An Attempt to Generalize Onsager's Principle, and its Significance for Rheological Problems[1])

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1. Introduction

Recent developments in rheology emphasize the thermodynamic aspect of the problems treated. In thermoelasticity, for instance, the field of classical elasticity is extended to include influences of temperature differences and heat flow [1][3]). While the phenomena considered here are reversible (by definition), other trends of research are concerned with irreversible processes. A. P. Green [2] and W. Prager ([3], p. 83) have pointed out that in the solution of problems of plastic flow it is indispensable to assure a positive sign of the rate of dissipation work throughout the body. M. A. Biot [4] stressed the importance of irreversible thermodynamics for viscoelasticity. He used the relations of L. Onsager [5, 6] to establish a perfect analogy between problems of elastic deformation and viscous flow. This proof of the so-called viscoelastic analogy has the advantage of being independent of any conditions of symmetry or isotropy; it is restricted, however, to linear rheological laws, since Onsager's relations are meaningful only in the linear case.

In a recent paper [7][4]) the author suggested (without proof) a generalization of Onsager's theory for nonlinear phenomenological laws. Such a generalization is of particular interest in connection with rheology, since it allows to establish the viscoelastic analogy in full generality, and at the same time to lay a foundation for the theory of plastic potential of R. v. Mises [8] which, in the generalized form due to W. Prager ([3], p. 18), is one of the central pillars of the theory of plasticity.

This paper is an attempt to prove the suggested generalization of Onsager's relations. This can be done in full generality for arbitrary irreversible processes (sections 4 and 5). Since, however, the need for this generalization

[2]) ETH, 1956/57 Brown University, Providence, R. I., USA.

[3]) Numbers in brackets refer to References, page 762.

[4]) This paper was written in ignorance of Biot's work.

arose in connection with rheology, the exposition of the problem (sections 2 and 3) and the evaluation of the results (section 6) will be restricted to this particular field.

2. The Rheologic Problem

In certain rheologic bodies (Maxwell body, Prandtl-Reuss body) each of the deformations x_k $(k = 1, 2, \ldots)$ is the sum

$$x_k = x_k^e + x_k^i \tag{2.1}$$

of an elastic and an inelastic component, where the distinction between the two types of deformation is based on a definition to be given presently. If θ is the temperature of the body, the quantities x_k^e, x_k^i, and θ may be considered as the independent thermodynamic state-variables. In order to assure that the state of the body at any time is entirely determined by these quantities, it is necessary to confine the following considerations to sufficiently small bodies or to sufficiently slow changes of state.

The work of the external forces X_i in an arbitrary change of state is given by

$$dW = X_k \, (dx_k^e + dx_k^i) \; ^{5)}. \tag{2.2}$$

If dQ denotes the induced heat, the *first fundamental theorem* of thermodynamics takes the form

$$dW + dQ = dU \,, \tag{2.3}$$

where $U(x_k^e, x_k^i, \theta)$ is a single-valued state-function, called the *internal energy* of the body.

From (2.2) and (2.3) follows

$$dQ = dU - dW = \left(\frac{\partial U}{\partial x_k^e} - X_k \right) dx_k^e + \left(\frac{\partial U}{\partial x_k^i} - X_k \right) dx_k^i + \frac{\partial U}{\partial \theta} \, d\theta \,. \tag{2.4}$$

According to the *second fundamental theorem* of thermodynamics

$$dQ \leqq \theta \, dS \,, \tag{2.5}$$

where $S(x_k^e, x_k^i, \theta)$ is another single-valued state-function, called the *entropy* of the body. For reversible changes of state (2.5) is an equality; for irreversible processes it is an inequality.

We now distinguish between x_k^e and x_k^i by the definition that the elastic deformations be reversible changes of state, while the inelastic deformations are irreversible. From (2.4) and from relation (2.5), interpreted as an equation

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5) Throughout this paper the summation convention is adopted for subscripts.

for elastic processes $dx_k^i = 0$, we obtain

$$\left(\frac{\partial U}{\partial x_k^e} - X_k\right) dx_k^e + \frac{\partial U}{\partial \theta}\, d\theta = \theta\, dS\,. \tag{2.6}$$

It follows that

$$\frac{\partial S}{\partial x_k^e} = \frac{1}{\theta}\left(\frac{\partial U}{\partial x_k^e} - X_k\right), \qquad \frac{\partial S}{\partial \theta} = \frac{1}{\theta}\cdot\frac{\partial U}{\partial \theta}\,. \tag{2.7}$$

For the partial derivatives $\partial S/\partial x_k^i$ no similar relations hold.

