$$

and

$$(\partial d/\partial q_i) + \partial\epsilon/\partial q_i = p_i, \quad (2.3)$$

where

$$2d = T_R\dot{\sigma} = X_i\dot{q}_i = b_{ij}\dot{q}_i\dot{q}_j, \quad (i, j = 1, 2, \dots, n) \quad (2.4)$$

is the well-known *Rayleigh dissipation function per unit mass* whose positive definite character is guaranteed by the Onsager relations (1.23).

We now would like to see how the function ϵ changes in the neighborhood of equilibrium. We write (2.1) as

$$T_R d\sigma + d\epsilon = p_i dq_i. \quad (2.5)$$

At a state of equilibrium $d\sigma=0$; hence,

$$p_i^e = (\partial\epsilon/\partial q_i)_e, \quad (2.6)$$

where the index e represents the equilibrium value of the quantities. Let us imagine that q_i are changed so as

to take the system away from the point of equilibrium an infinitesimal amount, while the forces p_i are kept at their equilibrium values. From (2.5), we will have

$$T_R d\sigma + (\partial\epsilon/\partial q_i)_e dq_i + \frac{1}{2}(\partial^2\epsilon/\partial q_i\partial q_j)_e dq_i dq_j = p_i^e dq_i.$$

Using (2.6), this reduces to

$$T_R d\sigma = -\frac{1}{2}(\partial^2\epsilon/\partial q_i\partial q_j)_e dq_i dq_j.$$

Since $T_R d\sigma \leq 0$ for an unnatural process, this shows that

$$(\partial^2\epsilon/\partial q_i\partial q_j)_e \geq 0 \quad (2.7)$$

but, ϵ is a function of q_i alone and is independent of the way the forces are applied. Therefore, (2.7) must be valid generally.

Let us now expand ϵ into a power series of q_i and retain only the first three terms

$$\epsilon - \epsilon_0 = \beta_i q_i + \frac{1}{2}a_{ij}q_i q_j, \quad (2.8)$$

where ϵ_0 , β_i , and $a_{ij} = a_{ji}$ are constants, and according to the foregoing argument, $a_{ij} \geq 0$. Through (1.13), we get

$$p_i^r = \beta_i + a_{ij}q_j, \quad a_{ij} = a_{ji} \geq 0. \quad (2.9)$$

This shows that β_i are none other than the values of the reversible forces at the origin $q_i=0$

$$p_i^r = \beta_i \quad \text{at} \quad q_i = 0. \quad (2.10)$$

Carrying (2.9) into (2.2), we obtain

$$b_{ij}\dot{q}_j + a_{ij}q_j = P_i, \quad a_{ij} \geq 0, \quad b_{ij} \geq 0, \quad (2.11)$$

where

$$P_i = p_i - \beta_i. \quad (2.12)$$

Differential equations (2.11) are, in form, identical to those obtained by Biot in a different way.¹⁴ Here, however, P_i is much more general and is time-dependent. Moreover, our a_{ij} are different from those of Biot. The logical extension of the present quantities to systems and to continuous media makes one believe that the variables used here are natural ones. Let us also note that in Eqs. (2.2), by considering ϵ as any function of q_i rather than a quadratic function, the formulation of small irreversible changes superimposed on large reversible changes can be made. An example of this is the large deformation of an elastic solid accompanied by small irreversible changes (internal dissipation, etc.).

3. PHENOMENOLOGICAL RELATIONS FOR INTERNALLY CONSTRAINED SYSTEMS

The principles of irreversible thermodynamics lead us to the phenomenological relations

$$p_i = (\partial\epsilon/\partial q_i) + b_{ij}\dot{q}_j. \quad (3.1)$$

In this form, the phenomenological relations are capable of expressing the large reversible changes through the term $\partial\epsilon/\partial q_i$. When the equilibrium state is reached by a small change from an initial state, we have found that (3.1) gives

$$P_i = a_{ij}q_j + b_{ij}\dot{q}_j, \quad P_i = p_i - \beta_i, \quad (3.2)$$

where

$$a_{ij}=a_{ji}\geq 0, \quad b_{ij}=b_{ji}\geq 0 \quad (i, j=1, 2, \dots, n).$$

If some of the forces, say $P_{k+1}, P_{k+2}, \dots, P_n$ are zero, we see that the number of degrees of freedom of the system can be reduced to k by eliminating q_{k+1}, \dots, q_n from (3.2). This situation is the same as having internal constraints so that the system is nonholonomic.

An example for internal constraints may be provided by a simple linear Maxwellian solid. This solid is represented by a linear spring and a dashpot in series (Fig. 2). Let Q_1, Q_2 be the displacements of the end of the spring and dashpot; P the external force; and k and c the spring and dashpot constants. We have

$$P=kQ_1, \quad P=c(\dot{Q}_2-\dot{Q}_1).$$

Eliminating P from these equations we get

$$kQ_1=P, \quad kQ_1+c(\dot{Q}_1-\dot{Q}_2)=0,$$

which upon comparison with the form (3.2) shows that $P_1=P, P_2=0$. Hence, the simple Maxwell solid has one internal constraint. Note that this situation does not arise for the Voigt solid (parallel spring and dashpot) where we have a single degree of freedom system.

We now return to the set of Eqs. (3.2) and, using time domain analysis, give a quick solution. To get the general solution of the system (3.2), one solves the homogeneous equation

$$a_{ij}q_j+b_{ij}\dot{q}_j=0. \quad (3.3)$$

We try a solution:

$$q_j=C\phi_j e^{pt}, \quad (3.4)$$

where C and ϕ_j are constants, C being introduced for convenience. From (3.3) and (3.4), we get

$$(a_{ij}+pb_{ij})\phi_j=0, \quad (3.5)$$

which may have a nonzero solution if the characteristic equation is satisfied, i.e.,

$$|a_{ij}+pb_{ij}|=0. \quad (3.6)$$

For each root $p=-\lambda_s$ of (3.6) we must have (3.5) satisfied, i.e.,

$$(a_{ij}-\lambda_s b_{ij})\phi_j^s=0 \quad (\text{not summed over } s), \quad (3.7)$$

where ϕ_j^s is a mode corresponding to the root $-\lambda_s$. Next, one can prove that:

(i) The roots $-\lambda_s$ of the characteristic equation are real and negative.

