

New Variational-Lagrangian Irreversible Thermodynamics with Application to Viscous Flow, Reaction–Diffusion, and Solid Mechanics

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I. Introduction

Our purpose here is to present a comprehensive view of a distinct approach to the thermodynamics of irreversible processes that is based on a principle of virtual dissipation. It represents a generalization of d'Alembert's principle of classical mechanics to irreversible thermodynamics and leads to equations of evolution of thermodynamic systems. They are derived directly either as field equations or as Lagrangian equations.

This work originated in the years 1954–1955, first in the context of linear phenomena, and developed gradually along with its applications during the next 25 years. During this period it became evident that the concepts and methods are interdisciplinary. They extend far beyond pure mechanics and in particular should include chemistry. It therefore became necessary to reexamine some of the foundations of classical thermodynamics. This was accomplished more recently and has led to a restructuring of the thermodynamics of open systems. The approach is based on physical "thought experiment" procedures, in contrast with current standard formalism. It provides new definitions for the energy and entropy of open systems that bypass the fundamental difficulties of the classical Gibbs approach without recourse to quantum statistics. The well-known Gibbs paradox is avoided, and the Gibbs chemical potential is replaced by a "convective potential" that does not involve undetermined constants. The Gibbs–Duhem theorem is reformulated accordingly. Results in thermochemistry introduce the concept of "intrinsic heat of reaction," which is more representative of chemical energy than the concepts derived from standard definitions. It leads to a new expression for the affini-

ity and to a rigorous and complete generalization of the Kirchhoff formula.

Thus the work involves two distinct developments, constituted on the one hand by a new approach to classical thermodynamics and on the other by a variational-Lagrangian formulation of irreversible processes. The first provides a sound basis for the second. The same logical sequence will be followed here, and many applications to mechanics and coupled chemical reaction-diffusion will be presented.

Attention should be called to some of the more fundamental aspects of the concept of virtual dissipation and the associated Lagrangian formulation. *The concept itself does not postulate any particular kinetics of the phenomena involved.* This provides great flexibility in the applications, because one can introduce either a kinetics based on Onsager's principle or a more general one represented, for example, by nonlinear chemical reactions or a non-Newtonian viscosity. The extreme generality of this viewpoint opens a wide domain that does not exclude quantum kinetics.

The variational principle represents essentially a *probing* of the system in the vicinity of a frozen state of evolution. It is accomplished by applying virtual changes that obey constraints of mass and energy conservation and by evaluating the virtual entropy of an equivalent closed and adiabatic system that represents the virtual entropy produced. In this process the virtual work of the inertial forces is taken into account. This implies a generalization of d'Alembert's principle of mechanics to include the thermal energy. A fundamental aspect of the principle of virtual work in mechanics seems to have been overlooked. It is not merely a formal tool but embodies a physical law, sometimes called the third law of mechanics, namely that action and reaction forces are equal and opposite. This leads to the vanishing of virtual work between frictionless or adherent surfaces and the disappearance of interfacial forces from the equations. Its generalization involves the continuity of mass and energy flux and leads to a principle of interconnection of subsystems whereby the generalized interfacial forces, mechanical as well as thermodynamic, of interacting subsystems are eliminated from global equations.

The formulation of the principle was based on the introduction of a thermodynamic function that was shown by the author to be fundamental in irreversible thermodynamics. It was initially referred to as "generalized free energy." A formally similar expression was later given the name "exergy" in the literature. We have retained this term for the more precise definition required by the present context, using the concept of "hypersystem" as a basic model in the thermodynamics of open systems.

The viewpoint here is completely different from the purely formal conventional procedures that start from the differential field operators and

then derive corresponding variational principles. This implies a prior knowledge of the equations that govern the continuous field, and each particular case must then be treated separately with its own boundary conditions. In this context the deeper unitary physical insight is lost. By contrast, the principle of virtual dissipation introduces fundamental physical invariants that lead at the same time to field differential equations of evolution of the continuous system as well as to Lagrangian equations of collective evolution with generalized coordinates. In some problems new physical terms whose existence has been overlooked are thus obtained and are revealed essentially by the variational approach. *Prior knowledge of the field differential equations is thus not required.*

One may analyze very complex systems made up of components of physically very different natures. Lagrangian equations are then derived for each subsystem by simplified analysis, and the subsystems are coupled together using a principle of interconnection yielding Lagrangian equations for the global system from which the interfacial coupling forces have been eliminated. This includes *modal synthesis*.

Essentially the procedure also provides the foundation of a *large variety of finite-element methods without requiring the use or knowledge of the field equations of the continuum.*

The ideas embodied in this way of thinking may be considered as the natural extension to thermodynamics of those developed by Lagrange, d'Alembert, and Rayleigh in the more restricted domain of mechanics. The use of global generalized coordinates to describe the evolution of complex mechanical structures has been common practice, particularly among aeronautical engineers. A classic example is also provided by the Lagrangian equations of motion of a rigid solid immersed in a perfect incompressible fluid. The generalized coordinates are fundamentally more general than those obtained by a choice of basis in functional spaces. This is exemplified by the concept of "penetration depth" in diffusion where, starting from a linear problem, a nonlinear equation is obtained that is easier to solve than the original one. In analogy with Lagrangian mechanics, the generalized coordinates are chosen so that the mechanical constraints as well as global or local conservation of mass and energy are satisfied. This already solves part of the problem by the very choice of coordinates and gives the method a remarkable accuracy with very modest calculation requirements and rough approximations for assumed distributions of the intensive variables. One may add that the Lagrangian formulation is another procedure for achieving what has been one of the objectives of "computer algebra," whereby complicated analytical expressions describing physical systems are manipulated by a computer and simplified by elimination of negligible and physically nonrele-

vant terms. The Lagrangian equations directly provide such a formulation leading to simplified analytical results and improved physical insight. This character of simplicity is important, particularly in industrial problems, where a good grasp of physical reality as well as reliability and low cost are essential. The Lagrangian equations also lead naturally to general methods of bifurcation and related stability analyses. New stability criteria of evolution are obtained that are simpler and more general than those currently in use.

Some general remarks are in order regarding the use of spatial derivatives. In continuum theories of matter, because of the discontinuous molecular structure of matter, spatial derivatives are of only conventional significance. From the viewpoint of the physicist, it is just as rigorous to treat macroscopic problems dealing with matter by considering finite elements described by a finite number of coordinates, without using field differential equations. The size of the finite element simply must not be situated below a resolution threshold where the macroscopic laws break down because of fluctuations and molecular scale effects. On the other hand, the use of continuum models to represent material physical systems constitutes an extrapolation beyond the validity of physical laws. Furthermore, they create spurious mathematical difficulties by forcing the introduction of the concept of measure and associated properties of completeness of representation that have no physical relevance. In fact, it has been shown that much of the current fashionable continuum mechanics and thermodynamics represents purely formal exercises without physical foundation. These difficulties are eliminated if we use a description based on finite elements of suitable size to represent the macroscopic physics correctly. From this viewpoint, the corresponding Lagrangian equations provide a rigorous description of the physical evolution.

We should add that purely formal methods often tend to mask the more profound unitary aspect of the physical principles involved. It may even be said that it is sometimes in the context of physical applications that abstract generalizations are discovered. As an example, we may cite the extension of variational methods in terms of symbolic Heaviside operators and corresponding convolutions, which has played the role of catalyst in ulterior formal developments. The same remark can be made regarding the Lagrangian variational formulation, which has instigated much formal work on finite-element methods.

The general ideas discussed stand in contrast with methods based on prior knowledge of the field equations of evolution that derive variational properties for each particular case by manipulation in the context of functional spaces. *Such formal methods have their place, but their role should not be exclusive.* Removed from their physical context they may lead to

serious errors and stand in the way of intuitive understanding of physical problems as well as their analysis by simpler and more direct methods.

II. Restructured Thermodynamics of Open Systems and the Concept of Thermobaric Transfer

A new conceptual approach to the thermodynamics of open systems has been developed (Biot, 1976a, 1977a) that avoids the difficulties inherent in standard procedures without recourse to the axioms and ponderous methods of quantum statistics. It replaces the classic formalism by an operational approach using thought experiments on a physical model called a hypersystem. This model is constituted by primary cells ΣC_P (primary system), supply cells ΣC_{S_k} , and a thermal well TW. The supply cells are large and rigid and contain pure substances denoted by k , all at the same pressure p_0 and temperature T_0 , whereas TW is a large rigid isothermal reservoir at a temperature T_0 assumed for convenience to be the same as in the supply cells.

For the present we consider an open primary cell C_P constituted by a fluid mixture. Its state is determined by its volume v , its temperature T , and the masses M^k of each pure substance k added to it, starting from a given initial state. An infinitesimal change of state may be obtained as follows. We extract a mass dM^k of pure substance adiabatically from the supply cell C_{S_k} and compress and heat it gradually and reversibly to the temperature T of C_P and pressure p_k so that it is in equilibrium with C_P through a semipermeable membrane. We then inject it reversibly into C_P through the membrane. In addition we also inject into C_P a quantity of heat dh . This operation is called a *thermobaric transfer*. This type of thermobaric transfer does not involve the thermal well TW. Another type of thermobaric transfer that does involve TW will be considered later in connection with the concept of exergy. We may perform this operation for each pure substance and also increase the volume of the cell by the amount dv . These operations produce an increase of energy of the collective system $C_P + \Sigma C_{S_k}$ equal to

$$d^0u = -p dv + \sum_k \bar{\epsilon}_k dM^k + dh. \quad (2.1)$$

We denote by p the total pressure acting on C_P , and $\bar{\epsilon}_k$ is given by

$$\bar{\epsilon}_k = \int_{p_0 T_0}^{p_k T} \left(\frac{dp'_k}{\rho'_k} + T' ds'_k \right), \quad (2.2)$$

where p'_k , ρ'_k , T' , and $d\bar{s}'_k$ are, respectively, the pressure, density, temperature, and specific entropy differential of the mass dM^k along the path of integration. The value of $\bar{\epsilon}_k$ includes the work of extraction of dM^k from C_{S_k} and injection into C_P , and $T' d\bar{s}'_k$ is the heat injected into dM^k at every step of the thermobaric transfer.

Similarly, the increase of entropy of the subsystem $C_P + \sum C_{S_k}$ is

$$d\mathcal{S} = \sum_k \bar{s}_k dM^k + dh/T, \quad \bar{s}_k = \int_{p_0 T_0}^{p_k T} d\bar{s}'_k. \quad (2.3)$$

We called p_k the *injection pressure* and $\bar{\epsilon}_k$ and \bar{s}_k , respectively, the *injection enthalpy* and *injection entropy*. From Eq. (2.2) we derive the important differential relation for each substance

$$d\bar{\epsilon}_k = dp_k/\rho_k + T d\bar{s}_k, \quad (2.4)$$

where ρ_k is the density at the temperature T and pressure p_k .

By this thermobaric transfer process we may bring the cell C_P to any desired temperature T and increase the masses of each substance in the cell by arbitrary amounts M^k . Starting from a given initial state, the variables v , M^k , and T define the state of C_P . Because the M^k are the masses extracted from the supply cells, they also determine the state of the supply cells. Hence the state of the subsystem $C_P + \sum C_{S_k}$ and its increase of collective energy \mathcal{U} and entropy \mathcal{S} in the thermobaric transfer are determined by the same variables v , M^k , and T . As a consequence, we may adopt \mathcal{U} and \mathcal{S} as definitions of the energy and entropy of the primary cell C_P , keeping in mind that they refer to collective concepts.

To determine their values, we write the heat added dh in the form

$$dh = h_{mT}^v dv + \sum_k h_{vT}^k dM^k + C_{vm} dT. \quad (2.5)$$

We call h_{vT}^k the heat of mixing at constant temperature and volume; whereas C_{vm} is the heat capacity of C_P at constant volume and composition. The differential coefficients h_{mT}^v and h_{vT}^k may be evaluated without calorimetric measurements by generalizing a procedure leading to the classic Maxwell relations (Biot, 1982a). The result is obtained by substituting the value of dh from Eq. (2.5) into Eqs. (2.1) and (2.3) and noting that $d\mathcal{U}$ and $d\mathcal{S}$ are exact differentials. We obtain the relations

$$\frac{\partial}{\partial T} (h_{mT}^v - p) = \frac{\partial C_{vm}}{\partial v}, \quad (2.6)$$

$$\frac{\partial}{\partial T} \left(\frac{h_{mT}^v}{T} \right) = \frac{1}{T} \frac{\partial C_{vm}}{\partial v}. \quad (2.7)$$

Elimination of $\partial C_{vm}/\partial v$ between these equations yields

$$h_{mT}^v = -T \left(\frac{\partial p}{\partial T} \right)_{vm}. \quad (2.8)$$

The subscript vm indicates that the derivative is for v and M^k constant. Similarly, we obtain the relations

$$\frac{\partial}{\partial T} (\bar{\epsilon}_k + h_{vT}^k) = \frac{\partial C_{vm}}{\partial M^k}, \quad (2.9)$$

$$\frac{\partial}{\partial T} \left(\bar{s}_k + \frac{h_{vT}^k}{T} \right) = \frac{1}{T} \frac{\partial C_{vm}}{\partial M^k}. \quad (2.10)$$

Elimination of $\partial C_{vm}/\partial M^k$ between these equations yields

$$\frac{\partial \bar{\epsilon}_k}{\partial T} - T \frac{\partial \bar{s}_k}{\partial T} + \frac{h_{vT}^k}{T} = 0. \quad (2.11)$$

Taking into account the differential relation (2.4), we derive

$$h_{vT}^k = - \frac{T}{\rho_k} \left(\frac{\partial p_k}{\partial T} \right)_{vm}. \quad (2.12)$$

The derivatives in Eqs. (2.8) and (2.12) are obtained from relations

$$p = p(v, M^k, T), \quad (2.13)$$

$$p_k = p_k(v, M^k, T), \quad (2.14)$$

which may be considered as generalized equations of state derived experimentally or from kinetic theories. For perfect gas mixtures the injection pressure is

$$p_k = p\gamma_k, \quad (2.15)$$

where γ_k is the molar fraction of substance k in the mixture.

With the value of dh from Eq. (2.5), the differential coefficients of $d\mathcal{U}$ and $d\mathcal{S}$ are now known functions of v , M^k , and T . We may then integrate Eqs. (2.1) and (2.3) along any path, putting $\mathcal{U} = \mathcal{S} = 0$ for the initial state. We thus obtain

$$\mathcal{U} = \mathcal{U}(v, M^k, T), \quad \mathcal{S} = \mathcal{S}(v, M^k, T) \quad (2.16)$$

for the collective energy and entropy of the open cell C_p in terms of v , M^k , and T .

By eliminating dh between Eqs. (2.1) and (2.3), we obtain

$$d\mathcal{U} = -p dv + \sum_k \phi_k dM^k + T d\mathcal{S}, \quad (2.17)$$

where

$$\phi_k = \bar{\epsilon}_k - T\bar{s}_k \tag{2.18}$$

is the *convective potential* (Biot, 1976a, 1977a). Relation (2.17) is analogous to the Gibbs equation with ϕ_k replacing the chemical potential. In contrast with the classic procedure, Eq. (2.17) is *not used to define ϕ_k but constitutes a theorem*. In addition, $\phi_k, \bar{\epsilon}_k, \bar{s}_k$ do not involve undetermined constants as in the classic case. Note that these undetermined constants are not eliminated by taking differentials, because we then obtain

$$d\phi_k = d\bar{\epsilon}_k - T d\bar{s}_k - \bar{s}_k dT, \tag{2.19}$$

where, if we follow standard procedures, an undetermined constant still remains for nonisothermal transformations in the coefficient \bar{s}_k of dT . This difficulty was already recognized by Gibbs himself (Gibbs, 1906) as well as by others (see, e.g., Hatsopoulos and Keenan, 1965).