It is useful to introduce a third single-valued state function

$$F(x_k^e,\, x_k^i,\, \theta) = U - \theta S\,, \tag{2.8}$$

called the *free energy* of the body. According to (2.7) and (2.8)

$$X_k = \frac{\partial F}{\partial x_k^e}\,, \qquad -S = \frac{\partial F}{\partial \theta}\,. \tag{2.9}$$

Thus the dependent state-variables X_i, $-S$ can be obtained as partial derivatives of the free energy with respect to the corresponding independent variables x_k^e, θ. The function F therefore is sometimes called the *thermoelastic potential* of the body. According to (2.9) the thermoelastic behaviour (the elastic constants, the thermic deformation coefficients and the specific heats) is fully determined by the function F and generally depends on the inelastic deformations x_k^i.

From now on we confine ourselves to bodies the thermoelastic behaviour of which is independent of the inelastic deformations. On account of (2.9) the free energy of such a body is a sum of the form $F(x_k^e,\, \theta) + f(x_k^i)$. According to the last equation (2.9) the entropy has the form $S(x_k^e,\, \theta)$, and due to (2.8) the internal energy is given by $U(x_k^e,\, \theta) + f(x_k^i)$. Reviewing relations (2.1) through (2.9) we note that the function $f(x_k^i)$ only appears in (2.4). As a consequence of this the inelastic-thermic behaviour (e. g., the specific heats of the inelastic body and its response to given external forces) generally depends on the inelastic deformations. We exclude this dependence as well, setting $f(x_k^i) = 0$, so that $U = U(x_k^e,\, \theta)$ and $S = S(x_k^e,\, \theta)$.

In the discussion of the elastic behaviour it is customary to use the fact that the heat production is small. If the changes of state are isothermal, the temperature is no more a state-variable. The free energy, dependent on the elastic deformations x_k^e alone, becomes the elastic potential $\Phi(x_k^e)$, and the forces are given, according to (2.9), by

$$X_i = \frac{\partial \Phi}{\partial x_i^e}\,. \tag{2.10}$$

The changes of state, however, can also be considered as adiabatic. Setting $dx_k^i = 0$ and $dQ = 0$ in (2.2) and (2.3), we obtain in this case $dU = X_k\, dx_k^e$.

The internal energy again is independent of the temperature, and the forces follow once more from (2.10), where $\Phi(x_k^e)$ now is the internal energy.

Relation (2.10) represents the general rheologic law for isothermally or adiabatically elastic bodies. This law can be linearized for small deformations by assuming that Φ is a (positive definite) quadratic form

$$\Phi(x_k^e) = \frac{1}{2} a_{ik} x_i^e x_k^e \tag{2.11}$$

of the elastic deformations. The generality of (2.11) is not restricted by the further assumption that the matrix be symmetric, i. e., that

$$a_{ki} = a_{ik}. \tag{2.12}$$

The law (2.10) now takes the form

$$X_i = a_{ik} x_k^e, \tag{2.13}$$

and due to (2.12) we have

$$\frac{\partial X_k}{\partial x_i^e} = \frac{\partial X_i}{\partial x_k^e}. \tag{2.14}$$

If also inelastic deformations are present, (2.5) is to be interpreted as an inequality. According to (2.4) through (2.6)

$$dQ = \theta \, dS - X_k \, dx_k^i < \theta \, dS. \tag{2.15}$$

Thus the so-called *dissipation work* $dW^d = X_k \, dx_k^i$ is subject to the inequality

$$dW^d = X_k \, dx_k^i > 0, \tag{2.16}$$

and the increase of entropy is given by

$$dS = \frac{1}{\theta} (dQ + dW^d). \tag{2.17}$$

From (2.16) and (2.17) follows as expected that every adiabatic inelastic deformation increases the entropy.

According to CARNOT and CLAUSIUS the entropy increment dS may be considered as the sum

$$dS = dS^e + dS^i = \frac{dQ}{\theta} + dS^i \tag{2.18}$$

of the entropy supply $dS^e = dQ/\theta$ from outside and the entropy production inside the body which, according to (2.16) through (2.18), is given by

$$dS^i = \frac{\partial W^d}{\theta} = \frac{1}{\theta} X_k \, dx_k^i > 0. \tag{2.19}$$

While

$$L^d = X_k \, \dot{x}_k^i > 0 \tag{2.20}$$

represents the *rate of dissipation work*, the *rate of entropy production* is

$$\dot{S}^i = \frac{L^d}{\theta} = \frac{1}{\theta} X_k \dot{x}_k^i > 0 .$$ (2.21)

The foregoing considerations are based alone on the fundamental theorems of thermodynamics. As far as the thermoelastic behaviour is concerned, the results are complete, as soon as the free energy is known. Concerning the inelastic behaviour, however, little is known apart from the fact that the dissipation work is always positive.