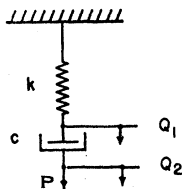


FIG. 2. Simple Maxwell solid.

(ii) Any two modes ϕ_i^r and ϕ_i^s corresponding to two distinct roots $-\lambda_r$ and $-\lambda_s$ are real and orthonormal, i.e.,

$$b_{ij}\phi_i^r\phi_j^s=\delta^{rs}, \quad \lambda_s\delta^{rs}=a_{ij}\phi_i^r\phi_j^s \quad (s \text{ not summed}). \quad (3.8)$$

To prove (i), one assumes that λ_s is complex, and hence its complex conjugate λ_s^* is also a root of (3.6); corresponding to these two roots, we have

$$(a_{ij}-\lambda_s b_{ij})\phi_j^s=0, \quad (a_{ij}-\lambda_s^* b_{ij})\phi_j^{s*}=0.$$

Now, multiply these equations by ϕ_i^{s*} and ϕ_i^s , respectively, and subtract one from the other. Since a_{ij} and b_{ij} are symmetric and $b_{ij}\phi_i^s\phi_j^{s*}\geq 0$, we get $\lambda_s-\lambda_s^*=0$, which proves that λ_s is real. We also solve this way for λ_s , giving us

$$\lambda_s=(a_{ij}\phi_i^s\phi_j^{s*})/(b_{ij}\phi_i^s\phi_j^{s*}),$$

which is the ratio of two positive quadratic forms. Thus $\lambda_s>0$ which proves (i).

To prove (ii), write (3.7) for two distinct roots $\lambda_s\neq\lambda_r$, multiply them, respectively, by ϕ_i^r and ϕ_j^s , and subtract one from the other. This gives the orthogonality of ϕ_i^r [i.e., the first of (3.8) with $r\neq s$]. Since, through (3.7), ϕ_j^s are determined up to a constant factor for each s , we can choose these constants to make $b_{ij}\phi_i^s\phi_j^s=1$ for each s , thereby, *orthonormalizing* ϕ_i^s . The second of (3.8) follows by using the first in one of these equations [i.e. (3.7)] multiplied by ϕ_i^r .

Introducing the *normal* coordinates ξ_r and expanding P_i into an expansion in terms of the normal modes

$$q_i=\phi_i^r\xi_r, \quad Z_s=P_i\phi_i^s \quad (3.9)$$

from (3.2) we get

$$\xi_s+\lambda_s\xi_s=Z_s \quad (\text{not summed over } s). \quad (3.10)$$

When this is solved and substituted into (3.9), we get

$$q_i=\sum_s C_s\phi_i^s e^{-\lambda_s t}+\sum_s K_{ij}^s \int_0^t P_j(\tau) e^{-\lambda_s(t-\tau)} d\tau, \quad (3.11)$$

where

$$K_{ij}^s=\phi_i^s\phi_j^s, \quad (3.12)$$

which, incidentally, is valid for repeated roots as well. Here, K_{ij}^s are completely determined since ϕ_i^s are all known through (3.7) and (3.8), while C_s are constants of integration to be determined from the initial conditions. This part, of course, dies out quickly with time. In the case of internal constraints, this result may be modified as follows. Write (3.2) as

$$(a_{ij}q_j+b_{ij}\dot{q}_j)+(a_{i\alpha}q_\alpha+b_{i\alpha}\dot{q}_\alpha)=P_i \quad (i, j=1, 2, \dots, k), \quad (3.13)$$

$$(a_{\alpha\beta}q_\beta+b_{\alpha\beta}\dot{q}_\beta)=- (a_{\alpha j}q_j+b_{\alpha j}\dot{q}_j)\equiv P_\alpha' \quad (\alpha, \beta=k+1, \dots, n), \quad (3.14)$$

where we assume that the Greek indices take the values $(k+1, \dots, n)$ and Latin ones $(1, 2, \dots, k)$. Then, the

solution of (3.14) is identical in form to (3.11). Hence,

$$q_\alpha = \sum_\sigma \left\{ C_\sigma \phi_\alpha^\sigma e^{-\lambda_\sigma t} - K_{\alpha\beta} \int_0^t [a_{\beta j} q_j(\tau) + b_{\beta j} \dot{q}_j(\tau)] e^{-\lambda_\sigma(t-\tau)} d\tau \right\}. \quad (3.15)$$

We thus expressed q_{k+1}, \dots, q_n [the left side of (3.15)] in terms of q_1, \dots, q_k . Now, substitute (3.15) into (3.13) and use the identity:

$$\int_0^t q_j(\tau) e^{-\lambda_\sigma(t-\tau)} d\tau = -\frac{1}{\lambda_\sigma} \int_0^t \dot{q}_j(\tau) e^{-\lambda_\sigma(t-\tau)} d\tau + \frac{1}{\lambda_\sigma} [q_j(t) - q_j(0) e^{-\lambda_\sigma t}].$$

This gives

$$P_i = A_{ij} q_j + B_{ij} \dot{q}_j + \sum_\sigma \int_0^t C_{ij}^\sigma \dot{q}_j(\tau) e^{-\lambda_\sigma(t-\tau)} d\tau + \sum_\sigma \{ [a_i^\sigma / (\lambda_\sigma)^{1/2}] - (\lambda_\sigma)^{1/2} b_i^\sigma \} \times [(\lambda_\sigma)^{1/2} C_\sigma + q_j(0) a_j^\sigma / (\lambda_\sigma)^{1/2}] e^{-\lambda_\sigma t}, \quad (3.16)$$

where

$$\begin{aligned} A_{ij} &= a_{ij} - \sum_\sigma (1/\lambda_\sigma) a_i^\sigma a_j^\sigma, \\ B_{ij} &= b_{ij} - \sum_\sigma b_i^\sigma b_j^\sigma, \\ C_{ij}^\sigma &= \{ [a_i^\sigma / (\lambda_\sigma)^{1/2}] - (\lambda_\sigma)^{1/2} b_i^\sigma \} \\ &\quad \times \{ [a_j^\sigma / (\lambda_\sigma)^{1/2}] - (\lambda_\sigma)^{1/2} b_j^\sigma \}, \\ a_i^\sigma &= \phi_\alpha^\sigma a_{i\alpha}, \quad b_i^\sigma = \phi_\alpha^\sigma b_{i\alpha}. \end{aligned} \quad (3.17)$$

