

The Thermodynamics of Irreversible Processes. IV. The Theory of Elasticity and Anelasticity*

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The traditional theory of the solid state rests on two false assumptions. One is the principle of a constant relaxed (or standard) state. The other is the principle of relaxability-in-the-large, first formulated mathematically by de Saint-Venant. His equations are essentially identical with Riemann's equations expressing the condition that a geometry be Euclidean-in-the-large. It is shown that a principle of relaxability-in-the-small is sufficient for the geometry of strain—which then becomes a three-dimensional Riemannian geometry. The kinematics of strain is next developed without introducing the principle of a constant relaxed state.

The ground is thus cleared for the construction of a classical theory of anelasticity. It is first shown that the variability of the relaxed state makes the density of the substance independent of the strains. Consequently, the internal energy can depend on the specific volume as well as on the strains and the entropy. The expression for the rate of increase of entropy is then derived. As usual, this suggests, but does not uniquely determine the form of the dissipative laws. In addition to the usual equations for the viscous stresses, one is led to another set of equa-

tions involving parameters that quantitatively describe the anelastic properties of the substance.

These results are used to derive the equations for the waves of distortion and dilation in an ideal isotropic anelastic medium. When the two coefficients of viscosity and two coefficients of anelasticity all vanish, these reduce to the usual equations for such waves. In addition to the four dissipative coefficients, the isotropic anelastic substance is characterized by four elastic moduli, rather than by the two that characterize an isotropic elastic substance. Thus, there are eight parameters whose values can be adjusted to describe the particular substance. When the four dissipative parameters do not vanish, the propagation of the waves can be described by five relaxation times. The ideal isotropic anelastic substance thus has a relaxation spectrum of about the same complexity as those of actual substances.

The kinematic independence of the density and the strains causes a hydrostatic pressure to have different dynamic effects than a uniaxial pressure. This is in accord with experiment—the latter being much more effective in producing anelastic deformation than the former.

1. INTRODUCTION

THE phenomena of anelasticity have been known for centuries. They are the basis of the metallurgical and other plastic arts. Possibly this has caused them to be too familiar to be easily analyzed from a theoretical point of view. In any case, there is a marked disparity between the amount of thought that has been expended on the theory of elasticity and that expended on the theory of anelasticity. There is a tendency among theoretical physicists to excuse this by claiming that there have, as yet, been no critical experiments in the field of anelasticity. This is scarcely a valid claim, for the experimental literature of this subject is more extensive than that of atomic spectra, and some of the greatest experimenters have contributed to it.

It is the purpose of this paper to indicate that the classical theory of elasticity can be extended

to include anelastic phenomena. To accomplish this, it must first be noted that the traditional theory rests on two false assumptions. It must then be shown that they can be eliminated without serious alteration of the concepts of the theory, and finally, the untenable assumptions must be replaced by definite laws of anelasticity whose consequences can be compared with experiment.

The first of the false assumptions may be called the principle of a constant relaxed state. It asserts that, if the strains of a solid object were to be completely relaxed at time t , the resulting state would be the same as if the strains had been relaxed at any other time t_0 . While some substances, such as spring steel, conform to this principle within wide limits, it is in direct conflict with all that we know about ductility, malleability, etc. There is little doubt that it should be replaced by some law of a quantitative nature, such substances as spring steel being characterized by extreme values of

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the parameters, and such substances as copper, by moderate values.

The second false assumption may be called the principle of relaxability-in-the-large. It asserts that the strains in a solid object can be completely relaxed by removing all external forces. It is trite to remark that the strains in an optical blank cannot be relaxed in this way: it must be carefully annealed and aged. Such counter-examples could be multiplied indefinitely, but one suffices to show that this principle, also, is an unsuitable basis for a theory of the solid state.

The principle of relaxability-in-the-large has an interesting history. It apparently entered the theory as a tacit assumption and remained unrecognized, until in 1864, de Saint-Venant criticized Maxwell for ignoring it in the development of a general method for the solution of elastic problems.¹ The former gave a precise and general mathematical formulation of the principle, and it has been accepted as basic ever since. His work is very closely related to that of his contemporary, Riemann. In 1861, the latter published his work on differential geometries, i.e., geometries that are Euclidean-in-the-small. He also formulated the necessary and sufficient conditions which such a geometry must satisfy in order to be Euclidean-in-the-large. It is a remarkable fact that de Saint-Venant's conditions for relaxability-in-the-large are essentially identical with Riemann's geometrical conditions. This relationship has become fairly well known, and physicists have become accustomed to dealing with geometries that are only Euclidean-in-the-small. It does not appear to have occurred to anyone that, by postulating only relaxability-in-the-small, the ground is cleared for the construction of a theory of anelasticity.