Gibbs's paradox is also eliminated, as shown by Eq. (2.3), because for identical substances the injection pressures p_k and hence also the injection entropies \bar{s}_k are the same, with the result that in Eq. (2.3) entropies become additive. It is important to note that, when two components become identical, Eq. (2.15) for the injection pressure in terms of the molar fraction loses its validity.

This is consistent with the physical fact that in that case a semipermeable membrane loses its ability to distinguish between components.

III. New Chemical Thermodynamics

The concept of thermobaric transfer has provided a new approach to chemical thermodynamics (Biot, 1976a, 1977a).

The first step is to introduce the new concept of intrinsic heat of reaction defined as follows. A chemical reaction is measured by a reaction coordinate ξ such that the masses of pure substances dm_k produced by a given chemical reaction $d\xi$ are given by

$$dm_k = \nu_k d\xi, \tag{3.1}$$

where ν_k are constants characteristic of the reaction that satisfy the condition $\sum_k \nu_k = 0$ of mass conservation. The coefficients are algebraic, so that the masses produced may be positive or negative. Consider a reaction $d\xi$ occurring in a rigid cell in such a way that the temperature is maintained constant while the products of the reaction are extracted reversibly through semipermeable membranes. Because the temperature and com-

position of the cell remain unchanged, its state and hence its pressure and volume do not vary. The constancy of the temperature is obtained by injecting into the cell a quantity of heat $\bar{h}_T d\xi$. This defines the *intrinsic heat of reaction* \bar{h}_T . How this is related to standard definitions can be shown by reinjecting into the cell the products of the reaction either at constant volume or at constant pressure, with T constant. We write

$$h_{vT} = \bar{h}_T + \sum_k \nu_k h_{vT}^k, \quad (3.2a)$$

$$h_{pT} = \bar{h}_T + \sum_k \nu_k h_{pT}^k, \quad (3.2b)$$

where h_{vT} and h_{pT} are the standard heats of reaction at constant temperature and, respectively, at constant volume and pressure. The heat of mixing h_{vT}^k at constant T and v is given by Eq. (2.12) and h_{pT}^k denotes the heat of mixing at constant temperature and pressure. By a method similar to the previous derivation of h_{vT}^k , we showed (Biot, 1982a) that the value of h_{pT}^k is

$$h_{pT}^k = - \frac{T}{\rho_k} \left(\frac{\partial p_k}{\partial T} \right)_{pm}. \quad (3.3)$$

The derivative $\partial/\partial T$ is for constant pressure and composition. For a perfect gas mixture, substitution of the value for p_k from (2.15) yields $h_{pT}^k = 0$. Hence in this case $h_{pT}^k = 0$, i.e., the standard and intrinsic heats of reaction coincide.

Note that the intrinsic heat of reaction is more representative of chemical properties than standard concepts, because it does not involve the heat of mixing or external work. For this reason its value is obtained by a very general formula relating the two heats of reaction for two different states. Consider a rigid cell in state 1 with values $p_k^{(1)}$, T_1 and another in state 2 with values $p_k^{(2)}$, T_2 . A reaction $d\xi$ occurs in cell 1 and $-d\xi$ in cell 2, while products of reaction are extracted from 1 and injected into 2 by thermobaric transfer. The temperatures of the cells are kept constant by injecting amounts of heat $\bar{h}_T^{(1)} d\xi$ and $-\bar{h}_T^{(2)} d\xi$, respectively, into each cell. Conservation of energy implies the relation (Biot, 1977a) generalizing Kirchhoff's formula

$$\bar{h}_T^{(2)} - \bar{h}_T^{(1)} = \sum_k \nu_k \int_{p_k^{(1)T_1}}^{p_k^{(2)T_2}} d\bar{\epsilon}_k. \quad (3.4)$$

Hence if we know the intrinsic heat of reaction for a single state, we may derive its value (as well as the standard values h_{vT} and h_{pT}) for any other state of arbitrary composition and temperature.

In the preceding section we showed how to evaluate the energy and entropy of an open cell by thermobaric transfer. The procedure may be extended to the case where a chemical reaction also occurs in the cell. This is accomplished by adding to the hypersystem a chemical supply cell C_{ch} in which the reaction takes place and is in equilibrium at the temperature T_{eq} , with injection pressures p_{keq} and an intrinsic heat of reaction \bar{h}_T^{eq} . We consider a reaction $d\xi$ to occur in C_{ch} while the products $\nu_k d\xi$ are extracted and injected into the primary cell C_P by thermobaric transfer. The temperature T_{eq} of C_{ch} is also kept constant by injecting the heat $\bar{h}_T^{eq} d\xi$. In this process the state of C_{ch} does not vary. At the same time we proceed as in the previous section by injecting masses dM^k from C_{Sk} into C_P , adding an amount of heat dh , and changing its volume by dv . *The change of state of the system through the reversible process of thermobaric transfer can be made to be the same as if a reaction $d\xi$ had occurred in the primary cell in addition to the other changes.*

The increase of energy and entropy of the subsystem $C_{ch} + \sum C_{Sk} + C_P$ is

$$d^0u = -p dv + \sum_k \nu_k d\xi \int_{p_{keq}T_{eq}}^{p_k T} d\bar{\epsilon}'_k + \bar{h}_T^{eq} d\xi + \sum_k \bar{\epsilon}_k dM^k + dh, \quad (3.5)$$

$$d\mathcal{S} = \sum_k \nu_k d\xi \int_{p_{keq}T_{eq}}^{p_k T} d\bar{s}'_k + \frac{\bar{h}_T^{eq}}{T_{eq}} d\xi + \sum_k \bar{s}_k dM^k + \frac{dh}{T}, \quad (3.6)$$

with

$$dh = h_{vT}^v dv + \sum_k h_{vT}^k (dM^k + \nu_k d\xi) + C_{vm} dT. \quad (3.7)$$

These results are obtained by adding to Eqs. (2.1), (2.3), and (2.5) the terms due to the masses $\nu_k d\xi$ transferred and the heat $\bar{h}_T^{eq} d\xi$ injected into C_{ch} . We have also taken into account the fact that C_{ch} is in equilibrium, so no change of entropy occurs in the system due to the chemical reaction in C_{ch} .

The differentials (3.5) and (3.6) may be integrated from a given initial state, yielding values

$${}^0u = {}^0u(v, \xi, M^k, T), \quad \mathcal{S} = \mathcal{S}(v, \xi, M^k, T), \quad (3.8)$$

functions of v , ξ , M^k , and T , considered as state variables of the primary cell C_P . The values in Eq. (3.8) define the energy and entropy of C_P in the presence of a chemical reaction. Note that, starting from a given initial

state $\xi = 0$, $M^k = 0$, the increase of masses of the various substances in the cell is

$$m_k = \nu_k \xi + M^k. \quad (3.9)$$

However, *the energy and entropy of the cell as defined by Eqs. (3.5) and (3.6) will vary even if m_k remains constant.* This is due to the collective definition of \mathcal{U} and \mathcal{S} , which involves the subsystem $C_{\text{ch}} + \sum C_{S_k} + C_P$. On the other hand, in the equations of state,

$$p = p(v, m_k, T), \quad (3.10)$$

$$p_k = p_k(v, m_k, T) \quad (3.11)$$

are functions of only v , m_k , and T .

Elimination of dh between Eqs. (3.5) and (3.6) yields

$$d^0\mathcal{U} = -p dv - A d\xi + \sum_k \phi_k dM^k + T d\mathcal{S}, \quad (3.12)$$

where

$$A = \sum_k \nu_k \left(T \int_{p_{k\text{eq}T_{\text{eq}}}}^{p_k T} d\bar{s}'_k - \int_{p_{k\text{eq}T_{\text{eq}}}}^{p_k T} d\bar{\varepsilon}'_k \right) + \left(\frac{T}{T_{\text{eq}}} - 1 \right) \bar{h}_T^{\text{eq}}. \quad (3.13)$$

Equation (3.12) generalizes Eq. (2.17) in the presence of a chemical reaction. When a reaction occurs adiabatically in a rigid closed cell we put $d^0\mathcal{U} = dv = dM^k = 0$, and Eq. (3.12) yields

$$A d\xi = T d\mathcal{S}. \quad (3.14)$$

This corresponds to De Donder's formula (1936) and shows that A is the affinity whereas $d\mathcal{S}$ is the entropy produced by the reaction and defined here precisely in a new way as a collective concept.

We may write the affinity in a way formally identical to a standard expression by putting

$$\bar{h}_T^{\text{eq}} = \sum_k \nu_k \left(\int_0^{p_{k\text{eq}T_{\text{eq}}}} d\bar{\varepsilon}'_k + \bar{\varepsilon}_k(0) \right), \quad (3.15)$$

$$\frac{\bar{h}_T^{\text{eq}}}{T_{\text{eq}}} = \sum_k \nu_k \left(\int_0^{p_{k\text{eq}T_{\text{eq}}}} d\bar{s}'_k + \bar{s}_k(0) \right). \quad (3.16)$$

The integrals at the lower limit are evaluated by extrapolating gaseous classic properties of $\bar{\varepsilon}_k$ and \bar{s}_k to absolute zero, with $\bar{\varepsilon}_k(0)$ and $\bar{s}_k(0)$ constants assumed to be characteristic of the substance and independent of any particular chemical reactions. We may consider these assumptions as *basic axioms*. Substitution of the values from Eqs. (3.15) and (3.16) into Eq. (3.13) yields

$$A = -\sum_k v_k \mu_k, \quad (3.17)$$

where

$$\mu_k = \int_0^{p_k T} d\bar{\varepsilon}'_k - T \int_0^{p_k T} d\bar{s}'_k + \varepsilon_k(0) - T s_k(0). \quad (3.18)$$

The constants $\varepsilon_k(0)$ and $s_k(0)$ are determined experimentally from chemical reactions. This provides a novel definition of the chemical potentials μ_k .

The values of $\varepsilon_k(0)$ and $s_k(0)$ may also be defined and evaluated by introducing the axioms of quantum statistics and physical properties of matter in the cryogenic range. However, in practice, in most cases this leads to many difficulties, as shown by Fowler and Guggenheim (1952).

According to expression (3.13) and the value of p_k from Eq. (3.11), the affinity

$$A = A(v, m_k, T) \quad (3.19)$$

is a function of v , m_k , and T . With the value of m_k from Eq. (3.9) it also becomes a function of v , ξ , M^k , and T :

$$A = A(v, \xi, M^k, T). \quad (3.20)$$

We considered a single chemical reaction, but the results are readily generalized to multiple simultaneous reactions by adding a set of chemical supply cells $C_{\text{ch}\rho}$, one for each reaction ρ . The masses produced by the reactions are then

$$dm_k = \sum_{\rho} v_{k\rho} d\xi_{\rho}. \quad (3.21)$$

With an affinity A_{ρ} for each reaction, Eq. (3.12) becomes

$$d^{\circ}u = -p dv - \sum_{\rho} A_{\rho} d\xi_{\rho} + \sum_k \phi_k dM^k + T d\mathcal{S}. \quad (3.22)$$

IV. Homogeneous Mixtures and Reformulation of the Gibbs–Duhem Theorem

The new restructured thermodynamics by thermobaric transfer provides a novel evaluation of the thermodynamic functions of a cell containing a homogeneous mixture of fluids. To evaluate the thermodynamic functions for this case we apply Eqs. (3.5) and (3.6) by writing them in the form

$$d\mathcal{U} = -p dv + \mathcal{U}_{\text{eq}} d\xi + \sum_k \bar{\varepsilon}_k dm_k + dh, \quad (4.1)$$

$$d\mathcal{S} = \mathcal{S}_{\text{eq}} d\xi + \sum_k \bar{s}_k dm_k + dh/T, \quad (4.2)$$

where we have put

$$\mathcal{U}_{\text{eq}} = \bar{h}_T^{\text{eq}} - \sum_k \nu_k \bar{\varepsilon}_k^{\text{eq}}, \quad \mathcal{S}_{\text{eq}} = \frac{\bar{h}_T^{\text{eq}}}{T_{\text{eq}}} - \sum_k \nu_k \bar{s}_k^{\text{eq}}, \quad (4.3)$$

$$\bar{\varepsilon}_k^{\text{eq}} = \int_{p_0 T_0}^{p_k \text{eq} T_{\text{eq}}} d\bar{\varepsilon}'_k, \quad \bar{s}_k^{\text{eq}} = \int_{p_0 T_0}^{p_k \text{eq} T_{\text{eq}}} d\bar{s}'_k, \quad (4.4)$$

and $dm_k = \nu_k d\xi + dM^k$. For simplicity we assume a single reaction, but the results may be readily generalized to multiple reactions. We start with a cell of zero volume. Its volume v is then increased gradually while maintaining constant the pressure p , the temperature T , and the concentrations of the various substances. Hence, $p_k \bar{\varepsilon}_k$ and \bar{s}_k also remain constant. The heat that must be injected is

$$dh = \sum_k h_{pT}^k dm_k, \quad (4.5)$$

where h_{pT}^k is the heat of mixing at constant pressure and temperature. Substitution of the value of dh from Eq. (4.5) into Eqs. (4.1) and (4.2) yields

$$d\mathcal{U} = -p dv + \mathcal{U}_{\text{eq}} d\xi + \sum_k \mathcal{U}_k dm_k, \quad (4.6)$$

$$d\mathcal{S} = \mathcal{S}_{\text{eq}} d\xi + \sum_k \mathcal{S}_k dm_k, \quad (4.7)$$

with

$$\mathcal{U}_k = \bar{\varepsilon}_k + h_{pT}^k, \quad \mathcal{S}_k = \bar{s}_k + h_{pT}^k/T. \quad (4.8)$$

During the transformation considered here, the value of h_{pT}^k remains constant, hence also the values of \mathcal{U}_k and \mathcal{S}_k as well as p and \mathcal{U}_{eq} . Thus integration of Eqs. (4.6) and (4.7) yields

$$\mathcal{U} = -pv + \mathcal{U}_{\text{eq}} \xi + \sum_k \mathcal{U}_k m_k, \quad (4.9)$$

$$\mathcal{S} = \mathcal{S}_{\text{eq}} \xi + \sum_k \mathcal{S}_k m_k. \quad (4.10)$$

These values are the energy and entropy of a homogeneous cell containing masses $m_k = \nu_k \xi + M^k$ of each substance.

For a pure gas mixture $h_{pT}^k = 0$, and without chemical reactions ($\xi = 0$) we obtain

$$\mathcal{U} + pv = \sum_k \bar{e}_k m_k, \quad \mathcal{S} = \sum_k \bar{s}_k m_k, \quad (4.11)$$

showing that *in this case the enthalpy of the mixture is the sum of the enthalpies of the individual components*, and likewise for the entropy (Biot, 1982a).

We note again that for identical components the injection pressures p_k are the same, hence also the values of s_k , so that *Gibbs's paradox is avoided*.

To reformulate the Gibbs–Duhem theorem in the present context, we differentiate Eqs. (4.9) and (4.10). Taking into account the values of these differentials from Eqs. (4.6) and (4.7), we derive

$$\sum_k m_k d\mathcal{U}_k = v dp, \quad (4.12)$$

$$\sum_k m_k d\mathcal{S}_k = 0. \quad (4.13)$$

Hence we may also write

$$\begin{aligned} v dp &= \sum_k m_k (d\mathcal{U}_k - T d\mathcal{S}_k) \\ &= \sum_k m_k d(\mathcal{U}_k - T\mathcal{S}_k) + \sum_k m_k \mathcal{S}_k dT. \end{aligned} \quad (4.14)$$

Using Eqs. (2.18) and (4.8) we also write

$$\mathcal{U}_k - T\mathcal{S}_k = \phi_k, \quad (4.15)$$

and Eq. (4.14) becomes

$$v dp = \sum_k m_k d\phi_k + \mathcal{S}^C dT, \quad (4.16)$$

where

$$\mathcal{S}^C = \sum_k m_k \mathcal{S}_k. \quad (4.17)$$

We call \mathcal{S}^C the *convective entropy* (Biot, 1982a), because it represents the value of the entropy obtained by pure convection of the masses m_k into the cell without chemical reaction.