In the expression (3.16), the terms containing the coefficients A_{ij} , B_{ij} , and C_{ij}^σ , respectively, correspond to elastic spring, Voigt damping, and Maxwell elements. Ignoring the transient effect of the initial conditions, we may write

$$P_i = \dot{p}_i - \beta_i = A_{ij} q_j + B_{ij} \dot{q}_j + \sum_\sigma \int_0^t C_{ij}^\sigma \dot{q}_j(\tau) e^{-\lambda_\sigma(t-\tau)} d\tau, \quad (3.18)$$

where from (3.17) we see also that the phenomenological coefficients A_{ij} , B_{ij} , and C_{ij}^σ are symmetric, i.e.,

$$A_{ij} = A_{ji}, \quad B_{ij} = B_{ji}, \quad C_{ij}^\sigma = C_{ji}^\sigma. \quad (3.19)$$

Thus, in a thermodynamic system with internal constraints, in addition to elastic and Voigt elements [the first two terms on the right of (3.18)], we must superpose a functional term representing the Maxwell Model. Let us note that the effect of the forces at the point $q_i = 0$ is taken into account by the term β_i which enables us to treat initial stress problems. Finally, it is meaningful to separate the purely reversible and irreversible

parts of the forces in (3.18) and those of the internal constraints and write

$$p_i = p_i^r + X_i, \quad p_\alpha = p_\alpha^r + X_\alpha, \quad (3.20)$$

where

$$p_i^r = \beta_i + A_{ij} q_j, \quad p_\alpha^r = \beta_\alpha + a_{\alpha j} q_j + a_{\alpha\beta} q_\beta, \quad (3.21)$$

$$X_i = B_{ij} \dot{q}_j + \sum_\sigma \int_0^t C_{ij}^\sigma \dot{q}_j(\tau) e^{-\lambda_\sigma(t-\tau)} d\tau, \quad (3.22)$$

$$X_\alpha = b_{\alpha i} \dot{q}_i + b_{\alpha\beta} \dot{q}_\beta, \quad (i, j = 1, 2, \dots, k),$$

$$(\alpha, \beta = k+1, \dots, n),$$

in which

$$q_\alpha = \sum_\sigma (1/\lambda_\sigma) C_{\alpha\beta}^\sigma \left[-a_{\beta j} q_j(t) + \int_0^t (a_{\beta j} - \lambda_\sigma b_{\beta j}) \dot{q}_j(\tau) e^{-\lambda_\sigma(t-\tau)} d\tau \right]. \quad (3.23)$$

According to (1.15) we may now calculate the entropy production by

$$T_R \dot{\sigma} = X_i \dot{q}_i + X_\alpha \dot{q}_\alpha. \quad (3.24)$$

In the following section, we show how this result may be applied to the mechanics of continuous media.

4. THERMODYNAMICS OF HOMOGENEOUS FLUIDS

We define a *homogeneous fluid* free from chemical and electrical phenomena by the *equation of state*:

$$\epsilon = \epsilon(s, 1/\rho). \quad (4.1)$$

Thus, our coordinates (state variables) are $q_1 = s$, $q_2 = 1/\rho$. Gibb's equation for densities now takes the form:

$$d\epsilon = T ds - p d(1/\rho), \quad (4.2)$$

which defines the thermodynamic temperature T and pressure p [just as in (1.13)] by

$$T = (\partial \epsilon / \partial s)_{\rho^{-1}}, \quad p = -(\partial \epsilon / \partial \rho^{-1})_s. \quad (4.3)$$

We would now like to compute the entropy production. To this end, we must use the well-known conservation equations of continuum mechanics:

$$\dot{\rho} + \rho v_{i,i} = 0 \quad (\text{conservation of mass}), \quad (4.4)$$

$$\sigma_{ij,i} + f_j = \rho a_j, \quad \sigma_{ij} = \sigma_{ji} \quad (\text{conservation of momentum}), \quad (4.5)$$

$$\rho \dot{\epsilon} = \sigma_{ij} \dot{d}_{ji} - \dot{q}_{i,i} \quad (\text{conservation of energy}), \quad (4.6)$$

where the time rate is now interpreted as the substantial derivative, and a subscript after a comma represents differentiation, i.e.,

$$\dot{F}_i \equiv \partial F_i / \partial t + (\partial F_i / \partial x_j) v_j, \quad v_i = dx_i / dt, \quad v_{i,j} = \partial v_i / \partial x_j,$$

and σ_{ij} , f_j , a_j , and \dot{q}_i are, respectively, the stress tensor, the body force per unit volume, the acceleration vector, and the heat input vector per unit surface area, and

d_{ij} is the deformation rate tensor; then,

$$2d_{ij} = v_{i,j} + v_{j,i}. \quad (4.7)$$

Eliminating ϵ between (4.2) and (4.6) and using (4.4), we have

$$\rho T \dot{s} = (p - \bar{p})v_{i,i} + s_{ij}d_{ij} - \hat{q}_{i,i}, \quad (4.8)$$

where we wrote

$$\sigma_{ij} = -\bar{p}\delta_{ij} + s_{ij}, \quad 3\bar{p} = -\sigma_{ii}, \quad (4.9)$$

in order to introduce the deviator stress s_{ij} and the mechanical pressure \bar{p} .