3. Onsager's Relations

In certain cases ONSAGER's theory [5, 6] supplies the additional information needed concerning the inelastic behaviour of the body under consideration. ONSAGER's theory applies to any kind of irreversible process. It is based essentially on the assumption of microscopic reversibility and can be stated as follows:
Let

$$L^d = X_k \dot{x}_k$$ (3.1)

be the rate of dissipation work of an irreversible process. Provided the 'velocities' $\dot{x}_k$ and the corresponding 'forces' X_i are connected by the linear relations

$$X_i = a_{ik} \dot{x}_k ,$$ (3.2)

then the matrix (a_{ik}) is symmetric, i. e.,

$$a_{ki} = a_{ik} .$$ (3.3)

The linear relations (3.2) are called the *phenomenological law* of the process, and (3.3) are ONSAGER's *reciprocal relations*.

In a rheologic process the $\dot{x}_k$ are the inelastic rates of deformation. Since the elastic behaviour has been disposed of, the superscript i can be suppressed from here on. The X_i are the external forces; (3.2) is the rheologic law of a linear inelastic body, and (3.3) represents the same symmetry as (2.12) in the case of a linear elastic body. The coincidence of (2.12) and (3.3) establishes the visco-elastic analogy for linear bodies (i. e., between a linear Newton body and a linear Hooke body or between the inelastic and elastic responses to external forces of a linear Maxwell body).

The symmetry expressed by (3.3) also holds for the inversion of the phenomenological law,

$$\dot{x}_k = b_{ki} X_i \quad \text{with} \quad b_{ki} = \frac{A_{ik}}{a} ,$$ (3.4)

where $a = |\, a_{ik}\,|$ and A_{ik} is the cofactor of a_{ik} in this determinant. For from the symmetry of (a_{ik}) follows $A_{ki} = A_{ik}$ and hence

$$b_{ik} = b_{ki}. \tag{3.5}$$

Due to (3.2) Onsager's relations (3.3) can also be written in the form

$$\frac{\partial X_k}{\partial \dot{x}_i} = \frac{\partial X_i}{\partial \dot{x}_k}. \tag{3.6}$$

It follows that the forces are the partial derivatives

$$X_i = \frac{\partial \Phi}{\partial \dot{x}_i} \tag{3.7}$$

of a function

$$\Phi(\dot{x}_k) = \frac{1}{2}\, a_{ik}\, \dot{x}_i\, \dot{x}_k. \tag{3.8}$$

This means that the force vector X_i is 'vortex-free' in the space $\dot{x}_k$ and hence is the gradient of a potential $\Phi(\dot{x}_k)$.

Similarly (3.4) and (3.5) yield

$$\frac{\partial \dot{x}_i}{\partial X_k} = \frac{\partial \dot{x}_k}{\partial X_i} \tag{3.9}$$

and thus

$$\dot{x}_k = \frac{\partial \Psi}{\partial X_i} \tag{3.10}$$

with

$$\Psi(X_i) = \frac{1}{2}\, b_{ki}\, X_k\, X_i. \tag{3.11}$$

The connection between the functions $\Phi(\dot{x}_k)$ and $\Psi(X_i)$ is, according to (3.11), (3.2), (3.4), (3.3) and (3.8),

$$\begin{aligned}
\Psi(X_i) &= \frac{1}{2}\, b_{ki}\, a_{kj}\, a_{il}\, \dot{x}_j\, \dot{x}_l = \frac{1}{2} \cdot \frac{A_{ik}}{a}\, a_{kj}\, a_{il}\, \dot{x}_j\, \dot{x}_l \\
&= \frac{1}{2}\, \delta_{ij}\, a_{il}\, \dot{x}_j\, \dot{x}_l = \frac{1}{2}\, a_{jl}\, \dot{x}_j\, \dot{x}_l = \Phi(\dot{x}_k)\,,
\end{aligned} \tag{3.12}$$

where $\dot{x}_k$ and X_i are values connected by the phenomenological law (3.2). This means that the velocity vector $\dot{x}_k$ is 'vortex-free' in the space X_i and hence is the gradient of a potential $\Psi(X_i)$.

The phenomenological law (3.2) supplies a reversibly single-valued transformation of the space $\dot{x}_k$ (the space of deformation rate) onto the space X_i (the force space). The inversion of this transformation is given by (3.4). From $\Phi = $ const follows, according to (3.12), $\Psi = $ const and vice versa: the potential surfaces in one space are the images of those in the other space. According to

(3.2) and (3.4) the rate of dissipation work is

$$L^d = a_{ik}\,\dot{x}_i\,\dot{x}_k = 2\,\Phi \quad \text{or} \quad L^d = b_{ki}\,X_k\,X_i = 2\,\Psi. \tag{3.13}$$

Due to (2.20), i. e., to the second fundamental theorem of thermodynamics, these expressions are positive for any nonvanishing vector $\dot{x}_k$ or X_i respectively. Hence the matrices (a_{ik}) and (b_{ki}) are positive definite, and the surfaces $\Phi = $ const and $\Psi = $ const are ellipsoids.