Equation (4.16) constitutes a reformulation of the Gibbs–Duhem theorem (Biot, 1982a). It is expressed here in terms of ϕ_k and the convective

entropy \mathcal{S}^C instead of the chemical potentials μ_k and the entropy used in the classical form. *The present formulation avoids the basic difficulties of the classical treatment, which involves undetermined constants in μ_k , and in the entropy.*

Expressions (4.9) and (4.10) are readily generalized for multiple reactions as

$$\mathcal{U} = -pv + \sum_{\rho} \mathcal{U}_{\text{cq}}^{\rho} \xi_{\rho} + \sum_k \mathcal{U}_k m_k, \quad (4.18)$$

$$\mathcal{S} = \sum_{\rho} \mathcal{S}_{\text{cq}}^{\rho} \xi_{\rho} + \sum_k \mathcal{S}_k m_k, \quad (4.19)$$

where

$$\mathcal{U}_{\text{cq}}^{\rho} = \bar{h}_T^{\text{cq}\rho} - \sum_k \nu_k \bar{\varepsilon}_k^{\text{cq}\rho}, \quad \mathcal{S}_{\text{cq}}^{\rho} = (\bar{h}^{\text{cq}\rho}/T_{\text{cq}\rho}) - \sum_k \nu_k \bar{s}^{\text{cq}\rho}. \quad (4.20)$$

The superscript ρ refers to values for the particular reaction ρ .

V. Nontensorial Virtual Work Approach to Finite Strain and Stress

The irreversible thermodynamics developed here is based on a principle of virtual dissipation. It constitutes a generalization of the traditional method of virtual work in classical mechanics. These methods in the field of solid mechanics have been used extensively by the author since 1934 (see Biot, 1965b); more recently, it was also emphasized by Washizu (1975). Because of the currently fashionable trends, the power and simplicity of this method have generally been overlooked. The method provides an approach to finite strain that is more general than that derived from tensor definitions and contains the latter as a particular case. At the same time, it is flexible and ideally suited to describe physical properties of anisotropic media such as laminated and fiber composites of technological importance.

We start from a homogeneous deformation defined by the linear transformation of the initial coordinates x_i of the material points to

$$\bar{x}_i = (\delta_{ij} + a_{ij})x_j, \quad (5.1)$$

where δ_{ij} is the unit matrix and a_{ij} are nine coefficients. Summation is implied for repeated tensor indices. We may consider the transformation to be equivalent to the following process (Biot, 1965b). First, a pure solid rotation is described by three degrees of freedom and written as

$$x'_i = R_{ij}x_j. \tag{5.2}$$

It is then followed by another transformation,

$$\bar{x}_i = (\delta_{ij} + \varepsilon_{ij})x'_j, \tag{5.3}$$

where the coefficients are not independent but satisfy three constraints, so that they contain only six degrees of freedom. For example, we may adopt the three constraints

$$\varepsilon_{ij} = \varepsilon_{ji} \tag{5.4}$$

and call ε_{ij} the six finite strain components defining the deformation (5.3). In this case, the transformation (5.3) is such that principal directions of strain remain invariant (Biot, 1965b).

Other choices may be made. For example, the transformation (5.3) may be chosen so that the material on the x'_1 axis remains on that axis while the material in the $x'_1x'_2$ plane remains in that plane. In this case, $\varepsilon_{21} = \varepsilon_{31} = \varepsilon_{32} = 0$, and the six remaining coefficients define the strain components. Other definitions may be chosen suitable to the particular physical properties of the material (Biot, 1973a).

For the method to be complete we must be able to express the six strain components ε_{ij} in terms of the nine coefficients a_{ij} . We have shown that this can easily be done to any order by a systematic procedure (Biot, 1965b). For example, to the second order, for the choice (5.4), we have

$$\varepsilon_{ij} = e_{ij} + \frac{1}{2} (e_{i\mu}\omega_{\mu j} + \varepsilon_{j\mu}\omega_{\mu i}) + \frac{1}{2} \omega_{i\mu}\omega_{j\mu}, \tag{5.5}$$

where

$$e_{ij} = \frac{1}{2} (a_{ij} + a_{ji}), \quad \omega_{ij} = \frac{1}{2} (a_{ij} - a_{ji}). \tag{5.6}$$

In two dimensions, for a choice of strain components such that $\varepsilon_{21} = 0$, the three strain components to the second order are (Biot, 1973b)

$$\varepsilon_{11} = e_{11} + \frac{1}{2} a_{21}^2, \quad \varepsilon_{22} = e_{22} - \frac{1}{2} a_{21}(2a_{12} + a_{21}), \tag{5.7}$$

$$\varepsilon_{12} = e_{12} + \frac{1}{2} a_{21}(a_{22} - a_{11}). \tag{5.8}$$

The second-order approximation is sufficient in a vast group of problems. We may also choose Green's definition of finite strain,

$$\varepsilon_{ij} = e_{ij} + \frac{1}{2} a_{\mu i}a_{\mu j}. \tag{5.9}$$

This has the advantage of providing the exact functional dependence in terms of a_{ij} . However, in practice this leads to difficulties because the strain components are nonlinearly related to extension ratios and introduce spurious purely geometric nonlinearities in the physical description.

The virtual work method readily provides the definition of six stress components τ_{ij} associated with the strain. A cubic element of unit size oriented along the coordinate axes is subject to the transformation (5.3) by forces applied on the six faces. A virtual deformation $\delta\varepsilon_{ij}$ produces a virtual work

$$\delta W = \tau_{ij} \delta\varepsilon_{ij} \quad (5.10)$$

with six coefficients τ_{ij} defining stress components conjugate to ε_{ij} . The quantity δW is a physical invariant, but the factors τ_{ij} and $\delta\varepsilon_{ij}$ need not be tensors. The indices i and j indicate a summation to all six independent terms whatever their nature. If ε_{ij} is expressed as a function of a_{ij} , we may write

$$\delta W = \tau_{\mu\nu} \partial\varepsilon_{\mu\nu} / \partial a_{ij} \delta a_{ij} = T_{ij} \delta a_{ij}, \quad (5.11)$$

where

$$T_{ij} = \tau_{\mu\nu} \partial\varepsilon_{\mu\nu} / \partial a_{ij} \quad (5.12)$$

are the nine components of the Piola tensor. We may also consider the stress σ_{ij} per unit area after deformation, referred to the initial axes x_i . A virtual transformation after deformation may be written in terms of final coordinates \bar{x}_i as

$$\delta\bar{x}_i = \bar{x}_j \delta\bar{a}_{ij}, \quad (5.13)$$

where $\delta\bar{a}_{ij}$ are nine suitable coefficients to be determined. The unit cube after deformation has become a parallelepiped, and the virtual work of the forces σ_{ij} in the virtual transformation (5.13) is

$$\delta W = J \sigma_{ij} \delta\bar{a}_{ij}, \quad (5.14)$$

where J is the Jacobian of the transformation of x_i to \bar{x}_i . To derive $\delta\bar{a}_{ij}$, consider the virtual transformation in terms of initial coordinates by substituting into Eq. (5.13) the value of \bar{x}_j from Eq. (5.1). We obtain

$$\delta\bar{x}_i = c_{jk} x_k \delta\bar{a}_{ij}, \quad c_{jk} = \delta_{jk} + a_{jk}; \quad (5.15)$$

and from Eq. (5.1),

$$\delta\bar{x}_i = x_k \delta a_{ik}. \quad (5.16)$$

Since Eqs. (5.15) and (5.16) are identical transformations, we derive

$$\delta a_{ik} = c_{jk} \delta \bar{a}_{ij}. \quad (5.17)$$

With this value, Eq. (5.11) becomes

$$\delta W = T_{ik} c_{jk} \delta \bar{a}_{ij}. \quad (5.18)$$

Comparing Eqs. (5.14) and (5.18) yields

$$\sigma_{ij} = (1/J) T_{ik} c_{jk}. \quad (5.19)$$

Since the virtual work (5.14) must vanish for a pure rotation $\delta \bar{a}_{ij} = -\delta \bar{a}_{ji}$, the tensor σ_{ij} is symmetric and satisfies the three relations

$$\sigma_{ij} = \sigma_{ji}, \quad (5.20)$$

which also expresses the conditions that the moments due to the nine stress components T_{ij} vanish.

Substitution in Eq. (5.19) of the values (5.12) of T_{ij} yields

$$\sigma_{ij} = (1/J) \tau_{\mu\nu} c_{jk} \partial \epsilon_{\mu\nu} / \partial a_{ik}. \quad (5.21)$$

This expression is valid for all definitions of $\tau_{\mu\nu}$, and the summation is extended to all six components of the stress $\tau_{\mu\nu}$ as defined above (Biot, 1981).

For a continuous deformation field, we write $\bar{x}_i = x_i + u_i(x_j)$, where the displacement u_i is a function of the initial coordinates x_j . The local infinitesimal transformation

$$d\bar{x}_i = (\delta_{ij} + \partial u_i / \partial x_j) dx_j \quad (5.22)$$

is the same as Eq. (5.1) provided we write

$$\partial u_i / \partial x_j = a_{ij}. \quad (5.23)$$

With a_{ij} representing the nine displacement gradients, the foregoing definitions of stress and strain remain valid as local values for a nonhomogeneous deformation.

VI. Thermodynamic Functions of Open Deformable Solids

The collective energy and entropy per unit initial volume of a deformable solid based on virtual work and nontensorial concepts were derived earlier (Biot, 1981). The results may be readily extended to an open solid with chemical reactions by proceeding as in Section III. We consider initially a cube of unit size. A homogeneous deformation is defined by the

six strain components ε_{ij} under the corresponding stresses τ_{ij} . The solid contains substances in solution. The increment of mass of each substance is

$$dm_k = \nu_k d\xi + dM^k, \quad (6.1)$$

where $\nu_k d\xi$ is due to a chemical reaction and dM^k is the mass acquired from an external source. For simplicity we assume a single reaction, because results are readily generalized for multiple reactions. An infinitesimal change is defined by $d\varepsilon_{ij}$, $d\xi$, dM^k and the temperature change dT . The corresponding changes in energy and entropy are obtained by thermobaric transfer and their values are derived from Eqs. (3.5) and (3.6) by replacing $-p dv$ by $\tau_{ij} \delta\varepsilon_{ij}$. This yields

$$d^0u = \tau_{ij} d\varepsilon_{ij} + \sum_k \nu_k d\xi \int_{p_{keq} T_{eq}}^{p_k T} d\bar{\varepsilon}'_k + \bar{h}_T^{eq} d\xi + \sum_k \bar{\varepsilon}_k dM^k + dh, \quad (6.2)$$

$$d\mathcal{S} = \sum_k \nu_k d\xi \int_{p_{keq} T_{eq}}^{p_k T} d\bar{s}'_k + \frac{\bar{h}_T^{eq}}{T_{eq}} d\xi + \sum_k \bar{s}_k dM^k + \frac{dh}{T}. \quad (6.3)$$

The value from Eq. (3.7) must also be changed to

$$dh = h_{mT}^{ij} d\varepsilon_{ij} + \sum_k h_{\varepsilon T}^k (\nu_k d\xi + dM^k) + C_{em} dT. \quad (6.4)$$

The terms $h_{mT}^{ij} d\varepsilon_{ij}$ represent the heat that must be injected when applying a deformation $d\varepsilon_{ij}$ under the constraint $dm_k = dT = 0$. Similarly, $h_{\varepsilon T}^k$ is the heat of mixing, where $h_{\varepsilon T}^k dM^k$ is the heat injected when adding a mass dM^k under the constraint $d\varepsilon_{ij} = dT = 0$. The heat capacity C_{em} is for $d\varepsilon_{ij} = dm_k = 0$. We may show that h_{mT}^{ij} and $h_{\varepsilon T}^k$ may be determined without calorimetric measurements when we know the equations of state

$$\tau_{ij} = \tau_{ij}(\varepsilon_{\mu\nu}, m_k, T), \quad (6.5)$$

$$p_k = p_k(\varepsilon_{\mu\nu}, m_k, T), \quad (6.6)$$

i.e., when we know the stress τ_{ij} and the injection pressures p_k as functions of the strain ε_{ij} , the masses m_k of each substance added by chemical reaction and transport, and the temperature T . From the conditions that Eqs. (6.2) and (6.3) are exact differentials, proceeding exactly as before in deriving Eqs. (2.8) and (2.12), we obtain

$$h_{mT}^{ij} = -T(\partial\tau_{ij}/\partial T)_{\varepsilon m}, \quad (6.7)$$

$$h_{\varepsilon T}^k = -T/\rho_k(\partial p_k/\partial T)_{\varepsilon m}, \quad (6.8)$$

where the subscripts indicate that the partial derivatives are for ε_{ij} and m_k constant.

The coefficients of the differentials in expressions (6.2) and (6.3) of $d\mathcal{U}$ and $d\mathcal{S}$ are now known as functions of ε_{ij} , $m_k = \nu_k \xi + M^k$, and T . Integration along any arbitrary path with initial conditions $\mathcal{U} = \mathcal{S} = 0$ yields the values

$$\mathcal{U} = \mathcal{U}(\varepsilon_{ij}, \xi, M^k, T), \quad (6.9)$$

$$\mathcal{S} = \mathcal{S}(\varepsilon_{ij}, \xi, M^k, T) \quad (6.10)$$

as functions of the state variables ε_{ij} , ξ , M^k , and T .

Replacing $-p dv$ by $\tau_{ij} d\varepsilon_{ij}$, Eq. (3.22) is generalized to

$$d\mathcal{U} = \tau_{ij} d\varepsilon_{ij} - \sum_p A_p d\xi_p + \sum_p \phi_k dM^k + T d\mathcal{S}. \quad (6.11)$$

VII. The Fluence Concept

In a fixed coordinate system x_i , a rate of mass flow or mass flux of a given substance is represented by a Cartesian vector \dot{M}_i^k . The component \dot{M}_i^k is the mass flux across a unit area normal to x_i : conservation of mass is expressed by

$$\dot{M}^k = -\partial \dot{M}_i^k / \partial x_i. \quad (7.1)$$

The total mass entering a domain Ω is then

$$-\int_{\Omega} \frac{\partial \dot{M}_i^k}{\partial x_i} d\Omega = -\int_A \dot{M}_i^k n_i dA, \quad (7.2)$$

where n_i is the unit normal to the boundary A . Since \dot{M}_i^k represents a time derivative, we may integrate the relations with respect to the time with zero initial values. Hence

$$M^k = -\partial M_i^k / \partial x_i, \quad (7.3)$$

where M_i^k is called the *mass fluence*. It constitutes a Cartesian vector.