We may further write (4.8) as

$$\rho \dot{s} + (\hat{q}_i/T)_{,i} = \rho \dot{\sigma}, \quad (4.10)$$

where

$$\rho T \dot{\sigma} = \tau_{ij}d_{ij} - (1/T)\hat{q}_i \partial T / \partial x_i, \quad (4.11)$$

and

$$\tau_{ij} = p\delta_{ij} + \sigma_{ij} = \pi\delta_{ij} + s_{ij}, \quad \pi \equiv p - \bar{p}. \quad (4.12)$$

Note that in this form $\dot{\sigma}$ is the entropy production per unit mass. In order to get back into macroscopic irreversible thermodynamics, we must multiply both sides of (4.10) by the volume element dV and integrate over the volume. Using the Green-Gauss theorem, the second term on the left of (4.10) is converted to a surface integral. Hence,

$$\dot{S} + \int_A (\hat{q}_i v_i / T) dA = d\Sigma / dt, \quad (4.13)$$

where A is the surface of B , v_i is the exterior normal, and

$$S = \int_V \rho s dV, \quad \Sigma = \int_V \rho \sigma dV \quad (4.14)$$

are the total entropy of our system (B) and the universe (B) + (R), respectively.

Clearly, $d\Sigma/dt \geq 0$, according to principle (ii) of the irreversible thermodynamics; then from (4.13) there follows the well-known Clausius-Duhem inequality:

$$\dot{S} + \int_A [(\hat{q}_i v_i) / T] dA \geq 0 \quad (4.15)$$

Truesdell¹⁹ includes (4.15) in the definition of homogeneous fluids.

From (4.11), it is clear that τ_{ij} and $T^{-1} \partial T / \partial x_i$ play the role of Onsager forces and d_{ij} and $-\hat{q}_i$ that of the fluxes. Phenomenological relations accordingly should read

$$\begin{aligned} T_{,i} / T &= -b_{ij}\hat{q}_j + c_{ijk}d_{jk}, \\ \tau_{ij} &= d_{ijk}\hat{q}_k + b_{ijk}d_{kl}, \end{aligned} \quad (4.16)$$

where b_{ij} , c_{ijk} , d_{ijk} , and b_{ijkl} are phenomenological coefficients of the Onsager theory and for which,

according to Onsager's principles, we have

$$b_{ij} = b_{ji} \geq 0, \quad b_{ijkl} = b_{klij} \geq 0. \quad (4.17)$$

The Onsager theory does not tell us anything about odd order coefficients c_{ijk} , d_{ijk} . In order to simplify the discussion, we consider only the isotropic fluids. In this case, the terms containing c_{ijk} and d_{ijk} drop out on account of symmetry conditions,²⁰ and

$$b_{ij} = \kappa^{-1}\delta_{ij}, \quad b_{ijkl} = \lambda_v \delta_{ij}\delta_{kl} + \mu_v (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \quad (4.18)$$

where δ_{ij} is the Kronecker delta and κ , λ_v and μ_v are constants. Substitution of (4.18) into (4.16) gives

$$\hat{q}_i = -(\kappa/T)(\partial T / \partial x_i), \quad (4.19)$$

$$\sigma_{ij} = (-p + \lambda_v d_{kk})\delta_{ij} + 2\mu_v d_{ij}. \quad (4.20)$$

The first relation is the well-known *Fourier's Law of Heat Conduction* and the latter is the stress-deformation rate relation of the Newtonian fluids. It is interesting to note that in (4.19) κ/T appears as a coefficient instead of κ .

In fluid dynamics often it is argued that $\pi = 0$ or $p = \bar{p}$. This is known as the *Stokes condition*.²¹ We would like to see precisely when this is permissible. From (4.20), writing $i = j$, we get

$$\pi = p - \bar{p} = (\lambda + \frac{2}{3}\mu)v_{i,i}. \quad (4.21)$$

In incompressible fluids $v_{i,i} = 0$; hence, $p = \bar{p}$. Now, the argument that for a compressible fluid $\lambda = -2\mu/3$ is contradictory to experimental facts. There is one more case in which $p = \bar{p}$; that is when the fluid is undergoing a reversible change only. In this case, Onsager forces $\tau_{ij} = 0$ which according to (4.12) is satisfied if

$$\sigma_{ij}^r = -p\delta_{ij}, \quad (4.22)$$

where superscripts r represents the reversible value of the stress tensor σ_{ij} . From (4.9), it now follows that

$$\sigma_{ij}^r = -p\delta_{ij} = -\bar{p}\delta_{ij} \quad \text{or} \quad p = \bar{p}^r. \quad (4.23)$$

Therefore, the Stokes condition is justified in two cases: Incompressible fluids and fluids undergoing reversible changes.

Next, we calculate the entropy production by simply substituting τ_{ij} and $T_{,i}/T$ back into (4.11). This gives

$$\sigma = \sigma_d + \sigma_T, \quad (4.24)$$

where

$$\rho T \dot{\sigma}_d = b_{ijk}d_{ij}d_{kl}, \quad \rho T \dot{\sigma}_T = b_{ij}\hat{q}_i\hat{q}_j, \quad (4.25)$$

and $\dot{\sigma}_d$ and $\dot{\sigma}_T$ are the entropy production due to deformation and heat input, respectively. They are positive definite on account of (4.17). Substituting (4.18) into (4.25) we get

$$\begin{aligned} \rho T \dot{\sigma}_d &= \lambda (d_{kk})^2 + 2\mu d_{ij}d_{ji}, \\ \rho T \dot{\sigma}_T &= (1/k)\hat{q}_i\hat{q}_i = (\kappa/T^2)(\partial T / \partial x_i)(\partial T / \partial x_i). \end{aligned} \quad (4.26)$$

²⁰ This is sometimes known as Curie's theorem [P. Curie, *Sur la symmetrie dans Les Phenomenes Physique*, Oeuvres (Gauthier-Villars, Paris 1908), p. 127].

²¹ For a discussion of this condition, see reference 19, p. 228.

¹⁹ C. Truesdell, J. Rational Mech. and Analysis 1, 163 and 228 (1952).

The pressure p can be determined from (4.3). For a van der Waal's gas, one has

$$p = [RT\rho/(1-b\rho)] - a\rho^2 \quad (4.27)$$

where a and b are constants. A few manipulations through classical thermodynamics produce

$$\epsilon = \int c_v dT - a\rho + \text{constant}, \quad (4.28)$$

$$s = R \ln[(1/\rho) - b] + \int c_v (dT/T) + \text{constant},$$

where c_v is the specific heat at constant volume.

$$c_v = (\partial\epsilon/\partial T)_{\rho^{-1}} = T(\partial s/\partial T)_{\rho^{-1}}, \quad (4.29)$$

which is a constant for an ideal gas; in such a case, we also have $a=b=0$.