In the following pages, a general theory of strain will be developed. It will first be shown that relaxability-in-the-small is sufficient for the discussion of its geometrical aspects. Next, the kinematics of strain will be developed without using the principle of a constant relaxed state. After these negative tasks have been completed, an attempt will be made to find positive laws of anelasticity. The only source of guidance in this phase of the work will be the second law of

thermodynamics; since this is an inequality rather than an equality, the equations will not be uniquely determined. This is, in a sense, fortunate. For, if it should prove that the equations do not correspond with the facts, there is always the possibility of replacing them by other, more complicated, equations. Finally, equations for the propagation of waves of distortion and dilatation in an isotropic anelastic medium are derived. These reduce to the usual equations when four coefficients of dissipation vanish. When these do not vanish, the propagation of the waves can be described by means of five relaxation times. Thus, even the simplest ideal anelastic substance has a relaxation spectrum comparable in its complexity to those of actual substances.

2. THE RIEMANNIAN GEOMETRY OF STRAIN

Let P and Q be two neighboring points of a material object that is under strain. Two lengths are associated to these points: one is dl , the actual distance between them, and the other is $d\lambda$, the distance that would separate them if all strains in the small region surrounding PQ were relaxed. If dx_i are the cartesian components of the vector $P \rightarrow Q$, then²

$$(dl)^2 = \delta_{ij} dx_i dx_j, \quad (1)$$

$$(d\lambda)^2 = g_{ij} dx_i dx_j, \quad (2)$$

where

$$\delta_{ij} = 0 \text{ if } i \neq j \text{ and } \delta_{11} = \delta_{22} = \delta_{33} = 1, \quad (3)$$

is the Euclidean metric tensor, and g_{ij} is a tensor that specifies the state of strain at the point P . Since a real value of $d\lambda$ (greater than zero), must be associated to every distinct pair of

² The indices $i, j, \dots$, have the values 1, 2, 3, and the summation convention for pairs of identical indices will be followed. Since the coordinates are cartesian throughout, there will be no need to distinguish between covariant and contravariant components; consequently inferior indices will be used by preference although not exclusively. The use of superior indices is convenient for the designation of the reciprocal g -matrix: i.e., the matrix g^{ij} is defined by the equation

$$g^{ij} g_{jk} = \delta_{ik}.$$

More generally, if $a_i \dots$ is any quantity, then

$$a^i \dots = g^{ij} a_j \dots$$

This convention makes it possible to use all of the ordinary formulae for the Riemann-Christoffel symbols, etc., while preserving the convenience of writing $a^i b^j$ instead of $\delta_{ik} a^k b^j$.

¹ A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), 4th edition, pp. 17, 49, 101.

points P, Q it follows that the symmetric tensor g_{ij} is positive definite.³

The question of a physical procedure for relaxing the strains in a given neighborhood immediately arises. For this purpose, it is not sufficient to relieve the object of all external forces: the various parts of the object may also be exerting forces on neighboring parts and thus causing "internal" strains to exist. Geometrically, there is no difference between internal strains and those produced by external forces. However, if a small bit of the matter surrounding P is cut out of the larger object, then all strains in this bit will be relaxed, since it will have no forces acting on it. There is no other general way of relaxing the strains at a point, although in special cases there may be simpler ways. Saint-Venant's problem was to characterize those cases in which the removal of the external forces is sufficient to relax all strains at every point of an extended object.

Let P, Q, Q' , etc., be points in a dissected bit of matter; it will be necessary to compare their configuration before and after the strains have been relaxed. Unmodified words, such as "length," "angle," will always refer to the former state, and the adjective "relaxed" will be prefixed to corresponding words referring to the latter state. The coordinate differentials will always, however, be in the cartesian system associated to the state before the strains have been relaxed, unless explicitly stated otherwise.

With these understandings, let dx_i be the vector $P \rightarrow Q$ and $d'x_i$ the vector $P \rightarrow Q'$; their lengths and relaxed lengths will be given by Eqs. (1) and (2). Let α be the angle QPQ' and α the relaxed angle QPQ' ; then it is clear that,

$$\cos \alpha = (dx_i/dl)(d'x_i/d'l), \quad (4)$$

and it can be proven⁴ that

$$\cos \alpha = g_{ij}(dx_i/d\lambda)(d'x_i/d'\lambda). \quad (5)$$

For this purpose note that the relaxed length, $d'\lambda$, of $Q \rightarrow Q'$ is given by

$$(d'\lambda)^2 = g_{ij}(d'x_i - dx_i)(d'x_j - dx_j) \\ + \text{terms of third order.}$$

To second order, therefore, the Euclidean definition

$$\cos \alpha = \frac{(d''\lambda)^2 - (d'\lambda)^2 - (d\lambda)^2}{2d\lambda d'\lambda}$$

will be identical with Eq. (6). The neglect of the terms of third order is justified, since the formula is to be applied only "in the small."

Let $x_i = x_i(h)$ be any curve, Γ (not closing on itself), in the strained object. Then it is reasonable to suppose that, if a filament having Γ as axis could be cut out of the object, the strains in this filament would be completely relaxed. Let P and Q be points on Γ ; then the length of this curve in the strained state will be

$$l = \int_P^Q \left(\frac{dx_i}{dh} \frac{dx_i}{dh} \right)^{\frac{1}{2}} dh, \quad (6)$$

and the relaxed length of the filament axis will be

$$\lambda = \int_P^Q \left(g_{ij} \frac{dx_i}{dh} \frac{dx_j}{dh} \right)^{\frac{1}{2}} dh. \quad (7)$$

One problem of the geometry of strains will be to determine the shape of the relaxed filament; the determination of its length is only one part of this problem.