Figure 1 illustrates the results in two dimensions, the quadratic forms (3.13) being transformed on normal coordinates.
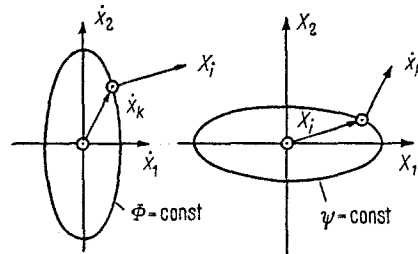

Figure 1

ONSAGER's law (3.7), (3.8) and its inversion (3.10).

4. A Generalization

In order to prove his relations (3.3), ONSAGER considered the statistical aspect of the fluctuations occuring in irreversible processes, making use of the following assumptions [6]: In the first place, the microscopic fluctuations about a state of equilibrium are assumed to be reversible. In the second place, it is supposed that the regression of fluctuations obeys the same laws as a macroscopic process.

For nonlinear phenomenological laws ONSAGER's relations are meaningless. In the form given by (3.6) or (3.7), however, the results can be generalized, if two assumptions are accepted that correspond in a certain sense to ONSAGER's postulates.

From the viewpoint of statistical mechanics, a thermodynamic system with the state variables x_k, θ is a mechanical system with a great number of degrees of freedom most of which are latent from the phenomenological point of view. Beside the external coordinates x_k there are a large number of internal coordinates q_λ ($\lambda = 1, 2, \ldots$). If T is the kinetic energy of the system and if the Q_λ are its generalized forces, the motion for given values of the external coordinates x_k may be obtained by LAGRANGE's differential equations

$$\frac{d}{dt}\,\frac{\partial T}{\partial \dot{q}_\lambda} - \frac{\partial T}{\partial q_\lambda} = Q_\lambda. \tag{4.1}$$

It is customary to assume [9] that the system is conservative and nongyro-scopic [10]. Clearly this assumption is equivalent to ONSAGER's first postulate (microscopic reversibility). The generalized forces then are the negative partial derivatives

$$Q_\lambda = - \frac{\partial}{\partial q_\lambda} V(q_\lambda, x_k) \qquad (4.2)$$

of a potential energy dependent on the internal and external coordinates.

Let us now assume that the external velocities $\dot{x}_k$ are prescribed constants. Then the partial derivatives $\partial V/\partial q_\lambda$ are known functions of the q_λ and of t. Integration of (4.1) supplies the q_λ as functions of the time and of the initial conditions. In other words: the motion of the system is entirely determined by the initial conditions and the velocities $\dot{x}_k$. Hence, also the rate of increase $\dot{U}$ of the total energy

$$U = T + V \qquad (4.3)$$

only depends on the initial conditions and on the $\dot{x}_k$.

From the phenomenological point of view the rate of energy increase can be considered as a mean value $\dot{U}$ over a sufficiently long time interval. It only depends on the $\dot{x}_k$, and this remains true in the case where the $\dot{x}_k$ are functions of the time, provided they vary so slowly that they can be considered constant over the time intervals needed for the averaging process just mentioned. The phenomenological rate of energy increase in an adiabatic process of this type thus is represented by a *dissipation function*

$$\dot{U} = D(\dot{x}_k) . \qquad (4.4)$$

This function, defined without reference to the external forces, can be represented in velocity space by means of surfaces $D = $ const (see Figure 2, illustrating this statement for two dimensions).

Let us now consider the case where instead of the $\dot{x}_k$ the external forces X_i are prescribed constants. The velocities $\dot{x}_k$ then fluctuate about certain mean values $\dot{x}_k^m$, and the connection between these mean values $\dot{x}_k^m$ and the X_i obviously represents the phenomenological law of the process. If we assume that the fluctuations

$$\delta \dot{x}_k = \dot{x}_k - \dot{x}_k^m \qquad (4.5)$$

are slow compared with the molecular velocities (this assumption corresponding to the second of ONSAGER's postulates), the energy increase (4.4) at any instant depends on the actual velocities $\dot{x}_k$. According to the first fundamental law the rate of work of the X_i in an adiabatic process must be equal to the rate of increase of the internal energy. We have therefore

$$X_k \dot{x}_k = \bar{\dot{U}} = D(\dot{x}_k) , \qquad (4.6)$$

and due to the second fundamental theorem this quantity is positive for any nonvanishing state of motion $\dot{x}_k$.

Let us now – still under the assumption that the X_i are kept constant – pick out two states of motion $\dot{x}_k^m$ and $\dot{x}_k = \dot{x}_k^m + \delta\dot{x}_k$ for which $D(\dot{x}_k^m) = D(\dot{x}_k)$, their representative points (Figure 2) thus lying on the same surface $D = $ const.
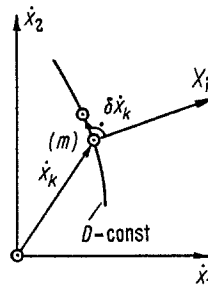

Figure 2

Vector X_i and surface $D = $ const.