5. HEAT CONDUCTION IN FLUIDS

The equation of heat conduction in fluids (Van der Waal's fluid) would be obtained through (4.10). From the second of (4.28), we have

$$\rho T \dot{s} = [-RT\dot{\rho}/(1-b\rho)] + c_v \rho \dot{T}.$$

Using the continuity equation (4.4), this gives

$$\rho T \dot{s} = [RT\rho/(1-b\rho)] v_{i,i} + c_v \rho \dot{T}. \quad (5.1)$$

Now, substitute (5.1) and (4.19) into (4.10).

$$c_v \rho \dot{T} + [R\rho T/(1-b\rho)] v_{i,i} - (\kappa T)_{,i} = \rho T \dot{\sigma}_d = \lambda d_{kk}^2 + 2\mu d_{ij} d_{ji}. \quad (5.2)$$

For an ideal gas, we have $a=b=0$, $R=c_p-c_v$, and $p=\rho RT$ where c_p is the specific heat at constant pressure. Writing

$$\dot{p} = RT\dot{\rho} + R\rho\dot{T} = -RT\rho v_{i,i} + \rho R\dot{T} = -RT\rho v_{i,i} + \rho(c_p - c_v)\dot{T},$$

in (5.2), we get

$$c_p \rho \dot{T} - \dot{p} - [(\kappa/T)T]_{,i} = \lambda d_{kk}^2 + 2\mu d_{ij} d_{ji}. \quad (5.3)$$

This reduces to the usual form of the equation of heat conduction if we write a new coefficient k in place of κ/T . Equations (4.4), (4.5), (4.18), (4.19), and (5.2) constitute the basic equations of fluid dynamics. The equations governing anisotropic fluids can be obtained in a similar fashion.

6. THERMODYNAMICS OF VISCOELASTIC SOLIDS

An elastic solid may be defined by an equation of state of the form

$$\epsilon = \epsilon(s, e_{ij}). \quad (6.1)$$

Now, Gibbs' equation is written as

$$\dot{\epsilon} = T\dot{s} + \rho^{-1} t_{ij} \dot{e}_{ij}, \quad (6.2)$$

which defines temperature T and thermodynamic

stresses t_{ij} as

$$T = (\partial\epsilon/\partial s)_{e_{ij}}, \quad t_{ij} = \rho(\partial\epsilon/\partial e_{ij})_{s, e_{km} \neq e_{ij}} = e_{ji}. \quad (6.3)$$

Substituting (6.2) into (4.6), we get

$$\rho \dot{s} + (\hat{q}_i/T)_{,i} = \rho \dot{\sigma}, \quad (6.4)$$

where

$$\rho T \dot{\sigma} = (\sigma_{ij} - t_{ij}) d_{ij} - \frac{1}{T} \hat{q}_i \frac{\partial T}{\partial x_i}. \quad (6.5)$$

The positive definite character of $\dot{\sigma}$ indicates that for a reversible change, i.e., $\dot{\sigma}=0$, we must have one member from each of the pairs $\sigma_{ij}-t_{ij}$, d_{ij} and Q_i , $T_{,i}/T$ zero. Four possibilities are

$$\begin{aligned} T_{,i}=0, \quad \sigma_{ij}=t_{ij} & \text{ isothermal process and vanishing dissipative stress,} \\ \hat{q}_i=0, \quad \sigma_{ij}=t_{ij} & \text{ totally adiabatic process and vanishing dissipative stress,} \\ T_{,i}=0, \quad d_{ij}=0 & \text{ isothermal process and rigid motion,} \\ \hat{q}_i=0, \quad d_{ij}=0 & \text{ totally adiabatic process and rigid motion.} \end{aligned} \quad (6.6)$$

The stress tensor in the first two cases takes its reversible value σ_{ij}^r , i.e., the form of (6.5) dictates that the Onsager forces are $\sigma_{ij}-t_{ij}$ and $T^{-1}(\partial T/\partial x_i)$ and fluxes d_{ij} and \hat{q}_i . Hence, postulate (iv) is expressed as:

$$\begin{aligned} (1/T)(\partial T/\partial x_i) &= -b_{ij} \hat{q}_j + c_{ijk} d_{jk}, \\ \sigma_{ij} - t_{ij} &= d_{ijk} \hat{q}_k + b_{ijk} d_{kl}. \end{aligned} \quad (6.7)$$

For an isotropic solid, this reduces to

$$\begin{aligned} -(\kappa/T)(\partial T/\partial x_i) &= \hat{q}_i, \\ \sigma_{ij} - t_{ij} &= \lambda_v d_{kk} \delta_{ij} + 2\mu_v d_{ij}. \end{aligned} \quad (6.8)$$

Let us note that through the t_{ij} -term this expression contains the potential for treating large reversible deformation problems. For these stresses, we have a stress potential $\rho\epsilon$ as expressed by (4.6) which is valid for large strains e_{ij} as well. The present method of approach also makes it possible to obtain fluid dynamics as a limiting case of a viscoelastic solid in which $t_{ij} = -p\delta_{ij}$. This amounts to using in the equation of state (6.1) $1/\rho$ for e_{ii} , which is permissible because of the continuity equation. To obtain t_{ij} and T for small strains and temperature rise, we expand $\rho\epsilon$ into a power series:

$$\rho(\epsilon - \epsilon_0) = U = \alpha_{ij} e_{ij} + \alpha s + \beta_{ijs} e_{ij} + \frac{1}{2} \beta s^2 + \frac{1}{2} \beta_{ijk} e_{ij} e_{kl} + \dots \quad (6.9)$$

where

$$\begin{aligned} \epsilon_0 &= \epsilon(0,0), \quad \alpha = \rho(\partial\epsilon/\partial s)_0, \quad \alpha_{ij} = \rho(\partial\epsilon/\partial e_{ij})_0, \\ \beta_{ij} &= \rho(\partial^2\epsilon/\partial s \partial e_{ij})_0, \quad \beta = \rho(\partial^2\epsilon/\partial s^2)_0, \\ \beta_{ijk} &= \rho(\partial^2\epsilon/\partial e_{ij} \partial e_{kl})_0, \end{aligned} \quad (6.10)$$

and a subscript zero indicates that the expansion is

about the *initial state* $s=0$, $e_{ij}=0$. Now, (6.3) gives

$$\begin{aligned} t_{ij} &= \alpha_{ij} + \beta_{ij}s + \beta_{ijkl}e_{kl}, \\ \rho T &= \alpha + \beta_{ij}e_{ij} + \beta s. \end{aligned} \quad (6.11)$$