Conversely, it may be required to determine the curve Γ so that the axis of the relaxed filament will have a given shape. If this is to be a straight line, the solution is simple: Γ must be a geodesic of the strain metric g_{ij} ; such a filament will therefore be called a geodesic filament. The proof follows: let P and Q be two points on the axis of a geodesic filament, and P', Q' two points in the neighborhood of P and Q such that $Q \rightarrow Q' = d''x_i$ and $P \rightarrow P' = d'x_i$, while the relaxed angles α' and α'' (see Fig. 1) are both $\pi/2$. The relaxed length of the axis between P and Q will be given by Eq. (8). Let Γ be any curve joining P' to Q' , provided only that it is everywhere close to the axis; its length will be⁵ $\lambda + \delta\lambda$, where

⁵ The proof follows readily from a slight modification of that given in *RG*, pp. 48-49. It is only necessary to replace Eq. (17.1) by $\epsilon\omega^i = d'x_i$ for $h = h_P$, and $\epsilon\omega^i = d''x_i$ for $h = h_Q$. On integrating Eq. (17.4) by parts and using Eq. (17.5), the equation in the text is obtained in a slightly different notation.

³ L. P. Eisenhart, *Riemannian Geometry* (Princeton University Press, Princeton, New Jersey, 1926), p. 23.

⁴ Reference 3, p. 38.

$$\begin{aligned}
\delta\lambda &= \left(g_{ij} \frac{dx_i}{d\lambda} \right)_Q d''x_j - \left(g_{ij} \frac{dx_i}{d\lambda} \right)_P d'x_i \\
&\quad + \text{terms of second order,} \\
&= d''\lambda \cos\alpha'' - d'\lambda \cos\alpha' + \dots, \\
&= 0 + \dots.
\end{aligned} \tag{8}$$

Hence the relaxed distance between any pair of points in the two cross sections perpendicular to the relaxed axis at P and Q is the same, to first order. This, however, is the condition that the planes of the two sections be parallel after relaxation. Since P and Q are arbitrary points on the axis, it follows that the latter must be a straight line.

The more general problem of determining the relaxed shape of an arbitrary filament will not be discussed, although the assumptions underlying the preceding discussion are presumably adequate for its treatment. Of greater interest is the remark that, if Γ is a closed (rather than an open) curve, and a closed filament be cut from the object with Γ as axis, the strains in the filament will not always be completely released. To prove this, consider a curvilinear triangle PQR in the object, whose sides are geodesics. Let this be the closed curve Γ , and cut a filament from the object with this as axis (see Fig. 2). If the strains in the filament were completely relaxed, its axis would become a plane triangle, and hence the sum of the angles at P , Q and R would be π . However, Eq. (5) affords the means of calculating these angles, and their sum will usually not be π , so that the triangle must be curvilinear, and the strains only partially relaxed. If one side of the filamentary triangle be cut, further relaxation will occur, and it will assume some such form as Fig. 3.

In general, the relaxation of the strains in thin sheets cut from the object will therefore also be incomplete. For, we may consider the above

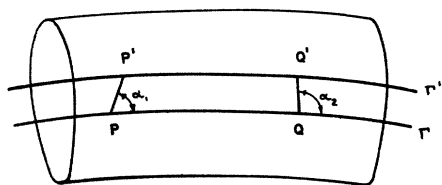


FIG. 1.

triangular filament to have been prepared by first cutting a thin sheet from the object, and then cutting out the triangle. Since each new cut will cause some further relaxation, the conclusion follows.

Finally, we may return to de Saint-Venant's problem, and consider the condition that the strains in an object may be completely relaxed by merely removing the external forces, without making any cuts. Let x_i be the cartesian coordinates of a point, P , in the object before relaxation and y_i those of P after relaxation. They will be related by equations of the form $y_i = f_i(x_1 x_2 x_3)$ and since points that were distinct but neighboring before relaxation will be so afterwards, the Jacobian of this transformation will not vanish. Moreover, the functions will be single-valued throughout the interior of the object. In terms of the dy_i , the relaxed distance between two neighboring points will be given by the Euclidean metric:

$$(d\lambda)^2 = \delta_{ij} dy_i dy_j, \tag{9}$$

while Eq. (2) will still hold for $d\lambda$ in terms of the dx_i . The conditions that must be satisfied by the g_{ij} , in order that the functions f_i shall exist, were investigated by Riemann⁶ as has been remarked above. The necessary and sufficient condition is the vanishing of the Riemann tensor formed from the g_{ij} and their derivatives with respect to the x_i . If the interior of the object is a simply-connected region, this condition is also sufficient for the complete relaxation of the strains. If the interior is multiply connected, it will, in addition, usually be necessary to cut the object along a sufficient number of surfaces to make it simply connected, before the strains can relax completely. The theory of such cuts has also been developed by Riemann. The filamentary triangles discussed above are a primitive example of the difference between simply and multiply connected regions.

Riemann's condition is thus the vanishing of complicated functions of the g_{ij} . If the strains are small, one may write

$$g_{ij} = \delta_{ij} - 2\sigma_{ij}, \tag{10}$$

and neglect the squares and products of σ_{ij} and its derivatives. Riemann's fourth-order tensor

⁶ Reference 3, pp. 23-25.

