

THERMOMECHANICS

BY

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1. Shortly before half-time of the period being celebrated at this conference, I had the privilege of spending a year as a guest of the Division of Applied Mathematics at Brown University. At that time, "applied mathematics" was virtually synonymous with "mechanics." A few years before, Prager, Drucker, and Greenberg had formulated their famous limit theorems in plasticity [1, 2], thus creating a basis for the practical application of the so-called theory of the plastic potential, suggested by v. Mises [3], developed by Prager [4] and refined by Koiter [5]. The next few years were marked by the application of limit analysis to a large variety of structures. As far as Brown University is concerned, much of this work was done by Drucker [6, 7], Haythornthwaite [8], Hodge [9], Hopkins [6, 10-13, 21], Lee [14], Onat [15-18], Pell [19]. Prager [4, 10, 13, 15, 16, 18, 19], Schumann [20], Shield [8], Symonds [14] and Wang [11, 21, 22]. Many other groups have contributed. The investigations were extended to soils, to large deformation, minimal weight and optimal design. Much of this work is still in progress.

2. It may be stated today without exaggeration that practically all of the results obtained in applied plasticity are based on the theorems of limit analysis and hence ultimately on the theory of the plastic potential. This is surprising in view of the fact that this theory, although easily accepted on account of certain similarities with the theory of elasticity, was a mere hypothesis from its very beginning, bare of any physical foundation.

To discuss this hypothesis, let us consider an element in a purely plastic continuum, and let us denote its strain rates by $d_{,i}$ and the corresponding stresses by $\sigma_{,i}$. Since both tensors are of rank 2 and symmetric, they may be represented by vectors \mathbf{d} and \mathfrak{d} , respectively, in a 9- or 6-dimensional coordinate system (Fig. 1). As long as the stresses are sufficiently small, the element does not deform. Plastic flow sets in when the end point of the vector \mathfrak{d} reaches a certain surface in stress space, the so-called yield surface, and the theory of the plastic potential states that the vector \mathbf{d} , representing the strain rates of the element, is orthogonal to the yield surface in the end point of the vector \mathfrak{d} and points away from the origin.

This statement is a mere postulate, although a certain similarity with elasticity is obvious. It can be shown, however [23], that the statement, provided it holds for the element, is also valid for the generalized strain rates and stresses used in many applications. This is also true, incidentally, for the observed fact that the yield surface is at least weakly convex. These invariance properties support the orthogonality condition to a certain extent, and the fact that it forms the basis of practically all of the progress

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in applied plasticity during the last two decades makes it worthwhile to look for a physical foundation.

3. An early step in this direction was taken by Drucker [24]. He considered a plastic body subjected to a given load and to an additional external agency which slowly applies and removes additional stresses. He then postulated that during application of the additional stresses as well as during the whole cycle of their application and their removal the work done by the external agency is non-negative. In other words, no useful energy can be extracted from the material and its load during the application of the external stresses nor during the whole cycle of applying and removing them.

On the basis of these postulates it follows from a discussion of Fig. 1, where σ^*

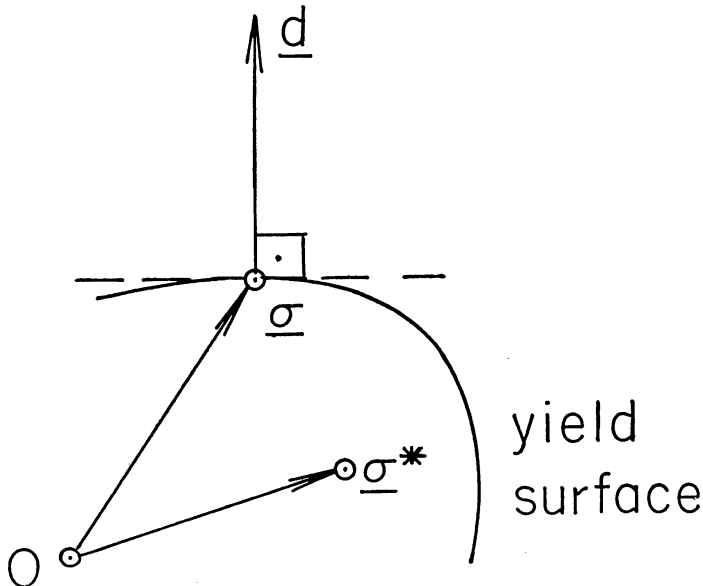


FIG. 1. Theory of the plastic potential.

represents the initial loading of the body and $\sigma - \sigma^*$ the additional stress, that (a) the yield surface is at least weakly convex and (b) the vector d is orthogonal to the yield surface in the end point of σ and points away from the origin. These two results are equivalent to the inequality

$$(\sigma - \sigma^*)d \geq 0. \quad (3.1)$$

Drucker's proof includes the more general case of an elastic-plastic body. However, some of his argumentation is questionable. In the first place, a finite body will generally not return to its initial state of stress after plastic deformation. Thus the change in elastic energy cannot be disposed of as easily as suggested in Drucker's proof. In the second place, an ideally plastic tensile specimen, loaded almost to its yield limit and triggered off by a small additional load, will contract during plastic flow. Since the contraction implies an increase in the stress, the additional load will initiate a flow of rapidly increasing speed which may be used to extract energy from the loaded specimen.

It is true that these difficulties can be avoided by restriction to an infinitesimal

element and by neglecting part of its deformation. This process, however, dilutes the physical content of the two postulates, so that the question arises whether they are really more fundamental than the inequality (3.1).