From (4.6) follows

$$X_k \, \dot{x}_k^m = X_k \, \dot{x}_k = X_k \, (\dot{x}_k^m + \delta \, \dot{x}_k) \tag{4.7}$$

or

$$X_k \, \delta\dot{x}_k = 0; \tag{4.8}$$

hence, the vector X_i must be normal to the surface $D = $ const in the domain of the values $\dot{x}_k$ compatible with X_i.

Phenomenologically, the fluctuations $\delta\dot{x}_k$ under a given vector X_i are imperceptible. From this point of view a force X_i defines a velocity $\dot{x}_k$, and the superscript m can now be dropped. If (4.6) is applied to this phenomenological velocity $\dot{x}_k$, we have

$$L^d = X_k \, \dot{x}_k = D(\dot{x}_k) \text{ positive definite.} \tag{4.9}$$

Condition (4.8) is equivalent to the statement that X_i is parallel to the gradient of D at $\dot{x}_k$. According to (4.9) the scalar product $X_k \, \dot{x}_k$ is positive in the whole space $\dot{x}_k$ with the exception of the origin. The surfaces $D = $ const therefore are concave with respect to the origin.

Analytically the fact that X_i is perpendicular to the surface $D = $ const at $\dot{x}_k$ is expressed by

$$X_i = f(\dot{x}_k) \, \frac{\partial D}{\partial \dot{x}_i}, \tag{4.10}$$

where $f(\dot{x}_k)$ is an arbitrary function. Due to (4.9), however, the functions $f(\dot{x}_k)$ and $D(\dot{x}_k)$ are connected by the condition

$$D = f \frac{\partial D}{\partial \dot{x}_k} \, \dot{x}_k. \tag{4.11}$$

It follows that the phenomenological law has the form

$$X_i = \left(\frac{\partial D}{\partial \dot{x}_k}\, \dot{x}_k\right)^{-1} D\, \frac{\partial D}{\partial \dot{x}_i}. \tag{4.12}$$

Relation (4.12) [or (4.10) together with one of the relations (4.9), (4.11)] is the generalization of ONSAGER's theory we were looking for. It represents the most general phenomenological law for a purely irreversible process subject to the two assumptions made in the derivation.

If we require that the X_i be linear functions

$$X_i = a_{ik}\, \dot{x}_k \tag{4.13}$$

of the $\dot{x}_k$. $D(\dot{x}_k)$, according to (4.9), is a quadratic form

$$D = a_{ik}\, \dot{x}_i\, \dot{x}_k, \tag{4.14}$$

positive definite, but not necessarily symmetric. Due to (4.10), however,

$$X_i = f(\dot{x}_k)\, (a_{ik} + a_{ki})\, \dot{x}_k. \tag{4.15}$$

Since (4.13) and (4.15) must be identical for any values of i and k, we obtain $f = 1/2$ and

$$a_{ki} = a_{ik}, \tag{4.16}$$

i. e., ONSAGER's relations (3.3).

5. An Important Special Case

From a physical point of view we are particularly (if not exclusively) interested in phenomenological laws of a special kind, namely in laws where the directions of the vectors $\dot{x}_k$ and X_i determine each other independently of their magnitudes. In other words: the vectors X_i for all points $\dot{x}_k$ on a radius from the origin in the space $\dot{x}_k$ have the same direction. It follows at once that in this case the surfaces $D =$ const are similar and similarly situated with respect to the origin.

Let us assume that an arbitrary function $G(\dot{x}_k)$ has similar surfaces $G =$ const, similarly situated with respect to the origin. If we start from different points $\dot{x}_k$ on an arbitrary surface $G =$ const and carry out small steps

$$d\dot{x}_k = \dot{x}_k\, d\varepsilon \tag{5.1}$$

in the directions and proportional to, the vectors $\dot{x}_k$, then, according to (5.1),

$$dG = \frac{\partial G}{\partial \dot{x}_k}\, d\dot{x}_k = \frac{\partial G}{\partial \dot{x}_k}\, \dot{x}_k\, d\varepsilon. \tag{5.2}$$

Due to the similarity assumed these steps end on another surface $G = $ const. Hence the right-hand side of (5.2) is the same for all starting points, i. e.,

$$\frac{\partial G}{\partial \dot{x}_k} \dot{x}_k = g(G).$$ (5.3)

Applying (5.3) to the dissipation function D and making use of (4.11), we obtain

$$\frac{D}{f} = g(D).$$ (5.4)

It follows that f is a function of D, i. e.,

$$f(\dot{x}_k) = \varphi(D).$$ (5.5)

Let a function Φ be defined by

$$\Phi = \int \varphi(D)\, dD$$ (5.6)

and let the additional constant contained in (5.6) be fixed by setting

$$\Phi(D = 0) = 0.$$ (5.7)

Then

$$\varphi = \frac{d\Phi}{dD},$$ (5.8)

and the rheologic law (4.10) becomes, due to (5.5) and (5.8),

$$X_i = \varphi\, \frac{\partial D}{\partial \dot{x}_i} = \frac{d\Phi}{dD} \cdot \frac{\partial D}{\partial \dot{x}_i}$$ (5.9)

or

$$X_i = \frac{\partial \Phi}{\partial \dot{x}_i}$$ (5.10)

as in (3.7). Hence, the force vector X_i again is the gradient of a potential $\Phi(\dot{x}_k)$ in velocity space, and since such a gradient is 'vortex-free', the generalized Onsager relations (3.6)

$$\frac{\partial X_k}{\partial \dot{x}_i} = \frac{\partial X_i}{\partial \dot{x}_k}$$ (5.11)

hold.