In deformable systems, a more general definition of the fluence has been found extremely useful (Biot, 1977b). We consider an area initially equal to unity and normal to the x_i axis. This area is then transported and deformed by the coordinate transformation

$$\bar{x}_i = \bar{x}_i(x_j, t). \quad (7.4)$$

We now call \dot{M}_i^k the mass flux across this transformed area. Obviously the mass flowing into a transformed element initially of unit volume is given

by (7.1), where \dot{M}_i^k represents the more general mass flux. Hence Eqs. (7.1)–(7.3) retain exactly the same form with this generalized definition of the mass flux \dot{M}_i^k and mass fluence M_i^k . In this case, however, \dot{M}_i^k is not a Cartesian vector. We denote by $\dot{M}_i^{\prime k}$ the corresponding Cartesian components, i.e., $\dot{M}_i^{\prime k}$ represents the mass flux per unit area in the space \bar{x}_i . An initial surface A is transformed into A' by transformation (7.4). The mass flux through it may be expressed in two different forms as

$$\int_A \dot{M}_i^k n_i dA = \int_{A'} \dot{M}_j^k C'_{ji} n'_i dA', \quad (7.5)$$

where the second integral is expressed in terms of the coordinates \bar{x}_i and C'_{ij} is the cofactor of $\partial x_i / \partial \bar{x}_j$ in the Jacobian

$$J' = \det|\partial x_i / \partial \bar{x}_j|. \quad (7.6)$$

Obviously, in the second integral of Eq. (7.5) the integrand $\dot{M}_j^k C'_{ji}$ is the Cartesian component $\dot{M}_i^{\prime k}$ of the mass flux in the space \bar{x}_i . Hence

$$\dot{M}_i^{\prime k} = \dot{M}_j^k C'_{ji}. \quad (7.7)$$

This relation may be given another useful form by considering the linear transformation of $d\bar{x}_i$ into dx_i and solving for $d\bar{x}_i$. We find

$$\partial \bar{x}_i / \partial x_j = C'_{ji} / J'. \quad (7.8)$$

Hence

$$\dot{M}_i^{\prime k} = J' \dot{M}_j^k \partial \bar{x}_i / \partial x_j. \quad (7.9)$$

Multiplying this equation by $\partial x_j / \partial \bar{x}_i$, we obtain (Biot, 1977b)

$$\dot{M}_j^k = J \dot{M}_i^{\prime k} \partial x_j / \partial \bar{x}_i, \quad (7.10)$$

where

$$J = 1/J' = \det|\partial \bar{x}_i / \partial x_j|. \quad (7.11)$$

These results show the mass flux, as defined above for a deformable coordinate system, to be a relative contravariant vector (Sokolnikoff, 1951, see pp. 58, 72). We shall refer to \dot{M}_i^k and M_i^k , respectively, as the *contravariant mass flux* and the *contravariant mass fluence*.

Similarly, consider the local Cartesian heat flux \dot{H}'_i at \bar{x}_i and a *contravariant heat flux* \dot{H}_i defined as the rate of heat flow across a transformed surface initially equal to unity and initially normal to the x_i axis. They satisfy the same relations as Eqs. (7.9) and (7.10), namely

$$\dot{H}'_i = J' \dot{H}_j \partial \bar{x}_i / \partial x_j, \quad \dot{H}_j = J \dot{H}'_i \partial x_j / \partial \bar{x}_i. \quad (7.12)$$

The time integral of \dot{H}_i is the contravariant heat fluence H_i . We may write a conservation condition analogous to Eq. (7.3) as

$$h = -\partial H_i / \partial x_i, \quad (7.13)$$

where h is the heat acquired by a deformed element of unit initial volume.

The entropy flux across an area is defined as (Biot, 1977b)

$$\dot{S}_i = \sum_k \bar{s}_k \dot{M}_i^k + \dot{H}_i / T. \quad (7.14)$$

Its time integral is the entropy fluence S_i . They are either Cartesian or contravariant components.

The fluence fields M_i^k are *state variables*, because they determine M^k by Eq. (7.3). However, the fluence fields H_i and S_i are not state variables.

Other fluence fields that are state variables may be introduced by putting

$$\mathcal{S} = -\partial S_i^+ / \partial x_i, \quad \mathcal{U} = -\partial \mathcal{F}_i^+ / \partial x_i, \quad (7.15)$$

where S_i^+ is called a *pseudo-entropy fluence* and \mathcal{F}_i^+ a *pseudo-energy fluence*. Using such concepts, the state of a system may be partially described by fluence vectors as further clarified below in several applications.

VIII. The Nature of Entropy Production and Its Evaluation

In order to formulate the principle of virtual dissipation in the next section, we must evaluate the entropy produced by an irreversible process. Entropy production is due to various phenomena, in particular thermomolecular diffusion, viscosity, and chemical reactions. We shall first consider the entropy produced by diffusion, using a derivation that brings out its physical significance (Biot, 1982b). Consider a medium that may or may not be deformable. The entropy increase per unit initial volume as given by Eq. (2.3) is written in variational form

$$\delta \mathcal{S} = \sum_k \bar{s}_k \delta M^k + \delta h / T, \quad (8.1)$$

where δh is an amount of heat *added reversibly, so as to produce the same change of state as the actual irreversible process*. This amount of heat may be written

$$\delta h = \delta h^P - \partial \delta H_i / \partial x_i, \quad (8.2)$$

where $-\partial \delta H_i / \partial x_i$ is the amount of heat added by the actual irreversible heat flow. We assume that this amount is added reversibly along with an additional heat δh^P so that the total generates the actual irreversible change of state. The heat δh^P defines the heat produced by the irreversibility and corresponds to Clausius' uncompensated heat. From Eq. (7.3) we also write

$$\delta M^k = -\partial \delta M_i^k / \partial x_i. \quad (8.3)$$

In these equations, H_i and M_i^k are fluence concepts either Cartesian or contravariant, as defined in Section VII, and are valid in a deformable system in terms of initial coordinates x_i . We substitute the values (8.2) and (8.3) into Eq. (8.1). The result may be written in the form

$$\delta \mathcal{S} = -\frac{\partial \delta S_i}{\partial x_i} + \delta s^{*TM}, \quad (8.4)$$

where

$$\delta S_i = \sum_k \bar{s}_k \delta M_i^k + \delta H_i / T \quad (8.5)$$

is the variation of entropy fluence as defined by Eq. (7.14), and

$$T \delta s^{*TM} = T \sum_k \frac{\partial \bar{s}_k}{\partial x_i} \delta M_i^k + \delta h^P - \frac{1}{T} \frac{\partial T}{\partial x_i} \delta H_i. \quad (8.6)$$

Equation (8.4), when integrated over a volume Ω with $n_i \delta H_i = n_i \delta M_i = n_i \delta S_i = 0$ at the boundary, yields

$$\int_{\Omega} \delta \mathcal{S} d\Omega = \int_{\Omega} \delta s^{*TM} d\Omega. \quad (8.7)$$

Hence δs^{*TM} is the virtual entropy produced per unit initial volume. It has three terms. The first is due to the masses convected δM_i^k , the second is due to the heat δh^P produced by the irreversibility, and the third is due to the heat flow δH_i across a temperature gradient.

It remains to evaluate the heat produced δh^P . This is obtained by considering energy conservation. Using the value (8.2) of δh , the variation of energy (2.1) per unit initial volume with $\delta v = 0$ is

$$\delta^0 u = \sum_k \bar{\varepsilon}_k \delta M^k + \delta h^P - \frac{\partial}{\partial x_i} \delta H_i. \quad (8.8)$$

Substitution of Eq. (8.3) for δM^k and integration over a domain Ω yields

$$\int_{\Omega} \delta^{\mathcal{Q}} u \, d\Omega = \int_{\Omega} \left[-\frac{\partial}{\partial x_i} \left(\sum_k \bar{\varepsilon}_k \delta M_i^k + \delta H_i \right) + \sum_k \frac{\partial \bar{\varepsilon}_k}{\partial x_i} \delta M_i^k + \delta h^P \right] d\Omega. \quad (8.9)$$

On the other hand, conservation of energy is expressed by

$$\int_{\Omega} \delta^{\mathcal{Q}} u \, d\Omega = \int_{\Omega} \left[-\frac{\partial}{\partial x_i} \left(\sum_k \bar{\varepsilon}_k \delta M_i^k + \delta H_i \right) + \sum_k (\mathcal{B}_i - a_i^k) \delta M_i^k \right] d\Omega. \quad (8.10)$$

This expression is based on the significance of $(\sum_k \bar{\varepsilon}_k \delta M_i^k + \delta H_i)n_i$ as representing the variation of diffusive energy flowing across a surface, and while \mathcal{B}_i is the body force per unit mass and a_i^k the acceleration of each substance. Note that Eq. (8.10) is actually based on a generalized d'Alembert principle, where $-a_i^k$ plays the role of a body force per unit mass. Comparing the values (8.9) and (8.10), which are valid for an arbitrary domain Ω , we derive for the heat produced

$$\delta h^P = \sum_k (\mathcal{B}_i - a_i^k - \partial \bar{\varepsilon}_k / \partial x_i) \delta M_i^k. \quad (8.11)$$

This provides a physical interpretation of δh^P as the heat produced by the irreversible mechanical work. When it is substituted in the variational relation (8.6), taking into account relation (2.4), we obtain

$$T \delta s^{*TM} = \sum_k X_i^k \delta M_i^k + X_i^T \delta H_i, \quad (8.12)$$

where

$$X_i^k = \mathcal{B}_i - a_i^k - \frac{1}{\rho_k} \frac{\partial p_k}{\partial x_i}, \quad X_i^T = -\frac{1}{T} \frac{\partial T}{\partial x_i} \quad (8.13)$$

are dissipative disequilibrium forces. They are functions of the mass fluxes \dot{M}_i^k and the heat flux \dot{H}_i . We write

$$X_i^k = \mathcal{R}_i^k(\dot{M}_j^l, \dot{H}_j), \quad X_i^T = \mathcal{R}_i^T(\dot{M}_j^l, \dot{H}_j). \quad (8.14)$$

It should be understood that these relations also depend on the local state variables, although this is not formulated explicitly. They *embody the irreversible kinetics* of the system and may be obtained either experimentally or theoretically from molecular kinetics. With the values (8.14),

equations (8.12) may be written

$$T \delta s^{*TM} = \sum_k \mathcal{R}_i^k \delta M_i^k + \mathcal{R}_i^T \delta H_i. \quad (8.15)$$

In many problems it is convenient to use the entropy flux \dot{S}_i instead of the heat flux \dot{H}_i . Solving Eq. (7.14) for \dot{H}_i and Eq. (8.5) for δH_i , and substituting these values into Eq. (8.15), we obtain

$$T \delta s^{*TM} = \sum_k \mathcal{R}_i^{Sk} \delta M_i^k + \mathcal{R}_i^{ST} \delta S_i, \quad (8.16)$$

where

$$\mathcal{R}_i^{Sk}(\dot{M}_j^l, \dot{S}_j) = \mathcal{R}_i^k - T \bar{s}_k \mathcal{R}_i^T, \quad (8.17)$$

$$\mathcal{R}_i^{ST}(\dot{M}_j^l, \dot{S}_j) = T \mathcal{R}_i^T. \quad (8.18)$$

The present derivation of entropy production is fully general and does not assume linearity or any dependence on Onsager's (1930, 1931) principle. For example, we may include nonlinear diffusion of a non-Newtonian fluid through a porous medium.

In the case of a linear dependence of \mathcal{R}_i^T on the fluxes and *in the absence of a temperature gradient* we obtain from (8.14) the linear relations

$$\mathcal{R}_i^T(\dot{M}_j^l, \dot{H}_j) = 0, \quad (8.19)$$

where \dot{H}_i is the coupled heat flux due solely to the mass flux. If we solve these equations for \dot{H}_i , the coefficients of \dot{M}_i^k constitute what is generally called the *heat of transport*.

Consider now the entropy produced in a primary cell by a chemical reaction. This is the entropy increase of a cell for $dv = dM^k = d^0u = 0$. In this case Eq. (3.22) is applicable and is written in variational form as

$$T \delta s^{*ch} = \sum_\rho A_\rho \delta \xi_\rho, \quad (8.20)$$

where δs^{*ch} is the entropy produced by the reactions $\delta \xi_\rho$. The values of the affinities are functions of v , m_k , T ,

$$A_\rho = A_\rho(v, m_k, T), \quad (8.21)$$

where $m_k = \sum_\rho \nu_{k\rho} \xi_\rho + M^k$ is the total mass of each substance added to the cell by reaction and transport. An expression similar to Eq. (8.14) is obtained by introducing the kinetics of the various reactions. The rates of reaction $\dot{\xi}_\rho$ are functions of v , m_k , and T ,

$$\dot{\xi}_\rho = f_\rho(v, m_k, T). \quad (8.22)$$

Using Eqs. (8.21) and (8.22) it is easily shown that A_ρ is of the form

$$A_\rho = \mathcal{R}_\rho(\dot{\xi}_\rho, v, m_k, T). \quad (8.23)$$

The affinities A_ρ are similar to the disequilibrium forces X_i^k and X_i^T and in analogy with (8.14); they are expressed by \mathcal{R}_ρ in terms of the irreversible kinetics. Equation (8.20) becomes

$$T \delta s^{*ch} = \sum_\rho \mathcal{R}_\rho \delta \xi_\rho. \quad (8.24)$$

The total entropy production δs^* due to simultaneous diffusion and chemical reactions, obtained by adding Eqs. (8.16) and (8.24), is given by

$$T \delta s^* = \sum_\rho \mathcal{R}_\rho \delta \xi_\rho + \sum_k \mathcal{R}_i^{Sk} \delta M_i^k + \mathcal{R}_i^{ST} \delta S_i. \quad (8.25)$$

This expression is applicable to a deformable cell with fluence concepts for M_i^k and S_i . It yields the virtual entropy production per unit initial volume. For an actual irreversible transformation we replace the variations by time derivatives and Eq. (8.25) becomes

$$T \dot{s}^* = \sum_\rho \mathcal{R}_\rho \dot{\xi}_\rho + \sum_k \mathcal{R}_i^{Sk} \dot{M}_i^k + \mathcal{R}_i^{ST} \dot{S}_i > 0. \quad (8.26)$$

This expression represents the rate of dissipation per unit initial volume and is positive. Note that Eq. (8.26) is a consequence of relation (8.25), which is more general and concerns a virtual change, whereas the *actual change* in Eq. (8.26) is a particular case.

When in addition to being linear the relations between the rates and the dissipative forces satisfy Onsager's reciprocity relations (1930, 1931), they may be written

$$\mathcal{R}_\rho = \partial \mathcal{D}^{ch} / \partial \dot{\xi}_\rho, \quad \mathcal{R}_i^{Sk} = \partial \mathcal{D}^{TM} / \partial \dot{M}_i^k, \quad \mathcal{R}_i^{ST} = \partial \mathcal{D}^{TM} / \partial \dot{S}_i, \quad (8.27)$$

where \mathcal{D}^{ch} is a quadratic form in $\dot{\xi}_\rho$ and \mathcal{D}^{TM} a quadratic form in \dot{M}_i^k and \dot{S}_i , with coefficients functions of the local state.

Applying Euler's theorem, we write Eq. (8.26) as

$$\begin{aligned} T \dot{s}^* = 2\mathcal{D} = & \sum_{\sigma\rho} \mathcal{B}_{\sigma\rho} \dot{\xi}_\sigma \dot{\xi}_\rho + \sum_{lk} C_{ij}^{lk} \dot{M}_i^k \dot{M}_j^l \\ & + 2 \sum_k C_{ij}^k \dot{M}_i^k \dot{S}_j + T \lambda_{ij} \dot{S}_i \dot{S}_j, \end{aligned} \quad (8.28)$$

where $\mathcal{D} = \mathcal{D}^{ch} + \mathcal{D}^{TM}$ is a combined dissipation function for chemical reactions and thermomolecular diffusion.

Other types of entropy production, such as that due to viscous effects, will be discussed below in the applications.