4. The inequality (3.1) may be interpreted as a principle of maximum dissipation rate, since it asserts that, once a strain rate \mathbf{d} is prescribed, the rate of dissipation work of the real stress $\boldsymbol{\sigma}$ associated with it is never less than the fictitious rate of work of an arbitrary stress $\boldsymbol{\sigma}^*$ below or at the yield limit. The principle has been stated independently by v. Mises [3], Taylor [25] and Hill [26].

Bishop and Hill [27] derived the principle of maximum dissipation rate from the slip plane theory of crystals and a few additional assumptions. The most notable amongst them is the postulate that slip along a preferred plane depends only on the corresponding shear stress. The approach has been recently generalized by Kestin and Rice [28, 29]. They start from the general concept of internal parameters and the corresponding forces and base their theory on the obviously quite restrictive assumption that it is always possible to find a set of internal parameters such that the rate of each one of them only depends on the corresponding force.

5. The work reviewed so far has one common feature: it is entirely based on mechanical considerations. Moreover, most of it is restricted to plastic bodies and rests, to a certain extent, on more or less plausible assumptions. A study of the foundations of continuum mechanics shows that, sooner or later, one is compelled to introduce thermodynamic concepts. For example, the general treatment of continuum mechanics requires that the energy theorem of mechanics be replaced by the first law of thermodynamics, and the formulation of constitutive equations often requires that restrictions imposed by the second law be observed. In short, continuum mechanics is in the process of developing into continuum thermodynamics, thus opening a vast field of interdisciplinary research which really deserves this name, in contrast to many other enterprises wearing this label.

Today, work in the border region between mechanics and thermodynamics is hampered by problems of communication. This seems amazing in view of the successful synthesis of the two fields in the past and in particular in the creation of statistical mechanics towards the end of the last century. Since then, however, the development has followed independent lines, and it turns out that today discussions are difficult between partners one of whom, to put it bluntly, shuns the entropy concept and the other of whom is used to concentrate on gases undergoing reversible processes.

It will be necessary, however, to bridge this gap. Thermodynamic concepts have proved to be extremely fruitful for continuum mechanics, and there is in particular no reason why the special problem of providing a physical basis for the theory of the plastic potential or, more generally, for the principle of maximum dissipation rate, cannot be solved by thermodynamic considerations. One might even expect that the solution will be useful in a far wider field than the one of our original interest.

6. From a thermodynamical viewpoint, the deformation of a plastic body or, in fact, of any real material, is always an irreversible process. In order to establish a connection between the stresses and the strain rates, one needs, however, more than the fundamental laws. Fortunately, thermodynamics is in a position to supply a more powerful tool in the form of Onsager's symmetry relations [30] which, for the last four decades, have served as the basis of the linear theory of irreversible thermodynamics. Biot [31-33] was the first to recognize the implications of Onsager's work for continuum mechanics.

He used it to establish a perfect analogy between problems of elastic deformation and viscous flow. This proof of the so-called viscoelastic analogy, discovered by Alfrey [34] and extended by Hoff [35], is quite general and hence in particular independent of any conditions of symmetry or isotropy.

In order to formulate Onsager's relations, we note that an irreversible process is always characterized by certain velocities \dot{a}_i and the corresponding forces A_i (for a precise definition of these concepts see [36]). Velocities and forces are connected by the expression of the rate of dissipation work,

$$P = A_i \dot{a}_i . \quad (6.1)$$

If, for example, the system considered is the unit volume of a viscous fluid, the \dot{a}_i are the strain rates and the A_i the stresses. Provided the velocities and the forces are connected by linear relations,

$$A_i = c_{ik} \dot{a}_k , \quad (6.2)$$

Onsager's theory asserts that the matrix c_{ik} is symmetric; i.e., that

$$c_{ki} = c_{ik} . \quad (6.3)$$

This condition restricts (6.2) and, in particular, the constitutive equations of viscous fluids.

7. It is obvious that the symmetry relations (6.3) are meaningful only as long as the velocities and forces are connected by linear relations (6.2). In fact, Onsager's theory is restricted to this case, and it has been claimed that it cannot be extended to nonlinear relationships. On the other hand, there are strong arguments in favor of such a generalization.

In the first place, we know that most problems in physics are nonlinear, although we linearize them for mathematical convenience. A theory with a true physical content, however, cannot be expected to be confined to linearized cases. In the second place, the symmetry relations can be replaced by an equivalent statement which remains meaningful for nonlinear relationships between velocities and forces [37] and is strongly supported by reasons of mathematical simplicity. In the third place, it has been possible [38] to prove this generalization on the basis of the fundamental concepts of Gibbs' statistical mechanics [39]. Finally, the generalization has been successfully applied to various problems, particularly in continuum mechanics [40–42]. One of the results, as expected, is the thermodynamic justification of the theory of the plastic potential.

In order to replace the symmetry condition by a statement that can be generalized, we insert (6.2) in (6.1), obtaining

$$P = A_i \dot{a}_i = c_{ik} \dot{a}_i \dot{a}_k = D(\dot{a}_i) . \quad (7.1)$$

The rate of dissipation work can thus be expressed as a quadratic form $D(\dot{a}_i)$ of the velocities. This form is called the dissipation function and is positive definite in view of the second law. On account of the symmetry relations (6.3)

$$\partial D / \partial \dot{a}_i = 2c_{ik} \dot{a}_k , \quad (7.2)$$

so that (6.2) may be written

$$A_i = \lambda (\partial D / \partial \dot{a}_i) , \quad (7.3)$$

where $\lambda = \frac{1}{2}$.