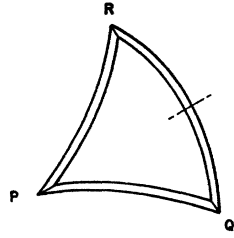


FIG. 2.

then simplifies to the approximate form

$$-R_{lijk} = \frac{\partial^2 \sigma_{kl}}{\partial x_i \partial x_j} + \frac{\partial^2 \sigma_{ij}}{\partial x_k \partial x_l} - \frac{\partial^2 \sigma_{ik}}{\partial x_l \partial x_j} - \frac{\partial^2 \sigma_{lj}}{\partial x_i \partial x_k}. \quad (11)$$

Since each of the four indices can take on any of three values, there are 81 components R_{lijk} . However, many of them are equal, especially because $\sigma_{ij} = \sigma_{ji}$, and others vanish identically. The distinct non-vanishing components are six in number and can be obtained from

$$-R_{1231} = \frac{\partial^2 \sigma_{11}}{\partial x_2 \partial x_3} - \frac{\partial}{\partial x_1} \left\{ \frac{\partial \sigma_{21}}{\partial x_3} + \frac{\partial \sigma_{31}}{\partial x_2} - \frac{\partial \sigma_{23}}{\partial x_1} \right\}, \quad (12.1)$$

$$-R_{1221} = \frac{\partial}{\partial x_1} \left(\frac{\partial \sigma_{22}}{\partial x_1} - \frac{\partial \sigma_{12}}{\partial x_2} \right) + \frac{\partial}{\partial x_2} \left(\frac{\partial \sigma_{11}}{\partial x_2} - \frac{\partial \sigma_{12}}{\partial x_1} \right), \quad (12.2)$$

by the cyclic permutation of 1, 2, 3. Except for a difference in notation, de Saint-Venant's equations are $R_{lijk} = 0$.¹

The rejection of the principle of relaxability-in-the-large permits the above six components of R_{lijk} to have any values whatever. However, this negative action is not sufficient for the construction of a complete theory of anelasticity. The six equations must be replaced by others, otherwise most problems will not have a unique solution. This is the valid portion of de Saint-Venant's criticism of Maxwell's work in this field.

3. THE KINEMATICS OF STRAIN

Thus far, only the momentary state of an object has been considered, and the relaxation of its strains has been supposed to be accomplished by an idealized destructive process. Actually, the changes in the state of strain of

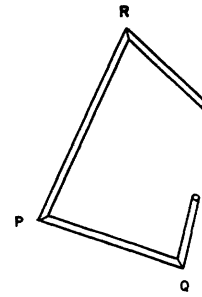


FIG. 3.

an object are very often accompanied by motions that leave its integrity unimpaired; obviously, exceptions to this rule do occur (rupture, fracture) but they will not be considered here.

Let $u_i(x_1 x_2 x_3 t)$ be the velocity of the matter that at time t occupies the point $P = x_i$; the velocity, at time t and at $Q = x_i + dx_i$ will be

$$u_i + \frac{\partial u_i}{\partial x_j} dx_j.$$

The relative velocity of the points P and Q will thus cause the vector $P \rightarrow Q$ to change; the rate of its change will be (to first order)

$$\frac{D dx_i}{Dt} = \frac{\partial u_i}{\partial x_j} dx_j \quad (13)$$

and its length will change according to the formula

$$\begin{aligned} \frac{D(dl)^2}{Dt} &= \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) dx_i dx_j \\ &= 2u_{(ij)} dx_i dx_j, \end{aligned} \quad (14)$$

where

$$u_{(ij)} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right). \quad (15)$$

Such changes in the distance separating neighboring points are called deformations: hence $u_{(ij)}$ may be called the deformation tensor. The corresponding anti-symmetric tensor is the vorticity:

$$u_{[ij]} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i} \right); \quad (16)$$

the identities

$$\frac{\partial u_i}{\partial x_j} = u_{(ij)} + u_{[ij]} \quad (17)$$

and

$$\frac{\partial u_i}{\partial x_i} = u_{(ii)} \quad (18)$$

will be needed below.

The rate at which the relaxed length of dx_i is changing may also be calculated, and is

$$\begin{aligned} \frac{D(d\lambda)^2}{Dt} &= \left\{ \frac{\partial g_{ij}}{\partial t} + u_k \frac{\partial g_{ij}}{\partial x_k} + g_{ik} \frac{\partial u_k}{\partial x_j} + g_{kj} \frac{\partial u_k}{\partial x_i} \right\} \\ &\quad \times dx_i dx_j = 2a_{ij} dx_i dx_j, \quad (19) \end{aligned}$$

where a_{ij} is an obvious abbreviation, and may be called the anelasticity tensor. The principle of a constant relaxed state would require that the relaxed length of dx_i be independent of t , and hence that $a_{ij}=0$ at all times and places. The rejection of this principle again has the negative effect of leaving a_{ij} physically indeterminate.