A fundamental entropy balance equation may be expressed in terms of entropy production by adding $\delta s^{*\text{ch}}$ in Eq. (8.4). The total entropy variation is then

$$\delta \mathcal{S} = - \frac{\partial}{\partial x_i} \delta S_i + \delta s^*, \quad \delta s^* = \delta s^{*\text{TM}} + \delta s^{*\text{ch}}. \quad (8.29)$$

We replace the variations by time derivatives and write

$$\dot{\mathcal{S}} = - \partial \dot{S}_i / \partial x_i + \dot{s}^*. \quad (8.30)$$

If we integrate this equation with respect to time, assuming zero initial values, we obtain the entropy balance equation

$$\mathcal{S} = - \partial S_i / \partial x_i + s^*. \quad (8.31)$$

It should be understood that in problems where we choose a nonzero initial \mathcal{S} , we must simply subtract this value of \mathcal{S} in Eq. (8.31).

The entropy production has been expressed here in terms of ξ_ρ , M_i^k , and S_i . While ξ_ρ and M_i^k are state variables, the entropy fluence S_i is not. In order to avoid this difficulty, it was shown (Biot, 1981, 1982b) that we may introduce the pseudofluence concepts (7.15) by proceeding as follows. We note that because Eq. (8.10) is valid for an arbitrary domain, we have

$$\delta^{\text{qu}} = - \frac{\partial}{\partial x_i} \left(\sum_k \bar{\varepsilon}_k \delta M_i^k + \delta H_i \right) + \sum_k (\mathcal{R}_i - a_i^k) \delta M_i^k. \quad (8.32)$$

Using Eqs. (8.13) and (8.14) and the definition (7.15) of \mathcal{F}_i^+ , this yields

$$- \frac{\partial}{\partial x_i} \delta \mathcal{F}_i^+ = - \frac{\partial}{\partial x_i} \left(\sum_k \bar{\varepsilon}_k \delta M_i^k + \delta H_i \right) + \sum_k f_i^k \delta M_i^k \quad (8.33)$$

with

$$f_i^k = \mathcal{R}_i^k + \frac{1}{\rho_k} \frac{\partial p_k}{\partial x_i}. \quad (8.34)$$

From Eqs. (8.14), we may obtain \dot{H}_i in terms of X_j^T and \dot{M}_i^k . Substituting these values of \dot{H}_i into \mathcal{R}_i^k determines the latter in terms of local state variables, their gradients and \dot{M}_i^k . Thus in the quantity

$$f_i^k = f_i^k(\dot{M}_j^k) \quad (8.35)$$

the only fluence fields are the state variables M_j^k . With $g_i(x_j, x_j^+)$ representing a fluence field due to a unit concentrated source at x_i^+ , Eq. (8.33) may be written

$$\delta H_i = \delta \mathcal{F}_i^+ - \sum_k \bar{\varepsilon}_k \delta M_i^k + \int_{\Omega^+} g_i(x_l, x_l^+) \sum_k f_j^k \delta M_j^k d\Omega^+, \quad (8.36)$$

where the integral is extended to the space Ω^+ of x_i^+ . Considering the value (8.5) of δS_i and (2.18) of ϕ_k , this may be written

$$T \delta S_i = \delta \mathcal{F}_i^+ - \sum_k \phi_k \delta M_i^k + \int_{\Omega^+} g_i(x_l, x_l^+) \sum_k f_j^k \delta M_j^k d\Omega^+. \quad (8.37)$$

With time derivatives, this becomes

$$T \dot{S}_i = \dot{\mathcal{F}}_i^+ - \sum_k \phi_k \dot{M}_i^k + \int_{\Omega^+} g_i(x_l, x_l^+) \sum_k f_j^k \dot{M}_j^k d\Omega^+. \quad (8.38)$$

Thus δS_i and \dot{S}_i are now expressed in terms of the fluence vectors \mathcal{F}_i^+ and M_i^k , which are state variables.

An important simplification occurs in problems where the effects of inertia and body forces are negligible, and more generally if f_i^k is negligible. In that case, with $f_i^k = 0$, Eq. (8.33) yields

$$-\frac{\partial}{\partial x_i} \delta \mathcal{F}_i^+ = -\frac{\partial}{\partial x_i} \left(\sum_k \bar{e}_k \delta M_i^k + \delta H_i \right), \quad (8.39)$$

where

$$\delta \mathcal{F}_i^+ = \delta \mathcal{F}_i = \sum_k \bar{e}_k \delta M_i^k + \delta H_i \quad (8.40)$$

or

$$\dot{\mathcal{F}}_i = \sum_k \bar{e}_k \dot{M}_i^k + \dot{H}_i. \quad (8.41)$$

Under these conditions $\dot{\mathcal{F}}_i^+$ coincides with the *actual physical energy flux* $\dot{\mathcal{F}}_i$ due to molecular and heat diffusion.

Relations (8.37) and (8.38) become

$$T \delta S_i = \delta \mathcal{F}_i - \sum_k \phi_k \delta M_i^k, \quad (8.42)$$

$$T \dot{S}_i = \dot{\mathcal{F}}_i - \sum_k \phi_k \dot{M}_i^k. \quad (8.43)$$

In many problems where f_i^k remains small these simplified results are applicable.

Another possibility is to introduce the pseudo-entropy fluence S_i^+ defined by Eq. (7.15). Equation (8.29) becomes

$$-\frac{\partial}{\partial x_i} \delta S_i^+ = -\frac{\partial}{\partial x_i} \delta S_i + \delta s^*. \quad (8.44)$$

Hence

$$\delta S_i = \delta S_i^+ + \int_{\Omega^+} g_i(x_l, x_l^+) \delta s^* d\Omega^+ \quad (8.45)$$

and

$$\dot{S}_i = \dot{S}_i^+ + \int_{\Omega^+} g_i(x_l, x_l^+) \dot{s}^* d\Omega^+. \quad (8.46)$$

In many problems we may neglect the entropy s^{*TM} produced by thermo-molecular diffusion. In that case, we write Eqs. (8.45) and (8.46) as

$$T\delta S_i = T\delta S_i^+ + \int_{\Omega^+} g_i(x_l, x_l^+) \sum_{\rho} \mathcal{R}_{\rho} \delta \xi_{\rho} d\Omega^+, \quad (8.47)$$

$$T\dot{S}_i = T\dot{S}_i^+ + \int_{\Omega^+} g_i(x_l, x_l^+) \sum_{\rho} \mathcal{R}_{\rho} \dot{\xi}_{\rho} d\Omega^+. \quad (8.48)$$

Thus δS_i and \dot{S}_i are now expressed in terms of state variables S_i^+ and ξ_{ρ} .

Another important simplification also applies for problems where the entropy produced does not contribute significantly to the total value of the entropy \mathcal{S} . In that case we may write

$$\mathcal{S} = -\partial S_i / \partial x_i, \quad (8.49)$$

and S_i itself becomes a state variable. This is the case for *quasi-reversible processes and in linear thermodynamics*.

IX. The Principle of Virtual Dissipation

Consider again a hypersystem constituted by a collection of primary cells (a primary system), a collection of supply cells including chemical cells, and a thermal well. In the process of thermobaric transfer as defined above, the thermal well did not play any role, because the source of the heat injected in the primary cells and the transferred masses is not specified. We now introduce a *modified thermobaric transfer*, in which the heat injected is provided by reversible heat pumps extracting heat from the thermal well. The mechanical work necessary to inject an amount of heat dh into an element at the temperature T is

$$dw = \theta/T dh, \quad (9.1)$$

where

$$\theta = T - T_0 \quad (9.2)$$

and T_0 is the thermal well temperature. A *thermobaric reversible transformation of the hypersystem is now accomplished entirely through mechan-*

ical work performed on the system, without any exchange of matter or heat with the environment. For such a transformation, the increase of energy of the hypersystem is equal to the mechanical work dW performed on the system. This may be written

$$dU - T_0 dS = dW, \tag{9.3}$$

where dU is the energy of the primary system defined above as a collective concept that includes the energy of the supply cells. The term $-T_0 dS$ is the energy acquired by the thermal well; its increase of entropy $-dS$, because of reversibility, must be equal and opposite in sign to the entropy increase dS of the primary system. We remember that dS is defined as a collective concept that includes the supply cells. We may write Eq. (9.3) as

$$dV = dW, \tag{9.4}$$

where

$$V = U - T_0 S \tag{9.5}$$

is a thermodynamic function shown by the author (Biot, 1954, 1955) to be the key concept that plays a fundamental role in irreversible thermodynamics. It was initially referred to as the “generalized free energy” because it coincides with the Helmholtz definition for the particular case of isothermal transformations. The term “exergy” was later introduced by others to designate a formally similar expression without defining more precisely the significance of U and S in the general case of open systems in terms of collective concepts, as we have done here. However, we shall keep the name exergy for the more general concept represented by Eq. (9.5).

Further physical insight is provided by considering the exergy of a single primary cell:

$$\mathcal{V} = \mathcal{U} - T_0 \mathcal{S}. \tag{9.6}$$

In order to simplify the writing, and without loss of generality, we may consider a rigid cell without chemical reactions. Using the values (2.1) and (2.3), with $dv = 0$, we may write the differential of the exergy as (Biot, 1976a, 1977a)

$$d\mathcal{V} = \sum_k \psi_k dM^k + \theta/T dh, \tag{9.7}$$

where

$$\psi_k = \bar{\varepsilon}_k - T_0 \bar{s}_k, \tag{9.8}$$

$$\bar{s}_k = \int_{\rho_0 T_0}^{\rho_k T} d\bar{s}'_k. \tag{9.9}$$

In a reversible transformation, $d^{\text{a}}V$ is the increase of energy of the hypersystem, and $(\theta/T) dh$ is the work accomplished by the heat pump in order to inject a quantity of heat dh into the primary cell. Hence the remaining term $\psi_k dM^k$ is the work required to bring the mass to equilibrium with the primary cell and inject it into the cell. We have called ψ_k the *thermobaric potential*. In terms of the convective potential (2.18), we write

$$\psi_k = \phi_k + \theta \bar{s}_k. \quad (9.10)$$

Note that ψ_k is defined purely in terms of mechanical work, which is not the case for ϕ_k , which involves the concept of entropy.

Until now we have been dealing with reversible transformations. However, the value of V is determined by the state variables, whether they follow a reversible or irreversible evolution. We therefore consider variations of the state variables for an irreversible change of state. These variations are arbitrary except for one condition. They must satisfy the constraint that the flow of heat and matter between cells is continuous. For a continuous system considered as a collection of infinitesimal cells, this means that the heat and mass fluence field must satisfy the constraint of continuity. At the boundary of the primary system, heat and matter may be injected into it by a modified thermobaric transfer within the hypersystem. Hence the *variation of the hypersystem occurs without exchange of matter and heat with the environment*. As a consequence, conservation of energy for the hypersystem is expressed by

$$\delta U + T_0 \delta S_{\text{TW}} = \delta W, \quad (9.11)$$

where δS_{TW} is the variation of entropy of the thermal well and $T_0 \delta S_{\text{TW}}$ its variation of energy. This relation differs from Eq. (9.3) in that the transformation is irreversible and we may not put $\delta S_{\text{TW}} = -\delta S$. With the value (9.5) of V we may write Eq. (9.11) as

$$\delta V + T \delta S^* = \delta W, \quad (9.12)$$

where

$$\delta S^* = \delta S_{\text{TW}} + \delta S \quad (9.13)$$

is the *variation of entropy produced* in the hypersystem. In terms of the local entropy produced δs^* , as evaluated in Section VIII, it is expressed by

$$T_0 \delta S^* = T_0 \int_{\Omega} \delta s^* d\Omega. \quad (9.14)$$

An important step results from a generalized interpretation of the value of δW , the virtual work of the external forces acting on the hypersystem.

It represents the work δW^M of the mechanical forces acting on the primary system plus the work δW^{TH} accomplished in the thermobaric transfer of heat and mass injected at the boundary. In addition, we generalize d'Alembert's principle by including in the external work the virtual work $-\sum_i I_i \delta q_i$ of the reversed inertial forces due to mass accelerations in the primary system at any particular instant of the evolution. The generalization involved here implies *the validity of d'Alembert's principle where U is a thermodynamic energy involving heat and not simply a mechanical potential as in classical mechanics*. Accordingly, we may write

$$\delta W = - \sum_i I_i \delta q_i + \delta W^M + \delta W^{TH}, \quad (9.15)$$

where

$$\delta W^{TH} = - \int_A \left(\sum_k \psi_k \delta M_i^k + \theta/T \delta H_i \right) n_i dA \quad (9.16)$$

represents the virtual work due to the thermobaric transfer of heat $\delta H_i n_i$ and masses $\delta M_i^k n_i$ at the boundary. Note that for a deforming boundary, M_i^k and H_i are the contravariant mass and heat fluences as defined in Section VII, whereas the surface integral is evaluated at the initial boundary A . Note also that Eq. (9.16) may be expressed in terms of the entropy fluence S_i at the boundary by substituting into Eq. (9.16) the value of δH_i extracted from Eq. (8.5). This yields

$$\delta W^{TH} = - \int_A \left(\sum_k \phi_k \delta M_i^k + \theta \delta S_i \right) n_i dA. \quad (9.17)$$

We have called δW^{TH} *the virtual work of thermodynamic forces at the boundary*.

With the value (9.15) of δW substituted in Eq. (9.12), we obtain

$$\sum_i I_i \delta q_i + \delta V + T_0 \delta S^* = \delta W^M + \delta W^{TH}. \quad (9.18)$$

This constitutes the *generalized principle of virtual dissipation (Biot, 1955, 1975, 1976b, 1982b) valid for arbitrary variations*, provided continuity of heat and mass flux is preserved.

If the system is in a potential field such as a gravity field, we denote by G the potential energy in this field. By including $-\delta G$ in the mechanical work of external forces, we may write Eq. (9.18) as

$$\sum_i I_i \delta q_i + \delta \mathcal{P} + T_0 \delta S^* = \delta W^M + \delta W^{GTH}, \quad (9.19)$$

where $\mathcal{P} = V + G$ (Biot, 1975, 1976b) is called the *mixed collective potential*, while δW^M denotes the work of forces other than gravity acting

directly on the primary system. The term

$$\delta W^{GTH} = - \int_A \left(\sum_k \varphi_k \delta M_i^k + \theta \delta S_i \right) n_i dA \quad (9.20)$$

now includes the work against the gravity field in the boundary thermobaric transfer. We have put

$$\varphi_k = \phi_k + \mathcal{G}, \quad (9.21)$$

where \mathcal{G} is the gravity potential field per unit mass chosen so that the supply cells are on the surface $\mathcal{G} = 0$. We have called φ_k the *mixed convective potential*.

With time derivatives instead of variations, Eq. (9.14) yields the total rate of dissipation as

$$T_0 \dot{S}^* = T_0 \int_{\Omega} \dot{s}^* d\Omega \quad (9.22)$$

It is interesting to compare $T_0 \dot{s}^*$ and $T \dot{s}^*$. For example, if $\partial \bar{s}_k / \partial x_i = \partial T / \partial x_i = 0$, writing Eq. (8.6) with time derivatives yields

$$T \dot{s}^* = \dot{h}^P, \quad (9.23)$$

where $\dot{h}^P \Delta t$ is the heat produced by the irreversibility in the time interval Δt . If we have a thermal well at a lower temperature T_0 , this heat is not entirely lost, because we may recover the mechanical work

$$\frac{T - T_0}{T} \dot{h}^P \Delta t \quad (9.24)$$

through a heat engine. The actual loss of useful energy is therefore

$$(T_0/T) \dot{h}^P \Delta t = T_0 \dot{s}^* \Delta t. \quad (9.25)$$

For this reason we have called $T \dot{s}^*$ the *intrinsic* dissipation, and $T_0 \dot{s}^*$ the *relative dissipation* (Biot, 1975, 1976b).