If (5.10) or (5.11) are interpreted as rheologic relations, either of these equations [by comparison with (2.10) or (2.14)] establishes the viscoelastic analogy for non-linear Newton and Maxwell bodies with rheologic laws satisfying the condition stated at the beginning of this section.

The potential $\Phi(x_k)$, however, is not an arbitrary function. According to (5.6) the surfaces $\Phi = $ const coincide with the surfaces $D = $ const. Hence, they are similar and similarly situated with respect to the origin. It follows that a relation of the type (5.3) also holds for Φ; the potential function thus must

satisfy the condition

$$\frac{\partial \Phi}{\partial \dot{x}_k} \, \dot{x}_k = h(\Phi).$$ (5.12)

It is easy to see that this condition is satisfied by any homogeneous function [11] of the $\dot{x}_k$, particularly by any entire rational function of arbitrary degree n. There are, however, more general solutions of (5.12).

By means of LEGENDRE's transformation [12][6]), these results can be extended. Let us assume for convenience that the phenomenological law (5.10) is single-valued. Due to (5.7) and to the fact that $D = 0$ at the origin o of the space $\dot{x}_k$, the function $\Phi(\dot{x}_k)$ vanishes at o. Relation (5.10) supplies a single-valued transformation of a domain g in the space $\dot{x}_k$ (the domain of definition of the function Φ) onto a domain G in the space X_i. Let us assume further that the inversion of the phenomenological law,

$$\dot{x}_k = \dot{x}_k(X_i),$$ (5.13)

is also single-valued, supplying a single-valued transformation of G onto g. Figure 3 illustrates these transformations in two dimensions. According to
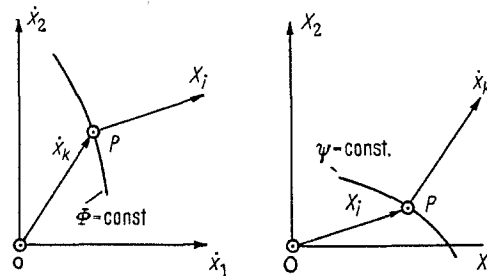

Figure 3
Generalization (5.10), (5.17) of ONSAGER's law.

section 2 there are no irreversible changes of state without dissipation. Hence the origin O in the space X_i is the image of o; consequently g contains o and G contains O.

Let c be an arbitrary curve in g, connecting o with a point p with coordinates $\dot{x}_k$. Let further the point P with coordinates X_k be the image of p in G. Then the image C of c in G connects the points O and P, and we have

$$\int_c X_i \, d\dot{x}_i + \int_C \dot{x}_i \, dX_i = \int d(X_i \, \dot{x}_i) = X_k \, \dot{x}_k.$$ (5.14)

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[6]) The analogous transformation for nonlinear Hooke bodies leads to the so-called complementary energy [13].

Making use of (5.10) and of the fact that Φ vanishes at o, we may write instead

$$\int_C \dot{x}_i \, dX_i = X_k \dot{x}_k - \Phi(\dot{x}_k). \tag{5.15}$$

If on the right-hand side $\dot{x}_k$ is expressed in terms of X_k by means of (5.13), the integral on the left-hand side appears as a function

$$\int_C \dot{x}_i \, dX_i = \Psi(X_k) \tag{5.16}$$

of the coordinates X_k of P, and from (5.16) follows

$$\dot{x}_k = \frac{\partial \Psi}{\partial X_k}. \tag{5.17}$$

Thus, also the inversion (5.13) of the rheologic law can be represented by means of a potential $\Psi(X_i)$ which, due to (5.16) and (5.15), vanishes at O. This potential may be called *complementary* to $\Phi(\dot{x}_k)$.

Due to (5.10) and (5.17), the dissipation function (4.6) may be written in either one of the two forms

$$D = \frac{\partial \Phi}{\partial \dot{x}_k} \dot{x}_k, \qquad D = \frac{\partial \Psi}{\partial X_i} X_i. \tag{5.18}$$

Thus, D in both spaces is the scalar product of the gradient of the potential and the radius vector. Since D is positive definite, both potentials increase monotonically on every radius from the origin. The potentials $\Phi(\dot{x}_k)$ and $\Psi(X_i)$ hence are single-valued functions of their arguments (obviously also in cases where the phenomenological law or/and its inversion are not single-valued).