In an n -dimensional cartesian coordinate system \dot{a}_i , the dissipation function can be represented by (hyper-)ellipsoids $D = \text{const}$ (Fig. 2). The relation (7.3) implies that the force vector A_i is orthogonal to the tangential plane of the D -surface in the end point of the velocity vector \dot{a}_i . Thus, the symmetry relations (6.3) are equivalent to an orthogonality condition which may be generalized for nonlinear cases.

8. Comparing Figs. 1 and 2, we note a marked similarity: both of the two figures

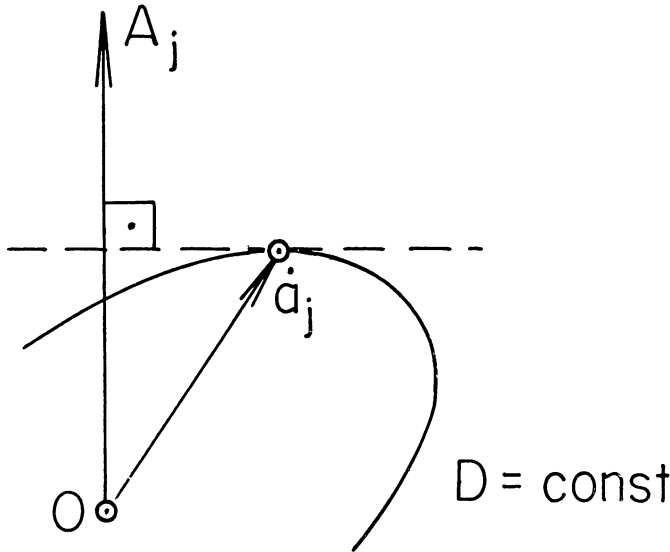


FIG. 2. Replacement of Onsager's symmetry relations by an orthogonality condition.

illustrate an orthogonality condition. This is an argument in favor of the thermodynamic approach. It is true that the roles of velocities and forces are interchanged between the two figures, but this is incidental and could easily be modified. The fact that, in Fig. 1, all of the D -surfaces appear to be concentrated in a single yield surface, is a particular feature of the plastic body. There remains the difference in the shape of these surfaces. The D -surfaces in Fig. 2 represent a linear theory and hence are ellipsoids. If, on the other hand, the relationships between velocities and forces are nonlinear, as in the case of a plastic body, we have to expect dissipation functions of a more general type. However, the orthogonality condition (7.3),

$$A_i = \lambda(\partial D / \partial \dot{a}_i), \quad (8.1)$$

remains meaningful, provided the factor λ is determined by means of the identity

$$A_i \dot{a}_i = D(\dot{a}_i) \quad (8.2)$$

following from (7.1).

Thus it turns out that, replacing the symmetry relations (6.3) by the orthogonality condition (8.1), (8.2), we obtain a form of Onsager's theory which is not restricted to linear cases.

9. The orthogonality condition is equivalent to various extremum principles. Such principles have been formulated for the linear case by Onsager [30], Biot [32], and by Prigogine and De Groot [43]; others have been added during the last decade [36, 44–48].

Of all these possibilities, the principle of maximum dissipation rate seems to be the most interesting one, aside from the fact that it is closely connected with the principle already discussed in connection with the theory of the plastic potential (Section 4). It states that, once the force vector A_i is prescribed, the actual velocity vector \dot{a}_i maximizes the rate of dissipation work $P = A_i \dot{a}_i$ or, equivalently, the dissipation function $D(\dot{a}_i)$ subject to the side condition (8.2).

To prove this, we note that for a given value of P , the equation $D(\dot{a}_i) = P$ represents an ellipsoid E (Fig. 3) with center O , whereas the equation $A_i \dot{a}_i = P$ represents a plane

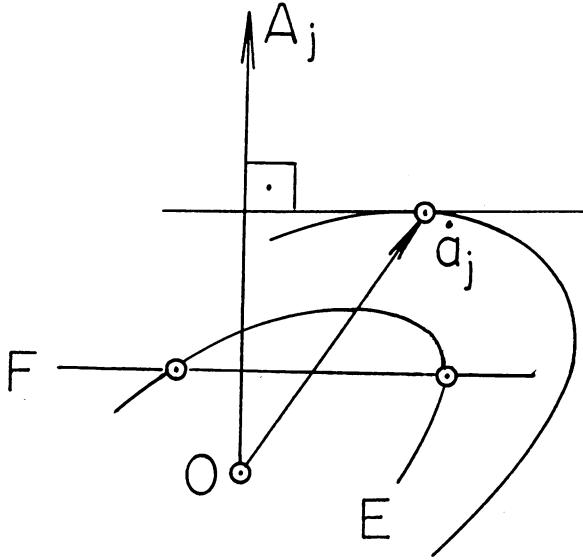


Fig. 3. Principle of maximum dissipation rate.

F perpendicular to the prescribed vector A_i . The distance of F from O is proportional to P whereas the semi-axes of E are proportional to \sqrt{P} . The side condition (8.2) requires that E and F have at least one point in common. This condition is clearly satisfied for sufficiently small values of P . It is further obvious that the direction of the exterior normal of E differs from the direction of A_i in the points of intersection with F but coincides with this direction in the point of contact. This point, however, corresponds to the largest value of P for which (8.2) is satisfied.

Some of the extremum principles, equivalent to the orthogonality condition in the linear case, retain this property in nonlinear cases, provided the dissipation function satisfies certain conditions which, from a physical point of view, are obvious. If gross ambiguities in the connection between velocities and forces are to be excluded, the D -surfaces must be at least weakly convex, and to avoid unstable situations, one has to assume that these surfaces are ordered in such a way that the value of D increases sufficiently fast on any radius from the origin [36, 46]. One of the theorems remaining valid under these conditions is the principle of maximum dissipation rate.