If the initial state is *stress-free* ($t_{ij}=0$ at temperature T_0), we find $\alpha_{ij}=0$, $\alpha=\rho T_0$. From (6.11) we solve for s and thus write in terms of temperature

$$\begin{aligned} s &= (\rho/\beta)\theta - (\beta_{ij}/\beta)e_{ij}, \quad \theta = T - T_0, \\ t_{ij} &= (\rho/\beta)\beta_{ij}\theta + [\beta_{ijkl} - (1/\beta)\beta_{ij}\beta_{kl}]e_{kl}. \end{aligned} \quad (6.12)$$

Constants α_{ij} , β_{ij} , and β_{ijkl} have obvious symmetries. For an isotropic medium, we have

$$\beta_{ij} = \gamma\delta_{ij}, \quad \beta_{ijkl} = \lambda\delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \quad (6.13)$$

Hence, we get

$$\begin{aligned} t_{ij} &= (\rho\gamma/\beta)\theta\delta_{ij} + (\lambda - \gamma^2/\beta)e_{kk}\delta_{ij} + 2\mu e_{ij}, \\ s &= (\rho/\beta)\theta - (\gamma/\beta)e_{ii}. \end{aligned} \quad (6.14)$$

Phenomenological relations thus become

$$\begin{aligned} \sigma_{ij} &= (\rho\gamma/\beta)\theta\delta_{ij} + (\lambda - \gamma^2/\beta)e_{kk}\delta_{ij} \\ &\quad + 2\mu e_{ij} + \lambda_v \dot{e}_{kk}\delta_{ij} + 2\mu_v \dot{e}_{ij}, \end{aligned} \quad (6.15)$$

$$\dot{q}_i = -(\kappa/T_0)(\partial\theta/\partial x_i).$$

We may now obtain various special cases of interest.

(a) *Isothermal deformation.* In an isothermal deformation the temperature at all instances is the same and is equal to the temperature of the initial state T_0 . Hence $\theta=0$. In this case (6.14) reduces to

$$\begin{aligned} s &= -(\gamma/\beta)e_{ii}, \\ t_{ij} &= (\lambda - \gamma^2/\beta)e_{kk}\delta_{ij} + 2\mu e_{ij}. \end{aligned} \quad (6.16)$$

In the expression (6.5) of $\dot{\sigma}$ the term containing \dot{q}_i vanishes thus indicating that the dissipative deformation energy is solely responsible for entropy production.

(b) *Isentropic deformation.* In this case, we have $s=0$. Hence, the isentropic values of temperature rise and stresses are given by

$$\begin{aligned} \theta &= (\gamma/\rho)e_{kk}, \\ t_{ij} &= \lambda e_{kk}\delta_{ij} + 2\mu e_{ij}. \end{aligned} \quad (6.17)$$

This is the usual form of the generalized Hooke's Law which is often confused with the adiabatic case in the literature. Through (6.4) and (6.5) we find that

$$\dot{q}_{i,i} = (\sigma_{ij} - t_{ij})d_{ij}.$$

Hence the heat input is fully used to balance the dissipative deformation energy.

(c) *Totally adiabatic deformation.* This means that during the deformation, the heat is not permitted to flow from one point to the next in the body, i.e., $\dot{q}_i=0$. This through (6.15)₂ gives $\theta_{,i}=0$, that is, the temperature in this case is uniform throughout the body and it may change only with time, $\theta=\theta(t)$. Phenomeno-

logical relations (6.14) and (6.15) otherwise retain their forms.

(d) *Locally adiabatic process.* This means $\dot{q}_{i,i}=0$. The heat conduction is steady. Again phenomenological relations (6.14) and (6.15) retain their forms except that now temperature θ is an analytic function, i.e.,

$$\nabla^2\theta=0. \quad (6.18)$$

We note in both cases (c) and (d), (6.4) and (6.5) reduce to

$$\dot{\sigma} = \dot{s} = (\sigma_{ij} - t_{ij})d_{ij}.$$

Hence, in both of these cases the entropy change \dot{s} is balanced with the dissipative deformation energy. It is customary to compare the elastic coefficient for various cases. If we express the thermodynamic stress-strain relations in a common form

$$t_{ij} = \lambda e_{kk}\delta_{ij} + 2\mu e_{ij}, \quad (6.19)$$

we see that the isothermal and adiabatic values λ^T and λ^s of the constant λ are

$$\lambda^T = \lambda - \gamma^2/\beta, \quad \lambda^s = \lambda, \quad (6.20)$$

or

$$\lambda^T = \lambda^s - \gamma^2/\beta. \quad (6.21)$$

Since $\beta>0$ we see that $\lambda^T \leq \lambda^s$. The elastic constant μ is not altered. By the same token, the isothermal value of stress t_{ij}^T is never greater than the isentropic value of the stress. The difference $-(\gamma^2/\beta)e_{kk}\delta_{ij}$ represents an extra pressure over the isentropic stress. Note also that adiabatic Lamé constants are the same as the isothermal ones. This is contrary to the known results in the literature. In the literature often the adiabatic process (\dot{q}_i or $\dot{q}_{i,i}=0$) is confused with the isentropic case ($s=0$).

On the other hand, for the isothermal case, $\dot{q}_{i,i}$ is set equal to ρTs ; then, the Helmholtz free energy $\epsilon - Ts$ is used as the stress potential for $T=\text{constant}$. This replacement for the irreversible changes is not acceptable.