Due to (5.16) and (5.15)

$$\Phi(\dot{x}_k) + \Psi(X_k) = X_k \dot{x}_k = D. \tag{5.19}$$

According to (5.6) the surfaces $D = $ const in the space $\dot{x}_k$ are also the surfaces $\Phi = $ const. If $\dot{x}_k$ varies on such a surface, $\Psi(X_k)$, according to (5.19), is constant as well. It follows that the surfaces $\Psi = $ const are the images of the surfaces $\Phi = $ const and vice versa, and that both types of surfaces also are the surfaces $D = $ const in the corresponding space.

Since $\Phi(\dot{x}_k)$ increases monotonically on each radius from o, a given radius intersects a given surface $\Phi = $ const in no more than one point p. Hence, there exists on the corresponding surface $\Psi = $ const only one point P the normal of which has a given direction. It follows that the surfaces $\Psi = $ const are convex. In an analogous way the convexity of the surfaces $\Phi = $ const may be proved.

6. An Application to Plasticity

Let the $\dot{x}_k$ be the plastic rates of deformation of a perfectly plastic body under the action of the stresses X_i, and let the yield locus H be regular and determined by the equation

$$\chi(X_i) = 1 , \tag{6.1}$$

where the function χ is chosen in such a manner that $\chi < 1$ inside H. It is physically evident that this surface is closed and containing the origin O. Moreover, it is generally accepted that the yield locus is convex. According to the theory of plastic potential of R. v. MISES [8], as generalized by W. PRAGER ([3], p. 18), the velocity vector $\dot{x}_k$ for a given stress vector X_i at the yield limit is given by

$$\dot{x}_k = \lambda \frac{\partial \chi}{\partial X_k} , \tag{6.2}$$

where λ is an arbitrary non-negative factor of proportionality.

In this theory two items are extremely probably, but have not been proved so far in a direct and convincing manner. The first one is the convexity of the yield locus[7]; in the second place there are the relations (6.2)[8]. In both cases a direct proof is possible on the basis of our theory if we make the plausible assumption that a Prandtl-Reuss body may be considered as the limiting case of a non-linear Newton body with a rheologic law of the type considered in section 5.

In the case of a perfectly plastic body the vector $\dot{x}_k$ is zero when the end point of X_i lies in the interior of the yield locus H. Thus the transformation supplied by the rheologic law is such that the whole interior of H in the space X_i corresponds to the origin o in the space $\dot{x}_k$. On the other hand, plastic flow occurs under vectors X_i with end points on H. Hence, the whole space $\dot{x}_k$ with the exception of the origin o is transformed onto the yield locus H in the space X_i. Thus the domain g of section 5 is the entire space $\dot{x}_k$; the domain G contains the yield locus H and its interior. Neither the rheologic law nor its inversion are single-valued. If

$$R = (X_i X_i)^{1/2} \tag{6.3}$$

is the magnitude of an arbitrary radius vector in the space X_i, the direction of this vector is determined by the ratios

$$a_i = \frac{X_i}{R} \quad (a_i a_i = 1). \tag{6.4}$$

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[7] In applications the yield locus is always convex, and from considerations of uniqueness it seems highly probable that this is always the case. A direct and convincing proof, however, has not been given so far.

[8] R. v. MISES gave no proof for his relations. W. PRAGER [14] showed that (6.2) is a sufficient condition for a certain uniqueness theorem. A proof given by D. C. DRUCKER [15] is based on an assumption which itself is hypothetical.

The yield locus (6.1) may be described also by an equation of the form

$$R = h(a_i).\tag{6.5}$$

If we set

$$\Psi(X_i) = \left[\frac{R}{h(a_i)}\right]^n,\tag{6.6}$$

Ψ is a function in the space X_i which equals 1 on the surface H and increases on any radius with the n-th power of the distance from O. If $R/h(a_i)$ is constant, Ψ is constant; the surface $\Psi = $ const therefore are similar and similarly situated with respect to O.

A comparison with section 5 shows that the function Ψ given by (6.6) defines a nonlinear Newton body with the rheologic law

$$\dot{x}_k = \frac{\partial \Psi}{\partial X_k}.\tag{6.7}$$

If we assume that $n > 1$, the gradient of Ψ is zero at O and increases towards H; hence, the body defined by (6.7) has a viscosity decreasing with increasing stress. If n is increased, the region K where the magnitude of the gradient of Ψ exceeds an arbitrary small quantity ε spreads out more and more towards the surface H. At the same time, the magnitude of the gradient increases more and more on H. By increasing n sufficiently, the region K can be made as small as desired, and at the same time the magnitude of the gradient can be made arbitrarily large at any point P of H. On a radius connecting O and P, therefore, the gradient assumes all values of an interval tending to $0 \cdots \infty$ with increasing n in a vicinity of P tending to zero, and its direction, perpendicular to the surfaces $\Psi = $ const, is that of the normal to H at P. Hence, in the limit, (6.7) assumes the form (6.2) with $\lambda \geqq 0$. Thus, the relation of R. v. MISES is justified under the assumption that the Prandtl-Reuss body is a limiting case of a nonlinear Newton body with a rheologic law of the type treated in section 5. Moreover, this assumption requires that H be a convex surface. According to section 5 the surfaces $\Psi = $ const must be convex, and it is clear that they cannot supply in any limit process a non-convex yield limit.