Dividing the dissipation function by the temperature, one obtains the rate of entropy production within the system. It follows that the last theorem can also be stated as the principle of maximum rate of entropy production. From a physical point of view, this

form is particularly appealing since it represents a simple extension of the second law. In fact, if a closed system tends towards its state of maximum entropy, it seems reasonable that the rate of entropy increase under prescribed forces be a maximum; i.e., that the system should approach its final state on the shortest possible path.

10. In most cases and, in particular, in systems of the type we are considering here, the velocities \dot{a}_i are the time derivatives of certain parameters a_i which, together with the temperature θ , define the state from the point of view of a macroscopic observer. In a viscous fluid, e.g., the a_i are the strain components, representing the shape of the element.

From a microscopic point of view, the system may be considered as purely mechanical, the q_κ being the coordinates of its atoms and the p_κ the corresponding momenta. Under certain assumptions ([46] or [38, p. 854]), the motion of this microsystem is determined by Hamilton's equations

$$\dot{q}_\kappa = \partial H / \partial p_\kappa, \quad \dot{p}_\kappa = -(\partial H / \partial q_\kappa), \quad (10.1)$$

where the Hamiltonian

$$H(q_\kappa, p_\kappa, a_i) \quad (10.2)$$

represents its total energy. On account of (10.1) the time derivative of H is

$$\dot{H} = (\partial H / \partial a_i) \dot{a}_i. \quad (10.3)$$

It follows that H is modified through the a_i alone.

In contrast to the microsystem, the macrosystem is a thermodynamic system with parameters a_i which may be assumed to vary slowly compared with the micro-coordinates q_κ . This assumption clearly implies that the macrosystem is to be considered as adiabatically isolated, since a heat flow through the boundary cannot be represented by slow variations of the a_i .

In order to obtain useful results for the macrosystem, the statements (10.1) through (10.3) must be interpreted statistically. According to Gibbs ([39, p. 5]), this is achieved by (a) associating a large number of microsystems with the given macrosystem and (b) by inferring the behavior of the macrosystem from the average behavior of the ensemble of microsystems. It is clear that the history of the a_i must be the same for the whole ensemble, and it is equally obvious that the average behavior of the ensemble and hence the behavior of the macrosystem (and, in particular, the temperature history) are entirely determined by the history of the a_i .

It follows that, e.g., the dissipation function at any time t is completely determined by the way the macroscopic constraints a_i vary up to the time t . If the history is represented by internal parameters (to be counted among the a_i), the dissipation function depends on the state of the macrosystem and the velocities \dot{a}_i , and if we suppose that the state is prescribed, the dissipation function assumes the form $D(\dot{a}_i)$.

The forces A_i do not appear in this discussion. In fact, the statistical treatment shows that the dissipation function plays the decisive role in irreversible processes and that the forces appear as derived quantities. In order to connect the forces with the velocities by means of the dissipation function, we note that the choice of the velocities \dot{a}_i describing the irreversible process is somewhat arbitrary. The corresponding forces A_i are subject to the condition that the scalar product $A_i \dot{a}_i$ represents their rate of work. Restricting ourselves to linear transformations of the velocities, and considering the \dot{a}_i

as contravariant, we conclude from (8.2) that the A_i define a covariant vector. The simplest covariant vector connected with the dissipation function is its gradient. Multiplying it by the scalar λ , which itself may depend on D , we obtain (8.1), and the inclusion of the factor λ makes it possible to satisfy (8.2). Thus it turns out that the orthogonality condition represents the simplest invariant connection between the dissipation function and the force vector.

11. The last result supports the orthogonality principle but does not prove it. For a formal proof, we now definitively turn to thermodynamics. Here, we encounter a first obstacle in the form of the common argument that thermodynamics, notwithstanding its name, deals with equilibrium states and not with the evolution of systems in the course of time. This objection, however, is not only disproved by the description of processes in all texts on thermodynamics, but also by Onsager's theory, and it is by no means more realistic in connection with an extension of this theory to nonlinear processes. In fact, the inclusion of nonlinear terms does not necessarily imply that the velocities are greater than the ones considered by Onsager. The essential condition obviously is that the a_i vary slowly compared with the q_α . It is this assumption, and not the requirement that the a_i be constant, which governs all of Gibbs' work.

The emphasis placed on equilibrium states stems from the fact that, until lately, thermodynamics, rather than being conceived as a field theory in the spirit of continuum mechanics, has been based on the fiction of homogeneous states, i.e., of finite bodies in which the state variables are the same throughout the volume. This fiction implies that if, e.g., a mole of a gas is heated by contact with an external body, the heating process has to be considered as infinitesimally slow (since otherwise transient temperature differences would develop). This has the additional consequence that the entropy production due to heat exchange inside the volume is negligible and that the process, therefore, is practically reversible.

It is clear that a field theory, based on the notion of state variables depending on position and time, is far more realistic. It has been shown by Traupel [49] that there is no reason why this approach, which has been extremely fruitful in mechanics for approximately two centuries, should not be equally justified and useful in thermodynamics. Within the frame of such a field theory the restriction to infinitesimally slow processes is unnecessary; it is replaced, so to speak, by the concept of a body consisting of infinitesimal elements. Moreover, the treatment of irreversible processes becomes as straightforward as the discussion of reversible ones.