Before attempting to find positive laws governing the anelasticity tensor, certain purely kinematic equations connecting it to other quantities will be derived. The Eq. (19) may be written

$$a_{ij} = \frac{1}{2} \frac{Dg_{ij}}{Dt} + U_{(ij)} \quad (20)$$

where

$$U_{(ij)} = \frac{1}{2} \left(g_{ik} \frac{\partial u_k}{\partial x_j} + g_{kj} \frac{\partial u_k}{\partial x_i} \right). \quad (21)$$

It should be noted that because of Eq. (17), $U_{(ij)}$ depends on the vorticity as well as on the deformation of the motion:

$$U_{(ij)} = \frac{1}{2} (g_{ik} u_{(kj)} + g_{kj} u_{(ki)}) + \frac{1}{2} (g_{ik} u_{[kj]} + g_{kj} u_{[ki]}). \quad (22)$$

The matrix reciprocal to g_{ij} is denoted by g^{ij} where (see reference 2)

$$g^{ij} g_{jk} = \delta_{ik}; \quad (23)$$

hence Eq. (21) results in

$$g^{ij} U_{(ij)} = u_{(ii)} = \frac{\partial u_i}{\partial x_i}, \quad (24)$$

which is analogous to Eq. (18). Consequently Eq. (20) leads to

$$\frac{\partial u_i}{\partial x_i} = g^{ij} \left(a_{ij} - \frac{1}{2} \frac{Dg_{ij}}{Dt} \right). \quad (25)$$

The determinant of the matrix g_{ij} is denoted by g ; the rule for the differentiation of a determinant results in

$$\frac{D}{Dt}(\log g) = g^{ij} \frac{Dg_{ij}}{Dt} \quad (26)$$

and hence Eq. (25) becomes

$$\frac{\partial u_i}{\partial x_i} = g^{ij} a_{ij} - \frac{1}{2} \frac{D}{Dt}(\log g), \quad (27)$$

an equation that will prove important below.

4. THE THERMODYNAMICS OF STRAIN

The general equations of thermodynamics will be briefly summarized in the present notation, and their implications for anelastic phenomena discussed. The conservation of matter is expressed by

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho u_i) = 0,$$

where ρ is the density of the substance. This may also be written

$$\frac{D\rho}{Dt} = -\rho \frac{\partial u_i}{\partial x_i}. \quad (28)$$

Introducing the specific volume, $v=1/\rho$, this becomes, on referring to the previous equations,

$$\frac{D}{Dt}(\log v) = \frac{\partial u_i}{\partial x_i}. \quad (29)$$

Combining this with Eq. (27), the important equation

$$\frac{D}{Dt}(\log v g^{\frac{1}{2}}) = g^{ij} a_{ij} \quad (30)$$

is obtained. One consequence of the principle of a constant relaxed state would thus be that the product $vg^{\frac{1}{2}}$ is constant for each bit of the substance. It is the most commonly used consequence of this principle. In the present theory, the quantities v and g become independent, and must both be specified before the state of the substance is known.

The conservation of momentum is expressed by

$$\rho \frac{Du_i}{Dt} = \frac{\partial S_{ij}}{\partial x_j} \quad (31)$$

where $S_{ij}=S_{ji}$ is the stress tensor; and the conservation of energy is expressed by

$$\rho \frac{D}{Dt} (\frac{1}{2} u_i u_i + \epsilon) + \frac{\partial q_i}{\partial x_i} = \frac{\partial}{\partial x_j} (u_i S_{ij}) \quad (32)$$

where ϵ is the internal energy in ergs per gram of the substance and q_i is the heat flow, in ergs per $\text{cm}^2 \text{ sec.}^{-1}$ Equation (31) combines with Eq. (32) to give the first law of thermodynamics:

$$\rho \frac{D\epsilon}{Dt} + \frac{\partial q_i}{\partial x_i} = S_{ij} u_{(ij)}. \quad (33)$$

It is worth noting that only the deformation tensor enters into the expression, $S_{ij} u_{(ij)}$, for the rate of thermodynamic work.

From the previous discussion, it follows that the internal energy must be a function of, at least, the entropy, η ; the specific volume, v ; and of the strain metric, g_{ij} . In the traditional discussions, v is assumed to be expressible as a function of g , and thus does not appear explicitly in ϵ . The rejection of the principle of a constant relaxed state thus finds a first positive expression in the equation

$$\frac{D\epsilon}{Dt} = \frac{\partial \epsilon}{\partial v} \frac{Dv}{Dt} + \frac{\partial \epsilon}{\partial g_{ij}} \frac{Dg_{ij}}{Dt} + \frac{\partial \epsilon}{\partial \eta} \frac{D\eta}{Dt}. \quad (34)$$

The various terms on the right can be transformed into more interesting expressions. Using the usual thermodynamic definition of the hydrostatic pressure:

$$p = - \frac{\partial \epsilon}{\partial v}, \quad (35)$$

and referring to Eq. (29),

$$\rho \frac{\partial \epsilon}{\partial v} \frac{Dv}{Dt} = -p u_{(ii)}. \quad (36)$$

The usual definition of the absolute temperature, θ , is equivalent to

$$\rho \frac{\partial \epsilon}{\partial \eta} \frac{D\eta}{Dt} = \rho \theta \frac{D\eta}{Dt}. \quad (37)$$