The internal energy function is obtained by putting (6.14) into (6.9).

$$U = \rho(\epsilon - \epsilon_0) = \frac{1}{2}t_{ij}e_{ij} + \frac{1}{2}\rho\theta s + \rho T_0 s, \quad (6.22)$$

which may also be expressed either completely in terms of e_{ij} and T , or in terms of e_{ij} and s , by using expressions of stresses and entropy. The first two terms in (6.22) are the internal energies due to straining and heating the body from an initial state of zero strain and zero entropy ($s=e_{ij}=0$). The last term is the energy which is due to an initial temperature T_0 at the initial state. If we set $T_0=0$ at this state, we eliminate the last term on the right of (6.22). The internal energy U now becomes a positive definite quadratic form having its minimum at the initial state. This situation appears to be closely related to the third law of thermodynamics in which we have $s=0$ as $T \rightarrow 0$.

To obtain the equation of heat conduction, we substitute (6.14) and \hat{q}_i of (6.8) into (6.4).

$$(\rho T/\beta)(\rho\dot{\theta} - \gamma\dot{e}_{kk}) - (\kappa T_{,i}/T)_{,i} = (\sigma_{ij} - t_{ij})d_{ij}. \quad (6.23)$$

If we set $T = T_0 + \theta$ when $T_0 = \text{constant} \gg \theta$ and linearize (6.23), thus dropping the second order Rayleigh dissipation term on the right, we obtain:

$$c\rho\dot{\theta} - c\gamma\dot{e}_{kk} - \nabla^2\theta = 0, \quad c = \rho T_0^2/\kappa\beta. \quad (6.24)$$

According to the Lagrangian point of view, for solids the time differentiation is taken as the partial differentiation, i.e., $\dot{F} \equiv \partial F/\partial t$. We must now add to the basic equations obtained above the equation of the conservation of mass.

$$\rho - \rho_0 = \rho_0 e_{ii}. \quad (6.25)$$

The basic equations of general Voigt solids therefore consist of the conservation of mass (6.25), conservation of momentum (4.5), the phenomenological relations (6.15), and the equation of heat conduction (6.24).

All of this analysis must be modified for the fluids and solids having internal constraints. In the following section, we carry out the analyses for solids only. The situation is very similar for the fluids.

7. SOLID WITH INTERNAL CONSTRAINTS

When the solid has internal constraints we must add the Maxwellian terms, similar to those of (3.18), to the phenomenological equations. Therefore, we write

$$\begin{aligned} \frac{1}{T} \frac{\partial T}{\partial x_i} = & -b_{ij}\hat{q}_j + c_{ijk}d_{jk} + \sum_{\sigma} \int_0^t [c_{ijk}^{\sigma}d_{jk}(\tau) \\ & - b_{ij}^{\sigma}\hat{q}_j(\tau)]e^{-\lambda_{\sigma}(t-\tau)}d\tau, \\ \tau_{ij} = & \sigma_{ij} - t_{ij} - d_{ijk}\hat{q}_k \\ & + b_{ijk}d_{kl} + \sum_{\sigma} \int_0^t [c_{ijk}^{\sigma}d_{kl}(\tau) \\ & + d_{ijk}^{\sigma}\hat{q}_k(\tau)]e^{-\lambda_{\sigma}(t-\tau)}d\tau, \end{aligned} \quad (7.1)$$

where the even-order coefficients satisfy the Onsager symmetry condition. For a linear isotropic medium, these relations become

$$\begin{aligned} -\frac{1}{T_0}\theta_{,i} = & -\frac{1}{\kappa}\hat{q}_i + \sum_{\sigma} \int_0^t \frac{1}{\kappa^{\sigma}}\hat{q}_i(x,\tau)e^{-\lambda_{\sigma}(t-\tau)}d\tau, \\ \sigma_{ij} = & \frac{\rho\gamma}{\beta}\theta\delta_{ij} + \left(\lambda - \frac{\gamma^2}{\beta} + \lambda_v\frac{\partial}{\partial t}\right)e_{kk}\delta_{ij} \\ & + 2\left(\mu + \mu_v\frac{\partial}{\partial t}\right)e_{ij} + \sum_{\sigma} \int_0^t [\lambda_v^{\sigma}\dot{e}_{kk}(x,\tau)\delta_{ij} \\ & + 2\mu_v^{\sigma}\dot{e}_{ij}(x,\tau)]e^{-\lambda_{\sigma}(t-\tau)}d\tau, \end{aligned} \quad (7.2)$$

where $\theta = T - T_0$, and κ^{σ} , λ_v^{σ} , μ_v^{σ} are the additional

constants due to internal constraints. They are the isotropic values of b_{ij}^{σ} and c_{ijk}^{σ} , i.e.,

$$b_{ij}^{\sigma} = (1/\kappa^{\sigma})\delta_{ij}, \quad c_{ijk}^{\sigma} = \lambda_v^{\sigma}\delta_{ij}\delta_{kl} + \mu_v^{\sigma}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}). \quad (7.3)$$

The first of Eqs. (7.2) is an extension of the Fourier law of heat conduction. To the best of my knowledge, I do not recall seeing in the literature the *history* terms involved under the integral sign on the right. It is reasonable and logically compatible with the Maxwellian terms arising from damping to argue in favor of this heat term. We shall only remark, however, that this term implies the change of the material conduction constants with heating through its heat capacity. The final justification of it must, however, await experimental verification.

The equation of heat conduction again follows from (4.10) upon using (7.2) and linearizing the result. This time, however, \hat{q}_i is not expressible in a simple way in terms of $\partial\theta/\partial x_i$. The heat conduction equation is included in the set of

$$\begin{aligned} (\rho_0 T_0/\beta)\dot{\theta} - (\gamma T_0/\beta)\dot{e}_{ii} + \hat{q}_{i,i} = & 0, \\ -\frac{1}{T_0}\frac{\partial\theta}{\partial x_i} = & -\hat{q}_i + \sum_{\sigma} \int_0^t \frac{1}{\kappa^{\sigma}}\hat{q}_i(x,\tau)e^{-\lambda_{\sigma}(t-\tau)}d\tau, \end{aligned} \quad (7.4)$$

of which, the first is the same as (6.4) when linearized, and the second is the new heat conduction law which reduces to that of Fourier when $\kappa^{\sigma} = \infty$. We may eliminate $\hat{q}_{i,i}$ between the two expressions of (7.4) leading to an integro-differential equation for the heat conduction:

$$\begin{aligned} -\nabla^2\theta + (\rho_0 T_0^2/\kappa\beta)\dot{\theta} - (\gamma T_0^2/\kappa\beta)\dot{e}_{ii} \\ + \sum_{\sigma} \int_0^t [(\rho_0 T_0^2/\beta\kappa^{\sigma})\dot{\theta}(\tau) - (\gamma T_0^2/\kappa^{\sigma}\beta)\dot{e}_{ii}(\tau)] \\ \times e^{-\lambda_{\sigma}(t-\tau)}d\tau = 0. \end{aligned} \quad (7.5)$$