12. In continuum thermodynamics the primary object of investigation is the unit of mass. Considering it as the macrosystem in the sense of Sec. 10, we notice that its state is described by the temperature θ together with certain mechanical variables a_i , which include the strain components and possibly a set of internal parameters representing the history. Let us denote these quantities, which depend on position and time, as independent state variables. Any function of a_i and θ may be called a dependent state variable or a state function. Examples are the free energy $\Psi(a_i, \theta)$, the reversible forces $A_i^{(r)}$ which we define by

$$A_i^{(r)} = \partial\Psi/\partial a_i, \quad (12.1)$$

and the entropy

$$S = -(\partial\Psi/\partial\theta). \quad (12.2)$$

It follows from (12.1) and (12.2) that, in any change of state,

$$\dot{\Psi} = A_i^{(r)} \dot{a}_i - S\dot{\theta}. \quad (12.3)$$

The internal energy $U(a_i, \theta)$ is another state function, defined by

$$U = \Psi + \theta S. \quad (12.4)$$

On account of (12.3) its rate is given by

$$\dot{U} = A_i^{(r)} \dot{a}_i + \theta \dot{S}. \quad (12.5)$$

In order to facilitate the statistical treatment (Sec. 13) we assume at present that the element is adiabatically isolated. In this case \dot{S} represents the rate of entropy production within the element. Besides, the first law reduces to

$$\dot{U} = A_i \dot{a}_i, \quad (12.6)$$

where the A_i represent the macro-forces (zero for internal parameters and proportional to the stresses for the corresponding strain rates). Comparing (12.5) and (12.6), we obtain

$$(A_i - A_i^{(r)}) \dot{a}_i = \theta \dot{S}. \quad (12.7)$$

If the element undergoes a reversible process, \dot{S} is zero, and it follows from (12.7) that in this case $A_i = A_i^{(r)}$. This justifies the term "reversible force" for $A_i^{(r)}$, and it further suggests the decomposition

$$A_i = A_i^{(r)} + A_i^{(i)}, \quad (12.8)$$

where the $A_i^{(i)}$ may be denoted as irreversible forces. According to (12.7), they are subject to

$$A_i^{(i)} \dot{a}_i = \theta \dot{S} = D \geq 0, \quad (12.9)$$

where D , by comparison with (8.2), is the dissipation function, and the inequality sign is a consequence of the second law.

It thus turns out that each force can be decomposed into a reversible and an irreversible part. The reversible force is a state variable since it is obtained, according to (12.1), by partial differentiation of the free energy. The irreversible force depends on the change of state and hence is a function of the \dot{a}_i . Relation (12.9) clearly establishes the connection with the original form of our problem. There, we dealt with the purely dissipative and hence purely irreversible case, represented, e.g., by a viscous fluid and characterized by $A_i = A_i^{(i)}$. The present representation is more general insofar as it admits reversible and irreversible forces and hence is applicable to more complicated continua as, e.g., the viscoelastic body.

The only condition for the $A_i^{(i)}$ so far is (12.9). It connects the irreversible force with the dissipation function but does not determine it completely.

13. The missing link in the determination of the $A_i^{(i)}$ is provided by the statistical interpretation outlined in Sec. 10. In phase space the ensemble of microsystems corresponding to a given macrosystem is represented by a great number of points $q_{\mathbf{x}}, p_{\mathbf{x}}$, each one of them moving on its H -surface which itself is in motion as long as the parameters a_i vary with time. According to Gibbs, the distribution of these phase points may be considered as canonical ([39, p. 33]) and, on account of the large number of points,

may be treated as a continuum ([39, p. 5n]). The canonical distribution is characterized by the distribution function

$$w = \exp (\Psi - H)/\theta, \quad (13.1)$$

where θ and Ψ are the temperature and the free energy of the macrosystem. Eq. (13.1) implies that the phase points are uniformly distributed along the layers formed by H -surfaces, whereas their density varies from layer to layer. The logarithm of the distribution function (Gibbs' index of probability) is given by

$$\eta = \ln w = (\Psi - H)/\theta. \quad (13.2)$$

Its negative mean value,

$$-\bar{\eta} = S, \quad (13.3)$$

taken over the whole ensemble, is the entropy of the macrosystem.

A simple calculation ([38, p. 856]) shows that

$$\dot{\bar{\eta}} = 0, \quad \text{whereas} \quad \dot{\eta} = -\dot{S}. \quad (13.4)$$

It follows that, in the presence of entropy production, the processes of differentiation with respect to time and averaging over the elements of an ensemble are not interchangeable. In fact, (13.2) shows that, if $\bar{\eta}$ is not constant, the distribution density of the layers bounded by H -surfaces must vary with time ([46, p. 119]) even though each single phase point moves on its proper H -surface. We have to conclude, therefore, that, in an irreversible process, a given macrosystem is not always represented by the same ensemble of microsystems. This means that any entropy production (as has been demonstrated in [46]) is accompanied by a reorganization of the ensemble, consisting in the addition of phase points and the disappearance of others or, in short, in a transport in phase space superposed on the regular flow.

The conclusion reached here clearly breaks with the traditions established in connection with reversible processes. However, the conclusion is inevitable and implies that, in dealing with irreversible processes, one has to sacrifice the concept of continuity in phase space. To confirm this, let us write (13.2) in the form

$$H = \Psi - \theta\eta. \quad (13.5)$$

A simple calculation shows that

$$\dot{\bar{H}} = \dot{\Psi} + \dot{\theta}S, \quad \text{whereas} \quad \dot{H} = \dot{\Psi} + \dot{\theta}S + \theta\dot{S}. \quad (13.6)$$

It follows that

$$\dot{H} = \dot{\bar{H}} + \theta\dot{S}, \quad (13.7)$$

and we note that again the processes of time derivation and averaging cease to be interchangeable as soon as the entropy production is non-zero.