The remaining term results in a more complicated expression; since g_{ij} is a symmetric tensor, it

depends only on the symmetric tensor

$$E_{ij} = - \rho \left(\frac{\partial \epsilon}{\partial g_{ij}} + \frac{\partial \epsilon}{\partial g_{ji}} \right) \quad (38)$$

which may be called the elastic stress. (It will appear below that the total stress is the resultant of three components: the hydrostatic pressure, the elastic stress, and the viscous stress.) Equation (38) results in

$$\begin{aligned} \rho \frac{\partial \epsilon}{\partial g_{ij}} \frac{Dg_{ij}}{Dt} &= - \frac{1}{2} E_{ij} \frac{Dg_{ij}}{Dt}, \\ &= - E_{ij} (a_{ij} - U_{(ij)}) \end{aligned}$$

by Eq. (20). Using Eq. (22), it becomes

$$\begin{aligned} \rho \frac{\partial \epsilon}{\partial g_{ij}} \frac{Dg_{ij}}{Dt} &= \frac{1}{2} [g_{ik} E_{kj} + g_{jk} E_{ki}] u_{(ij)} \\ &\quad - E_{ij} [a_{ij} - \frac{1}{2} g_{ik} u_{[kj]} - \frac{1}{2} g_{jk} u_{[ki]}]. \end{aligned} \quad (39)$$

Using these results, the first law may be transformed into

$$\begin{aligned} \rho \frac{D\eta}{Dt} + \frac{\partial}{\partial x_i} \left(\frac{q_i}{\theta} \right) &= - \left(\frac{1}{\theta} \right)^2 q_i \frac{\partial \theta}{\partial x_i} \\ &\quad + \left(\frac{1}{\theta} \right) u_{(ij)} [S_{ij} + p \delta_{ij} - \frac{1}{2} g_{ik} E_{kj} - \frac{1}{2} g_{jk} E_{ki}] \\ &\quad + \left(\frac{1}{\theta} \right) E_{ij} [a_{ij} - \frac{1}{2} g_{ik} u_{[kj]} - \frac{1}{2} g_{jk} u_{[ki]}]. \end{aligned} \quad (40)$$

The second law of thermodynamics asserts that, for all motions compatible with the laws of physics, the right side of this equation is greater than zero. If the physical laws are unknown, this imposes restrictions on their possible forms.⁷

One particular set of laws that satisfies these restrictions is

$$q_i = -k \frac{\partial \theta}{\partial x_i}, \quad (41)$$

$$\begin{aligned} S_{ij} &= -p \delta_{ij} + \frac{1}{2} g_{ik} E_{kj} + \frac{1}{2} g_{jk} E_{ki} \\ &\quad + N_{((ij)(kl))} u_{(kl)}, \end{aligned} \quad (42)$$

$$a_{ij} = \frac{1}{2} g_{ik} u_{[kj]} + \frac{1}{2} g_{jk} u_{[ki]} + M_{((ij)(kl))} E_{kl}, \quad (43)$$

⁷ Carl Eckart, Thermodynamics of irreversible processes, Phys. Rev. **58**, 267, 269, 919 (1940).

provided that $k > 0$ and the two quadratic forms

$$N_{((ij)(kl))}u_{(ij)}u_{(kl)} \quad \text{and} \quad M_{((ij)(kl))}E_{ij}E_{kl}$$

are positive definite.

The Eq. (41) will be recognized as Fourier's law of heat conduction, k being the thermal conductivity. Equation (42) is a generalization of the usual formulae for the total stress, the first term being the hydrostatic pressure, the second two the elastic stress, and the last, the viscous stress. This last depends only on the deformation tensor $u_{(ij)}$, and, since the fourth-order tensor $N_{((ij)(kl))}$ has 21 independent components, it is clearly that generalization of the Stokes-Navier formulae which is appropriate to an aeolotropic substance.

Since Eq. (43) involves the anelasticity tensor, it has no counterpart in the traditional theory, unless one wishes to consider the principle of a constant relaxed state ($a_{ij}=0$) as such. It can be given a more useful form by using Eq. (20) and (22):

$$\frac{1}{2} \frac{Dg_{ij}}{Dt} = -\frac{1}{2}(g_{ik}u_{(kj)} + g_{jk}u_{(ki)}) + M_{((ij)(kl))}E_{kl}. \quad (44)$$

In this form, it asserts that changes in the strain metric at a given bit of matter are caused, not only by the deformation of the matter, but also by the elastic stresses. It is very interesting to note that the hydrostatic pressure, p , does not contribute to these irreversible changes in the strain metric.

Perhaps this is the strongest argument for supposing that Eq. (44) will be found consistent with the experimental facts. There are indications that the permanent deformations produced by a purely hydrostatic pressure are second-order effects compared to those produced by uniaxial pressures. Thus, a cube of lead may be subject to great hydrostatic pressure without apparent anelastic deformation; a much smaller pressure exerted by the jaws of a vise will deform it noticeably and permanently.