In the modified thermobaric transfer heat is pumped from the thermal well and injected into the various elements and cells of the hypersystem. The process involves only mechanical work (given by Eq. 9.1) and provides purely mechanical definitions of ψ_k as well as the exergy and δW^{TH} . The pump may use matter, subject to a Carnot cycle. However, it is of interest to point out (Biot, 1976a) that *use of the Carnot cycle may be avoided* by using pure heat as blackbody radiation extracted from the thermal well and compressed adiabatically to the required temperature of injection.

X. General Lagrangian Equations

Consider a system going through an irreversible evolution. We shall assume that its state may be described at every instant by a finite set of parameters q_i , unknown functions of time called generalized coordinates. In particular, this may be accomplished by the use of fluence fields as state variables either exactly or approximately. Such fluence fields, along with material displacements and reaction coordinates, are then considered to be given functions of the initial coordinates and generalized coordinates q_i to be determined. Arbitrary variations δq_i generate field variations that may be called *holonomic* and may satisfy identically the condition of field continuity. We may write

$$\delta \mathcal{P} = \sum_i \frac{\partial \mathcal{P}}{\partial q_i} \delta q_i, \quad (10.1)$$

$$T_0 \delta S^* = \sum_i R_i \delta q_i, \quad (10.2)$$

$$\delta W^M + \delta W^{TH} = \sum_i Q_i \delta q_i. \quad (10.3)$$

Substitution of these values into Eq. (9.19), which expresses the principle of virtual dissipation, considering that δq_i is arbitrary, yields

$$I_i + \delta \mathcal{P} / \partial q_i + R_i = Q_i, \quad (10.4)$$

where I_i are generalized inertia forces, R_i are generalized dissipative forces, and Q_i are driving forces of a mixed mechanical and thermodynamic nature due to environmental conditions (Biot, 1975, 1976b). These equations are the *general Lagrangian equations of evolution of irreversible thermodynamics*. For systems that are quasi-reversible such that local states do not deviate much from a local equilibrium satisfying Onsager's (1930, 1931) principle, the total virtual dissipation may be expressed in terms of a dissipation function. For example, when the entropy production is due to thermomolecular diffusion and chemical reactions near local equilibrium, Eqs. (8.25), (8.27), and (9.14) yield

$$T_0 \delta S^* = \int_{\Omega} \frac{T_0}{T} \left(\sum_{\rho} \frac{\partial \mathcal{D}}{\partial \dot{\xi}_{\rho}} \delta \dot{\xi}_{\rho} + \sum_k \frac{\partial \mathcal{D}}{\partial \dot{M}_i^k} \delta \dot{M}_i^k + \frac{\partial \mathcal{D}}{\partial S_i} \delta S_i \right) d\Omega. \quad (10.5)$$

If ξ_{ρ} , M_i^k , and S_i are expressed as functions of q_i , this may be written

$$T_0 \delta S^* = \sum_i \frac{\partial D}{\partial \dot{q}_i} \delta \dot{q}_i \quad (10.6)$$

where D is the total dissipation function

$$D = \int_{\Omega} \frac{T_0}{T} \mathfrak{D} \, d\Omega = \frac{1}{2} T_0 S^* \quad (10.7)$$

and \mathfrak{D} is given by Eq. (8.28). Expression (10.7) is a quadratic form in \dot{q}_i with coefficients depending on q_i . The Lagrangian equations (10.4) for quasi-reversible evolution become

$$I_i + \partial\mathcal{P}/\partial q_i + \partial D/\partial \dot{q}_i = Q_i. \quad (10.8)$$

This form of the Lagrangian equations was initially derived in the linear context (Biot, 1954, 1955, 1956a).

In many problems it is possible to express the generalized inertial forces in the classical form

$$I_i = \frac{d}{dt} \left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i} \right) - \frac{\partial \mathcal{T}}{\partial q_i}, \quad (10.9)$$

where \mathcal{T} denotes the kinetic energy expressed as a function of q_i and \dot{q}_i . In this case the variational principle may be written in the *Hamiltonian form*

$$\int_t \left[\delta(\mathcal{T} + \mathcal{P}) + \sum_i (R_i - Q_i) \delta q_i \right] dt = 0. \quad (10.10)$$

For a quasi-reversible evolution we may write Eq. (10.8) as

$$\partial D/\partial \dot{q}_i = X_i, \quad (10.11)$$

with $X_i = Q_i - I_i - \partial\mathcal{P}/\partial q_i$. This equation shows that in any given state, when we consider all possible generalized velocity fields \dot{q}_i satisfying the constraint

$$\sum_i X_i \dot{q}_i = \text{const.}, \quad (10.12)$$

the actual velocity of evolution minimizes the dissipation function D . In view of relation (10.7), the rate of total entropy production is also a minimum (Biot, 1955, 1976b). As a simple physical illustration, consider a fluid under gravity seeping through a porous medium. At a given instant, of all possible velocity fields with the same rate of descent of the center of mass, the actual one minimizes the dissipation.

XI. Dynamics of Viscous Fluid Mixtures with Reaction–Diffusion and Radiation Pressure

Field and Lagrangian equations of viscous fluid mixtures with chemical reactions, thermomolecular diffusion, and radiation pressure have been

derived directly from the principle of virtual dissipation (Biot, 1979, 1982a). The results provide new and powerful methods in a large variety of technological problems as well as in stellar dynamics, in particular in the analysis of stability and oscillations of self-gravitating bodies.

The coordinate system x_i is Cartesian and fixed. The fluid flow through it is described by a Cartesian mass flux \dot{M}_i^k of each substance in the mixture. In addition, we consider a Cartesian entropy flux \dot{S}_i . The fluid is in a gravity field. Because the mixture is homogeneous we may apply the concepts of Section XIII, where a cell of unit volume is created by therobaric transfer from an initial state of zero volume at constant temperature T and pressure p . The energy \mathcal{U} and entropy \mathcal{S} per unit volume are then obtained from Eqs. (4.9) and (4.10) by putting $v = 1$. Actually, to conform with our general procedure, we add suitable constants so that $\mathcal{U} = \mathcal{S} = 0$ at the initial time $t = 0$. The values m_k represent the masses of each substance per unit volume in the mixture. They may be written as

$$m_k = m_{0k} + \sum_{\rho} v_{k\rho} \xi_{\rho} + M^k, \tag{11.1}$$

where m_{0k} are the initial masses at $t = 0$. We also put $\xi_{\rho} = 0$ at $t = 0$ and assume the chemical reactions to be initiated at that instant, whereas M^k are the masses per unit volume added by convection for $t > 0$. As before, we may write the mass conservation equation (7.3) as

$$M^k = -\partial M_i^k / \partial x_i, \tag{11.2}$$

where M_i^k is the Cartesian mass fluence.

In the present case, the entropy production is due to three causes: the chemical reactions, the thermomolecular diffusion, and the viscosity. The first two have been evaluated and expressed by Eq. (8.25). In order to evaluate the entropy produced by the viscosity we consider the viscous stresses due to strain rates. The strain rate of a mixture is expressed in terms of the barycentric velocity v_i defined by

$$\rho v_i = \sum_k \dot{M}_i^k, \quad \rho = \sum_k m_k, \tag{11.3}$$

where ρ is the density of the mixture. The viscous stresses are then written

$$\sigma_{ij} = \eta_1 (v_{ij} + v_{ji}) + \eta_2 \delta_{ij} v_{ll}, \quad v_{ij} = \partial v_i / \partial x_j, \tag{11.4}$$

where η_1 and η_2 are viscosity coefficients depending on the local state of the mixture. These stresses may be written in the form

$$\sigma_{ij} = \partial \mathcal{D}^V / \partial v_{ij}, \tag{11.5}$$

where

$$\mathcal{D}^V = \frac{1}{2} \sigma_{ij} v_{ij}, \quad (11.6)$$

the viscous dissipation function, is a quadratic form in v_{ij} .

When varying the mass fluence δM_i^k , we produce a virtual displacement derived from Eq. (11.3) as

$$\delta u_i = \frac{1}{\rho} \sum_k \delta M_i^k \quad (11.7)$$

and a virtual work

$$\delta h^P = \sigma_{ij} \partial \delta u_i / \partial x_j. \quad (11.8)$$

The variation δh^P is the virtual heat produced and is analogous to the value in Eq. (8.2), namely, the heat to be added reversibly in order to obtain the same change of state as was due to the irreversible process. Hence the virtual entropy δs^{*V} produced by the viscous stresses is given by

$$T \delta s^{*V} = \delta h^P = \sigma_{ij} \partial \delta u_i / \partial x_j. \quad (11.9)$$

We shall assume that the mass and heat flux obey locally linear laws and Onsager's principle. In that case the virtual entropy production due to thermomolecular diffusion as derived from Eqs. (8.26) and (8.27) is given by

$$T \delta s^{*TM} = \sum_k \frac{\partial \mathcal{D}^{TM}}{\partial \dot{M}_i^k} \delta M_i^k + \frac{\partial \mathcal{D}^{TM}}{\partial \dot{S}_i} \delta S_i \quad (11.10)$$

with a dissipation function \mathcal{D}^{TM} to be specified below. For the dissipation due to the chemical reactions we retain the general form of Eq. (8.24).

The total virtual entropy production is then obtained by adding the values of Eqs. (8.24), (11.9), and (11.10). We write

$$T \delta s^* = \sum_\rho \mathcal{R}_\rho \delta \xi_\rho + \sigma_{ij} \frac{\partial}{\partial x_j} \delta u_i + \sum_k \frac{\partial \mathcal{D}^{TM}}{\partial \dot{M}_i^k} \delta M_i^k + \frac{\partial \mathcal{D}^{TM}}{\partial \dot{S}_i} \delta S_i. \quad (11.11)$$

For a domain Ω under gravity the mixed collective potential is

$$\mathcal{P} = \int_\Omega (\mathcal{V} + \rho \mathcal{G}) d\Omega \quad (11.12)$$

where \mathcal{G} is the gravity potential field and \mathcal{V} the exergy per unit volume. The fixed-coordinate system defines cells whose volume is not varied. Hence from Eqs. (3.22) and (9.6) with $\delta v = 0$, we obtain

$$\delta \mathcal{V} = \delta \mathcal{U} - T_0 \delta \mathcal{S} = - \sum_\rho A_\rho \delta \xi_\rho + \sum_k \phi_k \delta M^k + \theta \delta \mathcal{S} \quad (11.13)$$

Also $\delta\rho = \sum_k \delta M^k$, and we may write

$$\delta\mathcal{P} = \int_{\Omega} \left(-\sum_{\rho} A_{\rho} \delta\xi_{\rho} + \sum_k \varphi_k \delta M^k + \theta \delta\mathcal{S} \right) d\Omega, \quad (11.14)$$

where φ_k is the mixed convective potential (9.21).

The virtual work of the inertial forces is evaluated by assuming that all accelerations are the same and equal to the barycentric value

$$a_i = \partial v_i / \partial t + v_j \partial v_i / \partial x_j \quad (11.15)$$

as determined by v_i . This amounts to neglecting the inertial forces due to the relative velocities of diffusion. We write

$$\sum_i I_i \delta q_i = \int_{\Omega} a_i \sum_k \delta M_i^k d\Omega. \quad (11.16)$$

We now apply the principle of virtual dissipation (9.19), considering variations *inside* the domain Ω . In this case $\delta W^M = \delta W^{TH} = 0$. With the values (11.14) and (11.16) and the value (8.29) for $\delta\mathcal{S}$, the principle of virtual dissipation becomes

$$\int_{\Omega} \left(a_i \sum_k \delta M_i^k - \sum_{\rho} A_{\rho} \delta\xi_{\rho} + \sum_k \varphi_k \delta M^k - \theta \frac{\partial}{\partial x_i} \delta S_i + T \delta s^* \right) d\Omega = 0. \quad (11.17)$$

We then introduce the value (11.11) of $T \delta s^*$ and the value (11.2) for M^k . After integration by parts we equate to zero the coefficients of the arbitrary variations and obtain

$$a_i - \frac{1}{\rho} \frac{\partial \sigma_{ij}}{\partial x_j} + \frac{\partial \varphi_k}{\partial x_i} + \frac{\partial \mathcal{D}^{TM}}{\partial \dot{M}_i^k} = 0, \quad (11.18)$$

$$\partial T / \partial x_i + \partial \mathcal{D}^{TM} / \partial \dot{S}_i = 0, \quad (11.19)$$

$$-A_{\rho} + \mathcal{R}_{\rho} = 0. \quad (11.20)$$

These are the field dynamical equations of the viscous fluid mixture with reaction-diffusion. They bring out a *fundamental coupling between diffusion and the viscous stress gradient* $\partial \sigma_{ij} / \partial x_j$. They contain the unknowns ξ_{ρ} , M_i^k , and S_i . According to Eqs. (8.31) and (11.2), they determine the state of the system as a function of time, if we may neglect the contribution of the entropy produced s^* to the value \mathcal{S} of the entropy. However, if this is not the case, we may determine s^* by adding the auxiliary equation

$$T \dot{s}^* = \sum_{\rho} \mathcal{R}_{\rho} \dot{\xi}_{\rho} + 2\mathcal{D}^V + 2\mathcal{D}^{TM}, \quad (11.21)$$

which expresses the rate of dissipation and is obtained from Eq. (11.11) by replacing the variations by time derivatives.

Use of s^* and the auxiliary equation (11.21) may be avoided by using pseudofluence vectors such as \mathcal{F}_i^+ or \mathcal{F}_i^+ discussed in Section VIII as state variables. For example, in the present case, if we use \mathcal{F}_i^+ , Eq. (8.33) must be completed to take into account an additional heat source $\sigma_{ij} \partial \delta u_i / \partial x_j$ corresponding to the energy of viscous dissipation. Hence expressions (8.37) and (8.38) for $T \delta S$ and $T \dot{S}_i$ remain valid, provided we add terms $\sigma_{ij} \partial \delta u_i / \partial x_j$ and $\sigma_{ij} \partial v_i / \partial x_j$ in the volume integrals. We obtain

$$T \delta S_i = \delta \mathcal{F}_i^+ - \sum_k \phi_k \delta M_i^k + \int_{\Omega^+} g_i(x_l, x_l^+) \left(\sum_k f_j^k \delta M_j^k + \sigma_{ij} \frac{\partial \delta u_i}{\partial x_j} \right) d\Omega^+ \quad (11.22)$$

$$T \dot{S}_i = \dot{\mathcal{F}}_i^+ - \sum_k \phi_k \dot{M}_i^k + \int_{\Omega^+} g_i(x_l, x_l^+) \left(\sum_k f_j^k \dot{M}_j^k + \sigma_{ij} \frac{\partial v_i}{\partial x_j} \right) d\Omega^+. \quad (11.23)$$

With these values the field equations become integro-differential equations, except if the integral terms in Eqs. (11.22) and (11.23) are negligible, which is usually the case.

An *energy flux theorem* was derived (Biot, 1979, 1982a) from the field equations (11.18), (11.19), and (11.20). This may be shown by adding these equations after multiplying the first set by \dot{M}_i^k , the second set by \dot{S}_i , and the third by $\dot{\xi}_\rho$. We obtain

$$\frac{\partial F_i}{\partial x_i} + \frac{1}{2} \frac{\partial}{\partial t} (\rho v_i v_i) + \dot{q}_i + \dot{\rho} \mathcal{G} = 0, \quad (11.24)$$

where

$$F_i = \frac{1}{2} v_j v_j \sum \dot{M}_i^k - v_j \sigma_{ij} + \sum_k \dot{M}_i^k (\bar{\epsilon}_k + \mathcal{G}) + \dot{H}_i \quad (11.24a)$$

represents the total energy flux. Note that in this expression the quantity $\sum_k \dot{M}_i^k \bar{\epsilon}_k + \dot{H}_i$ is the diffusive energy flux (8.41).