A fluid of density ρ , moving in space and subject to the continuity equation

$$\dot{\rho} + \rho v_{i,i} = 0, \quad (13.8)$$

satisfies the relation

$$\left(\int \rho H dV \right) \dot{\quad} = \int \rho \dot{H} dV, \quad (13.9)$$

where H is an arbitrary field function, dV denotes the volume element, the integral is extended over an arbitrary volume and the dot indicates material differentiation. Applying (13.9) to the "continuum" of phase points, interpreting H as their energy and replacing the density ρ by the distribution function w , we note that the two sides of (13.9) respectively represent the left-hand side and the first term on the right-hand side of (13.7). The presence of the second term on the right-hand side of (13.7) confirms that there is no continuity in phase space provided the entropy production is different from zero.

It follows from Hamilton's equations (10.1) that

$$(\partial \dot{q}_\alpha / \partial q_\alpha) + (\partial \dot{p}_\alpha / \partial p_\alpha) = 0. \quad (13.10)$$

The corresponding equation for the fluid considered above is

$$v_{i,i} = 0, \quad (13.11)$$

and this is equivalent to

$$\dot{\rho} = 0 \quad (13.12)$$

if the fluid satisfies the continuity equation (13.8). Interpreting (13.12) in phase space, we obtain Liouville's theorem $\dot{w} = 0$. For irreversible processes, however, there is no continuity in phase space. It follows that Liouville's theorem is restricted to the reversible case.

14. We noted at the end of Sec. 12 that, so far, the only connection between the vectors \dot{a}_i and $A_i^{(i)}$ is the condition (12.9). Let the state of the macrosystem, together with the macro-forces, be given at time t , and let us ask for the corresponding velocity \dot{a}_i . According to (12.1) the reversible part $A_i^{(r)}$ of A_i is a state variable. Thus, $A_i^{(r)}$ is given and it follows from (12.8) that also the irreversible force $A_i^{(i)}$ is known.

The velocity \dot{a}_i does not enter Hamilton's equations (10.1), (10.2). If, therefore, \dot{a}_i is varied at time t by the amount $\delta \dot{a}_i$, this variation is of arbitrarily small influence on the motion, during a sufficiently short time interval, of the various microsystems corresponding to the given macrosystem. In the irreversible case, though, there is also a transport in phase space, and the corresponding change of η in the layers bounded by H -surfaces may be different for the velocities \dot{a}_i and $\dot{a}_i + \delta \dot{a}_i$. However, for variations $\delta \dot{a}_i$ which do not affect the various sides of (12.9), the behavior of the macrosystem during the time interval considered is the same. It follows that not only a single velocity \dot{a}_i is compatible with the prescribed force A_i or, equivalently, with its irreversible part $A_i^{(i)}$, but also all those varied velocities $\dot{a}_i + \delta \dot{a}_i$ for which the dissipation function and hence also the scalar product with $A_i^{(i)}$ remain unchanged. However, this requires (see Fig. 3, where A_i has to be replaced by $A_i^{(i)}$) that, in general, $\delta \dot{a}_i$ is infinitesimal and that $A_i^{(i)}$ is orthogonal to the tangential plane of the dissipation surface passing through the end point of \dot{a}_i .

The last statement proves the orthogonality condition on the basis of statistical thermodynamics. Together with (12.9), it supplies the connection between the velocities \dot{a}_i and the irreversible forces $A_i^{(i)}$. It can be shown [38, 42] that the restriction to adiabatic processes may be dropped if the components q_i of the heat flow are considered as additional velocities with corresponding irreversible forces $-(1/\rho) (\ln \theta)_{,i}$. It follows that the behavior of the macrosystem is completely determined in any process by its set of

macrocoordinates and two scalar functions: the free energy Ψ and the dissipation function D .

15. It can be shown [46, p. 138] that the orthogonality condition still holds if the roles of the velocities and the irreversible forces are exchanged and the dissipation function is written in terms of the irreversible forces.

If the dissipation function is quadratic, the connection between the irreversible forces and the velocities is linear, and the orthogonality condition becomes equivalent with the symmetry relations (6.3). In the highly nonlinear case of a plastic element, where all D -surfaces are concentrated in a single yield surface, the orthogonality condition is equivalent with the theory of the plastic potential. As an example situated between these two limiting cases, let us consider a non-newtonian fluid of the Reiner–Rivlin type [51, 52].

The constitutive equations of the incompressible Reiner–Rivlin fluid may be written

$$\sigma_{ik}^{(r)} = -p\delta_{ik} \quad (15.1)$$

and

$$\sigma_{ik}^{(i)} = g(d_{(2)}, d_{(3)}) d_{ik} + h(d_{(2)}, d_{(3)})(d_{ij} d_{ik} - \frac{2}{3}d_{(2)} \delta_{ik}), \quad (15.2)$$

where $\sigma_{ik}^{(r)}$ and $\sigma_{ik}^{(i)}$ are the reversible and irreversible parts of the stress, p is an undetermined hydrostatic pressure, d_{ik} is the strain rate with basic invariants $d_{(2)}$, $d_{(3)}$, and δ_{ij} is the unit tensor. The functions g and h are arbitrary but subject to the condition that the rate of dissipation work,

$$P = (1/\rho)\sigma_{ik}^{(i)} d_{ik}, \quad (15.3)$$

referred to the unit mass by means of the density ρ , is non-negative.