5. THE PROPAGATION OF WAVES IN AN ISOTROPIC ANELASTIC MEDIUM

One method of obtaining information concerning a substance is to study the propagation of waves through it. In such experiments, the

strains are usually small, so that Eq. (10) is useful, and the equations can be simplified by neglecting second-order terms in the σ_{ij} . The specific volume, v , also departs only slightly from its normal value $v_0 = 1/\rho_0$. The abbreviations

$$s = 1 - \rho_0 v, \quad \sigma = \sigma_{ii}, \quad (45)$$

will be used; if the waves are purely elastic, $s + \sigma = 0$ to the present approximation. It will be supposed, for simplicity, that all thermal effects can be neglected, so that the internal energy can be treated as a function only of s and σ_{ij} . Since it must be a minimum for $s=0$, $\sigma_{ij}=0$, a quadratic function will suffice for the present purposes. It will also be supposed that the medium is isotropic, so that all of its 28 coefficients except four will vanish:

$$\epsilon = (1/2\rho_0)(\lambda_3 s^2 + 2\lambda_2 s\sigma + \lambda_1 \sigma^2 + 2\mu \sigma_{ij}\sigma_{ij}). \quad (46)$$

The condition that this be a positive definite form is

$$\lambda_3 > 0, \quad \mu > 0, \quad \lambda_3(3\lambda_1 + 2\mu) > 3\lambda_2^2. \quad (47)$$

It should be noted that, although the preceding discussion has been couched in terms of a theory of the solid state, it ought to be possible to apply it with little modification to fluids. For a completely fluid substance, the coefficient $\mu = 0$. It is likely that substances for which μ is small will have properties that differ only slightly from those of a completely fluid substance. The distinction between hydrodynamics and the theory of elasticity is merely quantitative and not qualitative.

Substituting Eq. (46) into the general equations, it is easily seen that

$$p = \lambda_3 s + \lambda_2 \sigma, \quad (48)$$

$$E_{kl} = (\lambda_2 s + \lambda_1 \sigma)\delta_{kl} + 2\mu \sigma_{kl}. \quad (49)$$

The total stress is

$$S_{kl} = [(\lambda_2 - \lambda_3)s + (\lambda_1 - \lambda_2)\sigma]\delta_{kl} + 2\mu \sigma_{kl} + 2Nu_{(kl)} + N'u_{(ii)}\delta_{kl}, \quad (50)$$

where N and N' are the two coefficients of viscosity of an isotropic substance, and $N > 0$, $3N' + 2N > 0$. For an ideal gas, $3N' + 2N = 0$.

The conservation of matter reduces to the equation

$$\frac{\partial s}{\partial t} = -u_{(ii)}. \quad (51)$$

The conservation of momentum becomes

$$\rho_0 \frac{\partial u_k}{\partial t} = (\lambda_2 - \lambda_3) \frac{\partial s}{\partial x_k} + (\lambda_1 - \lambda_2) \frac{\partial \sigma}{\partial x_k} + 2\mu \frac{\partial \sigma_{kl}}{\partial x_l} + N \nabla^2 u_k + (N + N') \frac{\partial}{\partial x_k} u_{(ii)}. \quad (52)$$

The isotropic nature of the substance reduces Eq. (44) to

$$-\frac{\partial \sigma_{kl}}{\partial t} = -u_{(kl)} + 2ME_{kl} + M'E_{ii}\delta_{kl} \quad (53)$$

where M and $3M' + 2M$ are both positive. The M 's may be called the coefficients of anelasticity. As yet, there is no kinetic theory of these constants, but it is possible that they do not vanish for an ideal gas. In that case, a kinetic theory would be possible. Because of Eq. (50), Eq. (53) reduces to

$$\left[\frac{\partial}{\partial t} + 4M\mu \right] \sigma_{kl} = u_{(kl)} - \{ (3M' + 2M)\lambda_2 s + [(3M' + 2M)\lambda_1 + 2M'\mu]\sigma \} \delta_{kl}. \quad (54)$$

Setting $k=l$ in Eq. (54) and summing, one obtains the simple equation

$$\frac{\partial}{\partial t}(s + \sigma) = -(3M' + 2M) \times [3\lambda_2 s + (3\lambda_1 + 2\mu)\sigma], \quad (55)$$

which shows that when the coefficients of anelasticity vanish, $s + \sigma$ is constant.

The terms in σ_{kl} can be eliminated between Eqs. (52) and (54), resulting in

$$\begin{aligned} & \left[\frac{\partial}{\partial t} + 4M\mu \right] \left[\rho_0 \frac{\partial u_k}{\partial t} + (\lambda_3 - \lambda_2) \frac{\partial s}{\partial x_k} + (\lambda_2 - \lambda_1) \frac{\partial \sigma}{\partial x_k} + (N + N') \frac{\partial^2 s}{\partial t \partial x_k} - N \nabla^2 u_k \right] \\ &= \mu \left[\nabla^2 u_k - \frac{\partial^2 s}{\partial t \partial x_k} \right] - 2\mu \left\{ (3M' + 2M)\lambda_2 \frac{\partial s}{\partial x_k} + [(3M' + 2M)\lambda_1 + 2M'\mu] \frac{\partial \sigma}{\partial x_k} \right\}. \quad (56) \end{aligned}$$

As in the traditional theory, the equation for the vorticity is comparatively simple, since most

of the terms in Eq. (56) are gradients. Taking the curl of this equation eliminates the gradients and results in

$$\left[\frac{\partial}{\partial t} + 4M\mu \right] \left[\rho_0 \frac{\partial u_{[kl]}}{\partial t} - N \nabla^2 u_{[kl]} \right] = \mu \nabla^2 u_{[kl]}. \quad (57)$$

If M and N vanish, this reduces to the well-known equation for the waves of distortion.