We have not yet mentioned the important fact that the dissipation function \mathcal{D}^{TM} for thermomolecular diffusion must be invariant under translation. It was shown (Biot, 1982a) that this condition is satisfied if we put

$$\mathcal{D}^{\text{TM}} = \frac{1}{2} \sum_{ik} C^{ik} v_i^{ik} v_i^{ik} + \frac{1}{2} \sum_k C^k v_i^{kS} v_i^{kS}, \quad (11.25)$$

where

$$v_i^{ik} = \dot{M}_i^k / m_l - \dot{M}_i^k / m_k, \quad v_i^{kS} = \dot{M}_i^k / m_k - \dot{S}_i / \mathcal{F}^C, \quad (11.26)$$

and \mathcal{S}^C is equal to the value (4.17). The coefficients C^{lk} and C^k are functions of the local state, and the values of C^k are chosen such that the coefficient of \dot{S}_i^2 is $T/2k$ where k is the local thermal conductivity of the mixture. The dissipation function (11.25) satisfies the identity

$$\sum_k m_k \frac{\partial \mathcal{D}^{TM}}{\partial M_i^k} + \mathcal{S}^C \frac{\partial \mathcal{D}^{TM}}{\partial \dot{S}_i} = 0. \quad (11.27)$$

Using this relation, we may verify that the field equations (11.18) and (11.19) satisfy the total momentum balance (Biot, 1982a) by multiplying Eq. (11.18) by m_k and Eq. (11.19) by \mathcal{S}^C . Adding the results and taking into account the identity (11.27) and the modified Gibbs–Duhem theorem (4.16) for $v = 1$, we obtain

$$\rho a_i - \partial \sigma_{ij} / \partial x_j + \partial p / \partial x_i + \rho \partial \mathcal{G} / \partial x_i = 0. \quad (11.28)$$

This result expresses the total momentum balance.

As shown in a detailed discussion (Biot, 1982a), the effect of radiation pressure may be taken into account in the present analysis by including it in the total pressure p and the injection pressures p_k as generalized equations of state. It was pointed out that kinetic and radiation pressures may not be additive in dense mixtures because the radiation group velocity in dense matter is smaller than the velocity of light (Brillouin, 1930).

The foregoing results neglect the accelerations due to diffusion. Equations that avoid this simplification and introduce partial viscous stresses were also derived (Biot, 1979) in the absence of chemical reactions. The latter condition is required if relative accelerations due to diffusion are to retain any physical meaning, because chemical reactions imply a form of impact and coalescence between molecular flows that are not taken into account in the present theory.

Lagrangian equations of evolution are obtained directly from the principle of virtual dissipation. The state of the system may be described by ξ_ρ and the fluence fields M_i^k and \mathcal{F}_i^+ expressed in terms of generalized coordinates q_i as

$$\xi_\rho = \xi_\rho(q_1, q_2 \dots x_l), \quad (11.29)$$

$$M_i^k = M_i^k(q_i, q_2, \dots x_l), \quad (11.30)$$

$$\mathcal{F}_i^+ = \mathcal{F}_i^+(q_i, q_2, \dots x_l). \quad (11.31)$$

We derive the Lagrangian equations using the general procedure of Section X. Instead of \mathcal{F}_i^+ we may also use the fluence fields \mathcal{F}_i , S_i^+ , or S_i according to the particular approximations involved (see Section VII). The virtual work of the inertial forces is

$$\int_{\Omega} a_j \sum_k \delta M_j^k d\Omega = \sum I_i \delta q_i. \quad (11.32)$$

Hence the generalized inertial force is

$$I_i = \int_{\Omega} a_j \sum \frac{\partial M^k}{\partial q_i} d\Omega. \quad (11.33)$$

The virtual dissipation is

$$T_0 \delta S^* = \int_{\Omega} T_0 \delta s^* d\Omega = R_i \delta q_i, \quad (11.34)$$

where δs^* is given by Eq. (11.11). Hence

$$R_i = R_i^{\text{ch}} + R_i^{\text{V}} + R_i^{\text{TM}}. \quad (11.35)$$

The term

$$R_i^{\text{ch}} = \int_{\Omega} \frac{T_0}{T} \sum_{\rho} \mathcal{R}_{\rho} \frac{\partial \xi_{\rho}}{\partial q_i} d\Omega \quad (11.36)$$

is the chemical dissipative force. It can be shown that the viscous dissipative force is

$$R_i^{\text{V}} = \frac{\partial D^{\text{V}}}{\partial \dot{q}_i}, \quad D^{\text{V}} = \int_{\Omega} \frac{T_0}{T} \mathcal{D}^{\text{V}} d\Omega, \quad (11.37)$$

where \mathcal{D}^{V} has the value in Eq. (11.6). The dissipation function D^{V} is a quadratic form in \dot{q}_i . The value of $\mathcal{R}_i^{\text{TM}}$ is the dissipative force due to thermomolecular diffusion. It is obtained by writing the variational relation

$$\sum_i R_i^{\text{TM}} \delta q_i = \int_{\Omega} \frac{T_0}{T} \left(\sum_k \frac{\partial \mathcal{D}^{\text{TM}}}{\partial M_i^k} \delta M_i^k + \frac{\partial \mathcal{D}^{\text{TM}}}{\partial S_i} \delta S_i \right) d\Omega \quad (11.38)$$

replacing δS_i and \dot{S}_i by the values obtained from Eqs. (8.37) and (8.38). This provides the exact value of R_i^{TM} as a nonlinear function of \dot{q}_i . However in most problems we may neglect the integral in the values (8.37) and (8.38). In this case we may write

$$R_i^{\text{TM}} = \frac{\partial D^{\text{TM}}}{\partial \dot{q}_i}, \quad D^{\text{TM}} = \int_{\Omega} \frac{T_0}{T} \mathcal{D}^{\text{TM}} d\Omega \quad (11.38a)$$

where D^{TM} is a quadratic form in \dot{q}_i representing the total dissipation of thermomolecular diffusion.

Determination of the generalized driving force Q_i is obtained from Eq. (10.3), written in the form

$$\sum_i Q_i \delta q_i = \delta W^M - \int_A \left(\sum_k \varphi_k \delta M_i^k + \theta \delta S_i \right) n_i dA, \quad (11.39)$$

where A is the boundary of Ω . On the right is the virtual work of all the mechanical forces. The integral represents the work due to thermobaric transfer at the boundary considered as fixed, whereas δW^M represents the virtual work of all other forces. Special care must be exercised here by noting that in the absence of viscous stresses $\delta W^M = 0$. In this case the virtual work due to boundary displacement δu_i against the local equilibrium pressure p is already included in $\varphi_k \delta M_i^k$ of the surface integral. Hence the remaining work δW^M is due only to the viscous stresses and is written

$$\delta W^M = \int_A \sigma_{ji} n_i \delta u_j dA. \quad (11.40)$$

This is also verified using a lengthier procedure (Biot, 1979, 1982a).

We substitute this value into Eq. (11.39) and use the values in Eqs. (11.22) and (11.23) for δS_i and \dot{S}_i . Again we may generally neglect the volume integrals in these expressions. Coefficients of δq_i yield Q_i .

With these results the Lagrangian equations are written

$$I_i + R_i^{\text{ch}} + \partial D / \partial \dot{q}_i + \partial \mathcal{P} / \partial q_i = Q_i, \quad (11.41)$$

where $D = D^V + D^{\text{TM}}$ is the dissipation function due to viscous and thermomolecular dissipation. For a quasi-reversible evolution including chemical reactions we may neglect s^* in describing the system and use the entropy fluence S_i as a state variable instead of \mathcal{F}_i^+ . In that case the dissipation is expressed by a single dissipation function and the Lagrangian equations assume the simpler form [Eq. (10.8)].

It was also shown (Biot, 1979, 1982a) that the inertial force may be expressed in terms of the kinetic energy

$$\mathcal{T} = \frac{1}{2} \int_{\Omega} \rho v_i v_i d\Omega \quad (11.42)$$

as

$$I_i = \frac{d}{dk} \left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i} \right) - \frac{\partial \mathcal{T}}{\partial q_i} + \mathcal{M}_i + \frac{1}{2} \int_A v_l v_l \frac{\partial M_j}{\partial q_i} n_j dA, \quad (11.43)$$

where

$$\mathcal{M}_i = \int_{\Omega} \mathcal{A}_j \frac{\partial M_j}{\partial q_i} d\Omega, \quad \mathcal{M}_i = \sum_k M_i^k, \quad (11.44)$$

and

$$\mathcal{A}_i = \int \dot{v}_j \omega_{ij}, \quad \omega_{ij} = \frac{1}{2} (v_{ij} - v_{ji}). \quad (11.45)$$

It is interesting to note that

$$\mathcal{A}_i v_i = 0, \quad \sum_i M_i \dot{q}_i = 0. \quad (11.46)$$

Hence M_i represents a generalized inertial force normal to the velocity, corresponding to a *Magnus effect*.

XII. Dynamics of Solids with Elastoviscous Stresses and Heat Conduction, and Thermoelasticity

The dynamics of a deformable solid will now be considered in the particular case where rate-dependent viscous stresses are present in addition to elastic stresses, with simultaneous heat conduction across the deforming medium. The problem was treated in detail earlier (Biot, 1976b, 1981) and we shall present here a short and simplified version of the results.

The field is described by mass point displacements u_i such that

$$\bar{x}_i = x_i + u_i(x_j, t), \quad (12.1)$$

where a solid mass point with initial coordinate x_i is displaced to a point with coordinate \bar{x}_i . We have seen (Section V) that the local deformation may be defined as an affine transformation relative to rotating axes by six components ε_{ij} , which are assumed to be known functions of the displacement gradients $\partial u_i / \partial x_j$. The corresponding stress components τ_{ij} are then derived from the principle of virtual work. In the absence of molecular diffusion and chemical reactions, the energy \mathcal{U} and entropy \mathcal{S} of the solid per unit initial volume are obtained from Eqs. (6.2) and (6.3) as

$$d\mathcal{U} = (\tau_{ij}^E + h_T^{\dot{ij}}) d\varepsilon_{ij} + C_\varepsilon dT, \quad (12.2)$$

$$d\mathcal{S} = (1/T)(h_T^{\dot{ij}} d\varepsilon_{ij} + C_\varepsilon dT), \quad (12.3)$$

where τ_{ij}^E is the elastic part of the stress for reversible deformations and C_ε is the heat capacity of the solid per unit initial volume with constant strain. The value of $h_T^{\dot{ij}}$ is given by Eq. (6.7) without calorimetric measurements as

$$h_T^{\dot{ij}} = -T(\partial \tau_{ij}^E / \partial T)_\varepsilon, \quad (12.4)$$

where

$$\tau_{ij}^E = \tau_{ij}^E(\varepsilon_{\mu\nu}, T, x_i) \quad (12.5)$$

represents the local equations of state of the solid with the elastic stresses expressed in terms of strain and temperature. The subscript ε in Eq. (12.4) indicates constant strain. Since the solid may be intrinsically nonhomogeneous, τ_{ij}^E may depend also on the initial coordinates x_i .

Integration of Eqs. (12.2) and (12.3) yields \mathcal{U} , \mathcal{S} , and $\mathcal{V} = \mathcal{U} - T_0\mathcal{S}$ as functions of ε_{ij} , T and x_i .

The entropy production arises from the viscous stresses and the thermal conduction. This provides another example of two distinct types of entropy production, the first being due to an irreversible production of heat while the second is not.

In order to apply the principle of virtual dissipation we must evaluate the virtual entropy production. We therefore replace the differentials by variations in Eqs. (12.2) and (12.3). They yield

$$\delta\mathcal{U} = \tau_{ij}^E \delta\varepsilon_{ij} + T \delta\mathcal{S}. \quad (12.6)$$

For an irreversible transformation, conservation of energy is expressed by

$$\delta\mathcal{U} = (\tau_{ij}^E + \tau_{ij}^V) \delta\varepsilon_{ij} - \partial \delta H_i / \partial x_i, \quad (12.7)$$

where τ_{ij}^V is the additional viscous stress and δH_i is the variation of contravariant heat fluence.

We recall that \dot{H}_i is the heat flux across a deforming material area initially normal to x_i and equal to unity, whereas H_i is its time integral. Equating (12.6) and (12.7) yields

$$\delta\mathcal{S} = \delta S^* - \partial \delta S_i / \partial x_i, \quad (12.8)$$

where

$$T \delta S^* = \tau_{ij}^V \delta\varepsilon_{ij} - \partial T / \partial x_i \delta S_i, \quad \delta S_i = \delta H_i / T. \quad (12.9)$$

We recognize the term $(-\partial T / \partial x_i) \delta S_i$ already derived in (8.6) for thermal diffusion. The first term may be interpreted as due to heat production (Biot, 1981, 1982b) by considering an adiabatic transformation where conservation of energy requires

$$\delta\mathcal{U} = (\tau_{ij}^E + \tau_{ij}^V) \delta\varepsilon_{ij}. \quad (12.10)$$

Obviously this is equivalent to a reversible transformation where an amount of heat $\delta h^P = \tau_{ij}^V \delta\varepsilon_{ij}$ is added in order to reproduce the same change of state as in the irreversible process. The heat corresponds to the concept of uncompensated heat of Clausius and illustrates the physical

difference between the two types of entropy production in Eq. (12.9). The same distinction was discussed above in Section VIII.

As in the case of thermomolecular diffusion (see Section VIII) we now introduce the kinetics of irreversibility. We write

$$\tau_{ij}^{\vee} = \tau_{ij}^{\vee}(\varepsilon_{\mu\nu}, \dot{\varepsilon}_{\mu\nu}, T, x_l), \quad (12.11)$$

$$-\partial T/\partial x_i = \Lambda_{ij} \dot{H}_j, \quad (12.12)$$

where

$$\Lambda_{ij} = \Lambda_{ij}(\varepsilon_{\mu\nu}, T, x_l) \quad (12.13)$$

is the thermal resistivity of the deformable solid expressed in terms of the contravariant heat flux \dot{H}_j . It is a function of the local state variable $\varepsilon_{\mu\nu}$ and T . If the material is nonhomogeneous, it is also a function of the initial coordinates x_i . The viscous stress τ_{ij}^{\vee} , as a function of the rate of deformation $\dot{\varepsilon}_{ij}$, embodies the kinematics of the mechanical irreversibility. Note that τ_{ij}^{\vee} and

$$-1/T \partial T/\partial x_i = \Lambda_{ij} \dot{S}_j, \quad (12.14)$$

with $\dot{S}_i = \dot{H}_i/T$, play the same role as the dissipative disequilibrium forces \mathcal{R}_ρ , \mathcal{R}_i^{Sk} , and \mathcal{R}_i^{ST} in Eq. (8.25) for the case of thermomolecular diffusion with chemical reactions. This can be seen by writing the virtual dissipation (12.9) in terms of rate variables in the form

$$T \delta s^* = \tau_{ij}^{\vee} \delta \varepsilon_{ij} + T \Lambda_{ij} \dot{S}_i \delta S_j, \quad (12.15)$$

where τ_{ij}^{\vee} is the rate function (12.11). Comparing with Eq. (8.25), we see that the viscous stress τ_{ij}^{\vee} may be considered as the *tensor equivalent of the affinity* \mathcal{R}_ρ .