As long as the functions g and h are arbitrary (except for the restriction $P \geq 0$) the constitutive equation (15.2) does not obey the orthogonality condition. It can be shown, however [40], that the orthogonality condition is satisfied if the two functions are given by

$$\begin{aligned} g &= \rho D \left(2 \frac{\partial D}{\partial d_{(2)}} d_{(2)} + 3 \frac{\partial D}{\partial d_{(3)}} d_{(3)} \right) \frac{\partial D}{\partial d_{(2)}}, \\ h &= \rho D \left(2 \frac{\partial D}{\partial d_{(2)}} d_{(2)} + 3 \frac{\partial D}{\partial d_{(3)}} d_{(3)} \right) \frac{\partial D}{\partial d_{(3)}}, \end{aligned} \quad (15.4)$$

where

$$\rho D = 2gd_{(2)} + 3hd_{(3)} \quad (15.5)$$

is the dissipation function per unit volume. These conditions clearly define a special class of Reiner–Rivlin fluids, simpler insofar as the two arbitrary functions are reduced to a single one with a precise physical meaning: the dissipation function D .

To treat specific applications, the dissipation function must be specified. On account of the nonlinearity we cannot expect exact solutions. A reasonable way to obtain approximations is based on the expansion of $\sigma_{ik}^{(i)}$ in terms of powers of d_{ik} . Truncating this series, one obtains successive approximations, containing an increasing number of coefficients, which are free except for the condition that D is non-negative. If one then subjects the polynomials obtained to conditions (15.4), the number of free constants is considerably reduced.

The first approximation is linear and characterized by the constitutive equation

$$\sigma_{ik}^{(i)} = 2\eta d_{ik} \quad (15.6)$$

of the newtonian fluid of viscosity $\eta > 0$. On account of the orthogonality condition the second approximation is still given by (15.6). In a third approximation we obtain

$$\sigma_{ik}^{(i)} = 2(\eta + \kappa d_{(2)}) d_{ik}, \tag{15.7}$$

i.e., the constitutive equation of a quasi-linear fluid with two material constants η and κ . The fourth approximation yields the constitutive equation

$$\sigma_{ik}^{(i)} = 2(\eta + \kappa d_{(2)} - \lambda d_{(3)}) d_{ik} + 4\lambda d_{(2)} (d_{ji} d_{ik} - \frac{2}{3} d_{(2)} \delta_{ik}) \tag{15.8}$$

of a truly nonlinear fluid characterized by three constants η, κ, λ . In this last case the orthogonality condition reduces the number of material constants from 5 to 3.

Comparing the various approximations, we note that the second one is still newtonian and that the terms containing the square of the strain rate tensor appear for the first time in the fourth approximation, whereas (15.2) already contains them in the second approximation if the orthogonality condition is neglected. Thus, the transition from the newtonian to the truly nonlinear fluid is considerably smoothed by the orthogonality condition.

Since, on the other hand, the square of the strain rate finally appears in the higher approximations, it is to be expected that the typical nonlinear effects observed in experiments and predicted by the theory of Reiner-Rivlin fluids may be fully explained by the simpler theory based on the orthogonality principle. This has been confirmed [40] for the Weissenberg effect [53] (climbing of a fluid along a rotating cylinder (Fig. 4)),

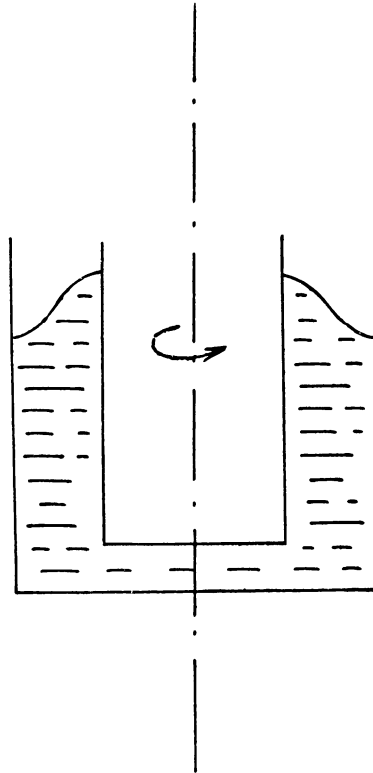


FIG. 4. Weissenberg effect.

the Green–Rivlin effect [54] (development of vortices in a parallel flow through an elliptical tube (Fig. 5)) and in other cases [41]. In the case of Fig. 5 it even turned out that the numerical results are exactly those of Green and Rivlin. This unexpected result is explained by the fact that, on account of the difficulties in the analytical treatment, Green and Rivlin had to simplify their fluid to such an extent that, for the problem considered, it became equivalent to a fluid obeying the orthogonality condition.