Let us finally remark that if the Laplace transforms of these expressions are used, a great deal of simplification can be achieved. Thus, for example, transforms of the phenomenological relations (7.2) give

$$\begin{aligned} \bar{\sigma}_{ij} + \sigma_{ij}^0 = & (\rho\gamma/\beta)\bar{\theta}\delta_{ij} + \tilde{\lambda}\bar{e}_{kk}\delta_{ij} + 2\tilde{\mu}\bar{e}_{ij}, \\ \bar{q}_i = & -(\kappa/T_0)\bar{\theta}_{,i}, \end{aligned} \quad (7.6)$$

where

$$\begin{aligned} \sigma_{ij}^0 = & \tilde{\lambda}e_{kk}(x,0)\delta_{ij} + 2\tilde{M}e_{ij}(x,0), \\ \tilde{\lambda} = & \lambda - (\gamma^2/\beta) + \tilde{\lambda}\zeta, \quad \tilde{\mu} = \mu + \tilde{M}\zeta, \\ \tilde{\lambda} = & \lambda_v + \sum_{\sigma} \lambda_v^{\sigma}/(\zeta + \lambda_{\sigma}), \\ \tilde{M} = & \mu_v + \sum_{\sigma} \mu_v^{\sigma}/(\zeta + \lambda_{\sigma}), \\ \frac{1}{\tilde{\kappa}} = & -\frac{1}{\kappa} + \sum_{\sigma} \frac{1}{\kappa^{\sigma}\zeta + \lambda_{\sigma}}, \end{aligned} \quad (7.7)$$

where ζ is the transform variable. By taking the Laplace transform of (7.5), we obtain

$$(\rho_0 T_0 / \beta) [\zeta \bar{\theta} - \theta(x, 0)] - (\gamma T_0 / \beta) \times [\zeta \bar{e}_{ii} - e_{ii}(x, 0)] + (\bar{\kappa} / T_0) \nabla^2 \bar{\theta} = 0, \quad (7.8)$$

where $\theta(x, 0)$ and $e_{ii}(x, 0)$ are the temperature and dilatation at $t=0$. It may be deduced from (7.6) and (7.8), and the fact that conservation laws are the same whether the medium has viscosity or not, that: *Theorem of Correspondence: The solution of the Laplace*

transform of basic equations of thermo-visco-elasticity is the same as that of the thermoelasticity with the transformed body forces \bar{f}_i and surface tractions $\bar{\sigma}_i$ in the latter replaced by $\bar{f}_i = \bar{f}_i - \sigma_{ji,j}^0$ and $\bar{\sigma}_i = (\bar{\sigma}_{ij} - \sigma_{ij}^0)n_j$, and λ , μ and κ replaced by $\bar{\lambda}$, $\bar{\mu}$ and $\bar{\kappa}$.

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Nuclear Spin Relaxation in Liquid He³. II*

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The nuclear spin thermal relaxation time, T_1 , of He³ nuclei in pure liquid He³ at its saturated vapor pressure has been measured at temperatures between 0.8°K and 3.1°K, at static magnetic fields from 1560 gauss to 12 200 gauss. No dependence of T_1 on the static magnetic field was observed. The measured relaxation times increase gradually from 300 seconds at 0.8°K to 650 seconds at 3.1°K. These measured relaxation times do not appear to have been significantly shortened by wall relaxation processes. These results, which do not agree with measurements made elsewhere, are in good agreement with the short correlation time form of the Bloembergen, Purcell, Pound theory of spin relaxation in liquids.

INTRODUCTION

RECENTLY we reported measurements¹ of the thermal spin relaxation time, T_1 , of He³ nuclei in pure liquid He³ at its saturated vapor pressure. Previous measurements in this laboratory^{2,3} had yielded different T_1 values depending on the container used. It had been concluded from these earlier measurements that in at least some of the containers used the relaxation time was being artificially shortened by wall relaxation or possibly by some impurity. The combination of the long relaxation time in liquid He³ and the large diffusion coefficient makes it difficult to avoid wall effects by simply using a very large sample. In these circumstances, the longest T_1 measured at any given temperature, pressure, etc., probably lies closest to the value characteristic of the bulk liquid, unless there is some systematic error which gives spuriously long T_1 values. The safest procedure seems to be to construct containers of a material believed to be relatively ineffective at relaxing He³ spins; if then approximately the same

results are obtained in two containers of quite different sizes, one has presumably measured something close to the "true" T_1 .

Fortunately, it was discovered early that Pyrex surfaces do not relax He³ spins very fast.² The measurements reported in I were therefore made in two Pyrex bulbs of different sizes and the results obtained from the two bulbs were in good agreement with each other. All the data in I were taken in a static magnetic field of 9000 gauss and seemed to be in reasonable agreement with the BPP⁴ theory of spin relaxation in liquids, provided that one makes the assumption that the correlation time for the motion of the atoms ($\tau_c \cong r^2/10D \cong 10^{-12}$ seconds, where r , a typical inter-atomic distance, is a few Å, and $D \cong 10^{-4}$ cm²/sec.^{5,6}) is much less than the Larmor period in available magnetic fields ($2\pi/\omega_0 \gtrsim 2 \times 10^{-8}$ seconds). The short τ_c approximation would appear to be an extremely good one for He³, particularly at high temperatures ($\sim 3.0^\circ\text{K}$).

Shortly after the completion of the measurements reported in I, the subject was re-opened by the report⁷ of a previously unsuspected magnetic field dependence of T_1 . Low and Rorschach, making measurements at

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