On taking the divergence of Eq. (56), one obtains the generalization of the dilatational wave equation:

$$\begin{aligned} & \left[\frac{\partial}{\partial t} + 4M\mu \right] \left[-\rho_0 \frac{\partial^2 s}{\partial t^2} + (\lambda_3 - \lambda_2) \nabla^2 s + (\lambda_2 - \lambda_1) \nabla^2 \sigma + (N' + 2N) \nabla^2 \frac{\partial s}{\partial t} \right] \\ &= -2\mu \nabla^2 \frac{\partial s}{\partial t} - 2\mu \{ (3M' + 2M)\lambda_2 \nabla^2 s + [(3M' + 2M)\lambda_1 + 2M'\mu] \nabla^2 \sigma \}. \quad (58) \end{aligned}$$

When the coefficients of viscosity and anelasticity vanish, and $s + \sigma = 0$, this reduces to

$$\frac{\partial}{\partial t} \left[-\rho_0 \frac{\partial^2 s}{\partial t^2} + (\lambda_1 - 2\lambda_2 + \lambda_3 + 2\mu) \nabla^2 s \right] = 0.$$

For simple harmonic waves, this is equivalent to the usual equation for the dilatational waves except that the coefficient of elasticity usually denoted by λ is replaced by $\lambda_1 - 2\lambda_2 + \lambda_3$.

These equations have plane wave solutions of the form $\exp i(kx - nt)$ where k is in every case, expressible as a function of n . These functions are such that k and n cannot both be real numbers. The ratio

$$c(n) = (n/k)^{\frac{1}{2}}$$

is also a complex number in general, but may still be called the velocity of the waves: for real values of n , its real part is the phase velocity and its imaginary part is related to the absorption coefficient of the waves. For certain real values of $in = 1/\tau$, $c(n) = 0$. These values of τ are called the relaxation times of the medium. It is an empirical fact that anelastic media have many widely different relaxation times: collectively they form the relaxation "spectrum." The num-

ber of lines in this spectrum depend on the crystalline structure and on the degree of chemical purity of the substance. It is therefore important to discuss the relaxation spectrum of the idealized medium considered above, in order to see whether it conforms to these general empirical facts about anelasticity.

The case of the distortional waves is quite simple; Eq. (57) yields the formula

$$\rho_0 c^2 = \mu(1 + 4NM) \frac{in[1 - in\tau_r]}{in - 4M\mu}, \quad (59)$$

where

$$\tau_r = N/\mu(1 + 4NM). \quad (60)$$

Therefore these waves contribute two lines to the relaxation spectrum: $\tau = \tau_r$ and $\tau = \infty$. The line at infinity would presumably move to a finite position if the thermal conductivity were not set equal to zero, and it might split up into several.

The case of the dilational waves results in a more complicated formula, since Eq. (55) and (58) must be treated simultaneously. The general result is that c is determined by the condition that the determinant of two linear equations vanish. These equations have the form

$$\begin{aligned} (in - a)s + (in - b)\sigma &= 0, \\ s\{(-in + 4M\mu)(-\rho_0 c^2 + A + Bin) - 2\mu in + C\} \\ &+ \sigma\{(-in + 4M\mu)(\lambda_2 - \lambda_1) + D\} = 0, \end{aligned}$$

where $a, b, A, \dots, D$ are functions of the coefficients of elasticity, anelasticity, and viscosity. It is readily seen that $\rho_0 c^2$ will be a rational function of in , the numerator being a cubic and the

denominator a quadratic. It is not easily proven that the roots of the numerator occur for real values of $1/in$, but this is probably a consequence of Eq. (47) and the restrictions on the coefficients of viscosity and anelasticity. Assuming this, the dilational waves contribute three lines to the relaxation spectrum. Again, a finite value of the thermal conductivity will undoubtedly introduce at least one additional line.

The present theory, therefore, predicts that a pure isotropic substance will have a minimum of five lines in its relaxation spectrum. If the substance is not chemically pure, but contains impurities that are capable of diffusing, their concentrations will enter into the expression for ϵ and their concentration gradients and chemical potentials will enter into the expression for the rate of increase of entropy. The equations for small departures from equilibrium will therefore contain additional variables, and increase in number. This will increase the number of relaxation times. In the same way, departures from isotropy will increase the number of types of waves and the number of kinds of dissipation, with a corresponding complication of the relaxation spectrum.

It would thus seem that the present theory is capable of explaining any given relaxation spectrum without resorting to the device of integro-differential equations. The crucial empirical test of the theory must therefore depend on its ability to explain changes in the relaxation spectrum caused by adding impurities, and similar phenomena.