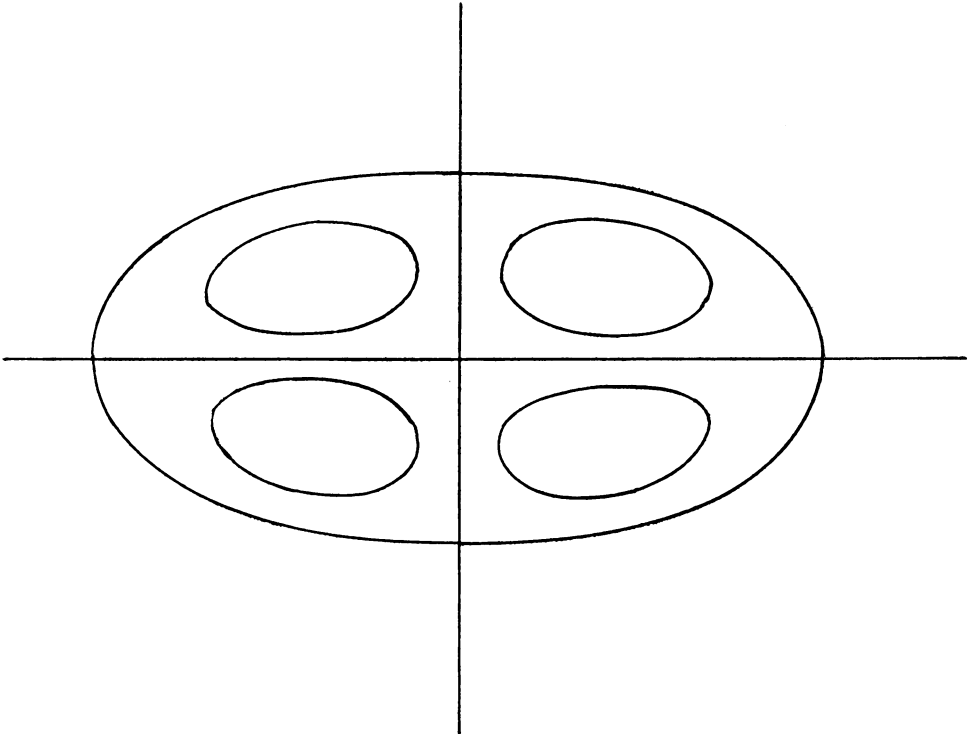


FIG. 5. Green–Rivlin effect.

16. The examples just treated were simple insofar as all of the macrocoordinates are external parameters. Besides, the free energy is identically zero. In other cases, e.g., in a viscoelastic material, the macrocoordinates are partly internal parameters, representing the history of the element, and the behavior of the element is determined by the free energy together with the dissipation function. The orthogonality condition, however, is not restricted to continuum mechanics. It may also be applied to chemical problems, and here the macrocoordinates are sometimes exclusively internal parameters. As an example, let us generalize the treatment [42] of a problem discussed on a linear basis in the recent editions of the text by Sommerfeld on theoretical physics [55], supplemented and edited by Bopp and Meixner.

Let us consider an isothermal gas consisting of

$$n = n_0 + n_1 + n_2 \quad (16.1)$$

moles of molecules in the respective energy levels U_0 , U_1 , and U_2 , confined in a closed container of constant volume. Its free energy [42] is

$$\Psi = \sum n_i [U_i - \theta S_i - R\theta \ln (n/n_i)], \quad (16.2)$$

where R is the gas constant, S_0 , S_1 , and S_2 are the entropies per mole of the three components, and the sum is extended over the indices 0, 1, and 2. Since θ and n are constant, the state of the mixture is determined by the internal parameters n_1 and n_2 . The problem is to determine the manner in which the system, released in an arbitrary state and left to itself, approaches the equilibrium state.

The free energy (16.2), as a state function, can be expressed in n_1 and n_2 by means of (16.1). According to (12.1) the reversible forces $A_k^{(r)}$ corresponding to the parameters n_k ($k = 1, 2$) are the partial derivatives of Ψ with respect to the n_k . Carrying out the differentiation we obtain

$$A_k^{(r)} = \Psi_k - \Psi_0 - R\theta \ln (n_0/n_k). \quad (16.3)$$

It can be shown that the $A_k^{(r)}$ vanish in the equilibrium state \bar{n}_k , \bar{n}_0 , and it follows that

$$A_k^{(r)} = R\theta (\ln (n_k/\bar{n}_k) - \ln (n_0/\bar{n}_0)). \quad (16.4)$$

The dissipation function D depends on the \dot{n}_k . According to (8.1) and (8.2), the irreversible forces are

$$A_k^{(i)} = \lambda(\partial D/\partial \dot{n}_k), \quad (16.5)$$

where λ follows from

$$A_k^{(i)} \dot{n}_k = D(\dot{n}_k), \quad (16.6)$$

if the summation convention is adopted for the index $k = 1, 2$. Since the n_k are internal parameters or, in other words, since the corresponding forces A_k do not contribute to the first law, we have $A_k = 0$. It follows from (12.8) that $A_k^{(r)} + A_k^{(i)} = 0$; i.e., that

$$\lambda(\partial D/\partial \dot{n}_k) = R\theta (\ln (n_0/\bar{n}_0) - \ln (n_k/\bar{n}_k)). \quad (\text{no summation}) \quad (16.7)$$

This equation connects the internal parameters with their rates and thus governs the approach of the system towards equilibrium.

In general, both sides of (16.7) are nonlinear in n_k and \dot{n}_k . In the vicinity of the equilibrium configuration the $n_k - \bar{n}_k$ and the \dot{n}_k are small, and by linearizing (16.7) we obtain the system

$$\dot{n}_k = -\gamma_{ki}(n_i - \bar{n}_i), \quad (16.8)$$

where the properties of the matrix γ_{ki} are governed by the orthogonality condition used on the left-hand side of (16.7). Taking this into account, one easily shows [42] that (16.8) is equivalent with the linear Fowler relations [56] including the so-called principle of detailed balance. Thus these last relations, usually considered as the basis of the theory, turn out to be consequences of the orthogonality condition in the linear case.

17. These are only a few particularly simple applications of the orthogonality condition. The connections established with existing theories in various fields appear encouraging. It seems reasonable to expect that the application to more complicated problems will contribute to render them more tractable. Finally, the fact that once again a close connection and an intensive mutual interaction between mechanics and thermodynamics become apparent, seems to me of particular interest.

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