REFERENCES

[1] M. A. BIOT, *Thermoelasticity and Irreversible Thermodynamics*, J. appl. Phys. 27, 240 (1956).
[2] A. P. GREEN, *The Plastic Yielding of Notched Bars Due to Bending*, Quart. J. Mech. appl. Math. 6, 223 (1953).
[3] W. PRAGER, *Probleme der Plastizitätstheorie*, (Basel 1955).
[4] M. A. BIOT, *Theory of Stress-Strain Relations in Anisotropic Viscoelasticity and Relaxation*, J. appl. Phys. 25, 1385 (1954); *Variational Principles in Irreversible Thermodynamics with Application to Viscoelasticity*, Phys. Rev. 97, 1463 (1955); *Variational and Lagrangian Methods in Viscoelasticity*,

IUTAM Colloquium Madrid (1955); *Deformation and Flow of Solids* (Berlin 1956), p. 251.

[5] L. ONSAGER, *Reciprocal Relations in Irreversible Processes*, Phys. Rev. *37* (II), 405 (1931) and *38* (II), 2265 (1931).

[6] H. B. G. CASIMIR, *On Onsager's Principle of Microscopic Reversibility*, Rev. modern Phys. *17*, 343 (1945).

[7] H. ZIEGLER, *Thermodynamik und rheologische Probleme*, Ing.-Arch. *25*, 58 (1957).

[8] R. v. MISES, *Mechanik der plastischen Formänderung von Kristallen*, Z. angew. Math. Mech. *8*, 161 (1928).

[9] J. W. GIBBS, *The Collected Works*, volume 2 (New Haven, 1948), p. 4.

[10] H. ZIEGLER, *On the Concept of Elastic Stability*, Adv. appl. Mech. *4*, 370 (1956).

[11] R. COURANT, *Vorlesungen über Differential- und Integralrechnung*, volume 2, (Berlin 1955), p. 96.

[12] R. COURANT and D. HILBERT, *Methoden der Mathematischen Physik*, volume 2 (Berlin 1937), p. 26.

[13] F. ENGESSER, *Über statisch unbestimmte Träger bei beliebigem Formänderungs-Gesetze und über den Satz von der kleinsten Ergänzungsarbeit*, Z. Arch. Ing.-Ver. Hannover *35*, 733 (1889).

[14] W. PRAGER, *Recent Developments in the Mathematical Theory of Plasticity*, J. appl. Phys. *20*, 235 (1948).

[15] D. C. DRUCKER, *Some Implications of Work Hardening and Ideal Plasticity*, Quart. appl. Math. *8*, 411 (1950).

Zusammenfassung

Wenn ein irreversibler Prozess durch die «Geschwindigkeiten» $\dot{x}_k$ und die «Kräfte» X_i (und somit durch die Dissipationsleistung $X_k \dot{x}_k$) charakterisiert ist und wenn das phänomenologische Gesetz $X_i = f_i(\dot{x}_k)$ dieses Prozesses linear, das heisst von der Form $X_i = a_{ik} \dot{x}_k$ ist, dann etabliert die Onsagersche Theorie die Symmetrie $a_{ki} = a_{ik}$ der Matrix (a_{ik}). Das phänomenologische Gesetz kann daher in der Form

$$X_i = \frac{\partial \Phi}{\partial \dot{x}_i} \tag{1}$$

geschrieben werden.

Diese Arbeit stellt einen Versuch dar, ONSAGERS Theorie für nichtlineare phänomenologische Gesetze zu verallgemeinern. Es stellt sich heraus, dass ein solches Gesetz von der Form

$$X_i = \left(\frac{\partial D}{\partial \dot{x}_k} \dot{x}_k\right)^{-1} D \frac{\partial D}{\partial \dot{x}_i} \tag{2}$$

sein muss und dass sich (2) im speziellen, aber praktisch wichtigen Falle, dass die Vektoren $\dot{x}_k$ und X_i ihre Richtungen gegenseitig unabhängig von den Beträgen bestimmen, auf (1) reduziert.

Ein wichtiges Anwendungsgebiet ist die nichtlineare Rheologie. Wenn etwa ein ideal-plastischer Körper als Grenzfall eines nichtlinearen Newton-Körpers aufgefasst wird, dann folgt die Konvexität der Fliessfläche und v. MISES' Theorie des plastischen Potentials aus dem rheologischen Gesetz (1).