Field equations may be obtained readily for the dynamics of the deformable solid by applying the principle of virtual dissipation (9.19). We vary the displacement u_i and the entropy fluence S_i . The virtual work of the inertial forces is

$$\sum_i I_i \delta q_i = \int_{\Omega} \rho \ddot{u}_j \delta u_j d\Omega, \quad (12.16)$$

where the volume integral is for the initial domain Ω of the space x_i and ρ is the initial density. The variation of \mathcal{P} is

$$\delta \mathcal{P} = \int_{\Omega} \left\{ \delta \mathcal{V} + \rho \partial \mathcal{G}(\bar{x}_i)/\partial \bar{x}_i \delta u_i \right\} d\Omega, \quad (12.17)$$

where $\mathcal{G}(\bar{x}_i)$ is the gravity potential field per unit mass at the point $\bar{x}_i = x_i + u_i$. The exergy variation per unit initial volume is

$$\delta\mathcal{V} = \delta\mathcal{Q} - T_0 \delta\mathcal{S} = \tau_{ij}^E \delta\varepsilon_{ij} + \theta \delta\mathcal{S} \quad (12.18)$$

($\theta = T - T_0$). The variations are applied only inside the domain Ω , and with the values (12.16), (12.17), and (12.18), the variational principle (9.19) is written

$$\int_{\Omega} (\rho \ddot{u}_i \delta u_i + \tau_{ij}^E \delta\varepsilon_{ij} + \theta \delta\mathcal{S} + \rho \partial^c \mathcal{G} / \partial \bar{x}_i \delta u_i + T_0 \delta s^*) d\Omega = 0. \quad (12.19)$$

Equation (8.29) is quite general, and with the value (12.15) it yields

$$\delta\mathcal{S} = -\partial \delta S_i / \partial x_i + \delta s^*. \quad (12.20)$$

Hence Eq. (12.19) becomes

$$\int_{\Omega} \left(\rho \ddot{u}_i \delta u_i + \tau_{ij} \delta\varepsilon_{ij} - \theta \frac{\partial}{\partial x_i} \delta S_i + \rho \frac{\partial^c \mathcal{G}}{\partial \bar{x}_i} \delta u_i + T \delta s^* \right) d\Omega = 0. \quad (12.21)$$

We replace $T \delta s^*$ by its value (12.15) and write

$$\delta\varepsilon_{\mu\nu} = \partial\varepsilon_{\mu\nu} / \partial a_{ij} \delta a_{ij}, \quad \delta a_{ij} = \partial\delta u_i / \partial x_j. \quad (12.22)$$

After integration by parts, we equate to zero the coefficients of the arbitrary variations δu_i , δS_i and obtain

$$\rho \ddot{u}_i - \frac{\partial}{\partial x_j} \left[(\tau_{\mu\nu}^E + \tau_{\mu\nu}^V) \frac{\partial\varepsilon_{\mu\nu}}{\partial a_{ij}} \right] + \rho \frac{\partial^c \mathcal{G}}{\partial \bar{x}_i} = 0, \quad (12.23)$$

$$\frac{\partial T}{\partial x_i} + T \Lambda_{ij} \dot{S}_j = 0. \quad (12.24)$$

These are the field equations for the deformable solid with elastic and nonlinear viscous stresses and with thermal conduction.

In solving the problem we may consider u_i and S_i as unknowns that determine the state through Eq. (8.30) if we also determine the entropy produced s^* . This may be done by adding to the field equations the auxiliary equation

$$T \dot{s}^* = \tau_{ij}^V \dot{\varepsilon}_{ij} + T \Lambda_{ij} \dot{S}_i \dot{S}_j \quad (12.25)$$

derived from Eq. (12.15). It extends Meixner's (1941) result to deformable solids with viscosity. Another procedure in analogy with the use of Eq. (8.36) for thermomolecular diffusion is to introduce a pseudoenergy fluence \mathcal{F}_i^+ defined by Eq. (7.15). The energy balance equation (12.7) is then written

$$-\partial \delta \mathcal{F}_i^+ / \partial x_i = (\tau_{ij}^E + \tau_{ij}^V) \delta\varepsilon_{ij} - \partial \delta H_i / \partial x_i. \quad (12.26)$$

Hence

$$\delta H_i = T \delta S_i = \delta \mathcal{F}_i^+ + \int_{\Omega^+} g(x_l, x_l^+) (\tau_{ij}^E + \tau_{ij}^V) \delta \varepsilon_{ij} d\Omega^+. \quad (12.27)$$

This becomes

$$T \dot{S}_i = \dot{\mathcal{F}}_i^+ + \int_{\Omega^+} g(x_l, x_l^+) (\tau_{ij}^E + \tau_{ij}^V) \dot{\varepsilon}_{ij} d\Omega^+. \quad (12.28)$$

With this value of \dot{S}_i Eqs. (12.23) and (12.24) become integro-differential equations in u_i and \mathcal{F}_i^+ , which are now state variables. A similar procedure has also been discussed in an earlier paper (Biot, 1981).

If the irreversible process is quasi-reversible, we may neglect the contribution of s^* to the value of \mathcal{S} and use S_i as a state variable. In that case Onsager's (1930, 1931) reciprocity relations are valid, and we may write

$$\tau_{ij}^V = \partial \mathcal{D}^V / \partial \dot{\varepsilon}_{ij}, \quad \partial T / \partial x_i = -\partial \mathcal{D}^T / \partial \dot{S}_i, \quad (12.29)$$

where \mathcal{D}^V is a quadratic form in $\dot{\varepsilon}_{ij}$ with coefficients that are functions of the local state variables ε_{ij} and T , and

$$\mathcal{D}^T = \frac{1}{2} T \Lambda_{ij} \dot{S}_i \dot{S}_j, \quad \text{for } \Lambda_{ij} = \Lambda_{ji}, \quad (12.30)$$

is a purely thermal dissipation function. The virtual dissipation (12.15) now becomes

$$T \delta s^* = \partial \mathcal{D}^V / \partial \dot{\varepsilon}_{ij} \delta \varepsilon_{ij} + \partial \mathcal{D}^T / \partial \dot{S}_i \delta S_i \quad (12.31)$$

and leads to the field equations

$$\rho \ddot{u}_i - \frac{\partial}{\partial x_j} \left(\tau_{\mu\nu}^E \frac{\partial \varepsilon_{\mu\nu}}{\partial a_{ij}} \right) - \frac{\partial}{\partial x_j} \left(\frac{\partial \mathcal{D}^V}{\partial \dot{\varepsilon}_{\mu\nu}} \frac{\partial \varepsilon_{\mu\nu}}{\partial a_{ij}} \right) + \rho \frac{\partial \mathcal{G}}{\partial \bar{x}_i} = 0, \quad (12.32)$$

$$\frac{\partial T}{\partial x_i} + \frac{\partial \mathcal{D}^T}{\partial \dot{S}_i} = 0. \quad (12.33)$$

The contravariant thermal resistivity Λ_{ij} may be expressed in terms of the local Cartesian thermal conductivity k_{ij} as follows. With the Cartesian resistivity

$$[\lambda_{ij}] = [k_{ij}]^{-1}, \quad (12.34)$$

we write the heat conduction law in the form

$$-\partial T / \partial \bar{x}_i = \lambda_{ij} \dot{H}'_j, \quad (12.35)$$

where \dot{H}'_j is the Cartesian heat flux in the \bar{x}_j coordinates. By using Eqs. (7.12) we introduce the contravariant heat flux and obtain

$$-\partial T / \partial \bar{x}_i = J' \lambda_{ij} \dot{H}_\mu \partial \bar{x}_j / \partial x_\mu. \quad (12.36)$$

Multiplying both sides by $\partial\bar{x}_i/\partial x_\nu$ this yields

$$-\frac{\partial T}{\partial x_\nu} = J' \lambda_{ij} \frac{\partial\bar{x}_j}{\partial x_\mu} \frac{\partial\bar{x}_i}{\partial x_\nu} \dot{H}_\mu. \quad (12.37)$$

Comparing with Eq. (12.12), we see that

$$\Lambda_{\mu\nu} = J' \lambda_{ij} \frac{\partial\bar{x}_j}{\partial x_\mu} \frac{\partial\bar{x}_i}{\partial x_\nu}, \quad (12.38)$$

showing the covariant nature of Λ_{ij} . Note that $\Lambda_{\mu\nu}$ is a function only of the strain ε_{ij} , T , and x_i , and hence represents an intrinsic physical property, whereas λ_{ij} is referred to the fixed axes x_i and depends also on the rotation of the material.

Lagrangian equations are immediately obtained from the principle of virtual dissipation. For simplicity, we shall assume that the entropy produced s^* does not contribute significantly to the state variables, so that the system may be described in terms of generalized coordinates q_i by the displacement field u_i and the contravariant entropy fluence S_i . We write

$$u_j = u_j(q_1, q_2, \dots, x_l), \quad (12.39)$$

$$S_j = S_j(q_1, q_2, \dots, x_l). \quad (12.40)$$

We apply arbitrary variations δq_i . The variation of the mixed collective potential is obtained from its value $\mathcal{P}(q_i)$ expressed as a function of q_i .

By a classical procedure the virtual work of the inertia forces yields

$$\sum_i I_i \delta q_i = \left[\frac{d}{dt} \left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i} \right) - \frac{\partial \mathcal{T}}{\partial q_i} \right] \delta q_i, \quad (12.41)$$

where

$$\mathcal{T} = \frac{1}{2} \int_\Omega \rho u_i \dot{u}_i d\Omega \quad (12.42)$$

is the kinetic energy, and Ω the initial domain.

We shall assume that the thermal conduction satisfies the reciprocity relations $\Lambda_{ij} = \Lambda_{ji}$ while the viscous stress remains a general nonlinear function $\tau_{ij}^V(\varepsilon_{\mu\nu}, \dot{\varepsilon}_{\mu\nu}, T)$. In this case, according to Eqs. (12.15) and (12.29), the virtual dissipation is

$$T \delta s^* = \tau_{ij}^V \delta \varepsilon_{ij} + (\partial \mathcal{D}^T / \partial \dot{S}_i) \delta S_i. \quad (12.43)$$

For the whole system we write

$$T_0 \delta S^* = \int_\Omega T_0 \delta s^* d\Omega = \sum_i \left(R_i^V \delta q_i + \frac{\partial D^T}{\partial \dot{q}_i} \delta q_i \right), \quad (12.44)$$

where

$$R_i^Y = \int \frac{T_0}{T} \tau_{\mu\nu}^Y \frac{\partial \varepsilon_{\mu\nu}}{\partial q_i} d\Omega. \quad (12.45)$$

The total thermal dissipation function D^T is a quadratic form in \dot{q}_i with coefficients being functions of q_i . It is obtained by writing

$$\int_{\Omega} \frac{T_0}{T} \frac{\partial \mathcal{D}^T}{\partial \dot{S}_j} \delta S_j d\Omega = \sum_i \int_{\Omega} \frac{T_0}{T} \frac{\partial \mathcal{D}^T}{\partial \dot{S}_j} \frac{\partial S_j}{\partial q_i} \delta q_i d\Omega. \quad (12.46)$$

By noting that $\partial S_j / \partial q_i = \partial \dot{S}_j / \partial \dot{q}_i$, we derive

$$\int_{\Omega} \frac{T_0}{T} \frac{\partial \mathcal{D}^T}{\partial \dot{S}_j} \delta S_j d\Omega = \sum_i \frac{\partial D^T}{\partial \dot{q}_i} \delta q_i, \quad (12.47)$$

where

$$D^T = \int_{\Omega} \frac{T_0}{T} \mathcal{D}^T d\Omega. \quad (12.48)$$

Finally we express the virtual work of the mechanical and thermodynamic forces applied at the boundary A . This is

$$\delta W^M + \delta W^{TH} = \sum_i Q_i \delta q_i = \int_A (f_j \delta u_j - \theta \delta S_j n_j) dA. \quad (12.49)$$

The integral is extended to the boundary A in the initial space x_i , while f_j is the boundary force per unit initial area at the deformed boundary. Values of θ and δS_j are also at the deformed boundary. The generalized mechanical and thermodynamic forces at the boundary are therefore

$$Q_i = \int_A \left(f_j \frac{\partial u_j}{\partial q_i} - \theta \frac{\partial S_j}{\partial q_i} n_j \right) dA. \quad (12.50)$$

With $\delta \mathcal{P}(q_i)$ and the values (12.41), (12.44), and (12.50), the principle of virtual dissipation (9.19) leads to the Lagrangian equations

$$\frac{d}{dt} \left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i} \right) - \frac{\partial \mathcal{T}}{\partial q_i} + R_i^Y + \frac{\partial D^T}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i. \quad (12.51)$$

The term R_i^Y is the generalized dissipative force due to the viscous stresses; it embodies the most general case where these stresses are non-linear functions of the strain ε_{ij} and the strain rate $\dot{\varepsilon}_{ij}$. If these stresses are linear functions of the strain rate and satisfy the Onsager reciprocity relations

$$\partial \tau_{\mu\nu} / \partial \dot{\varepsilon}_{ij} = \partial \tau_{ij} / \partial \dot{\varepsilon}_{\mu\nu}, \quad (12.52)$$

they may be expressed in terms of a dissipation function \mathcal{D}^V that is a quadratic form in $\dot{\varepsilon}_{ij}$. This leads to the Lagrangian equations

$$\frac{d}{dt} \left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i} \right) - \frac{\partial \mathcal{T}}{\partial q_i} + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i \tag{12.53}$$

with a total dissipation function

$$D = \int_{\Omega} \frac{T_0}{T} (\mathcal{D}^V + \mathcal{D}^T) d\Omega, \tag{12.54}$$

which represents the combined viscous and thermal dissipation.

We have simplified the Lagrangian formulation by neglecting s^* as a state variable. The accuracy may be improved in several ways. One way is to evaluate s^* as a function of time from the first approximation and introduce it in the value (8.31) of \mathcal{S} , which is now written

$$\mathcal{S} = - \partial(S_i + \Delta S_i) / \partial x_i + s^*, \tag{12.55}$$

whereas the displacement is $u_i + \Delta u_i$. The new unknowns are the corrections ΔS_i and Δu_i to the first approximations S_i and u_i . The corrections are expressed in terms of generalized coordinates as Eqs. (12.39) and (12.40), and the corresponding Lagrangian equations contain the time explicitly.

Another procedure is to use the pseudo energy fluence \mathcal{F}_i^+ and Eqs. (12.27) and (12.28) for δS_i and \dot{S}_i . The procedure is analogous to the one explained in Section VIII and discussed more extensively elsewhere (Biot, 1981).

If there are no viscous stresses the solid is *thermoelastic*. The field equations are obtained from Eqs. (12.23) and (12.24) by putting $\tau_{ij}^V = 0$. The Lagrangian equations are obtained from Eq. (12.51) by putting $R_i^V = 0$. In this case the exergy vV becomes the *thermoelastic potential* (Biot, 1973a).

XIII. Inhomogeneous Viscous Fluid with Convected Coordinates and Heat Conduction

The general case of a deforming solid, analyzed in the previous section, has a number of interesting applications that are better discussed separately. In particular, we shall consider the case of a compressible viscous fluid, Newtonian or non-Newtonian, with thermal conduction. For the homogeneous fluid, this may also be treated from an Eulerian viewpoint as in Section XI for the more general case of a mixture. The purpose here

is to develop equations using convected coordinates $\bar{x}_i = x_i + u_i$ for a fluid, which may be inhomogeneous. The energy \mathcal{U} and entropy \mathcal{S} per unit initial volume are functions

$$\mathcal{U} = \mathcal{U}(J, T, x_i), \quad \mathcal{S} = \mathcal{S}(J, T, x_i) \quad (13.1)$$

of the temperature T and the Jacobian J (7.11), which represents the ratio of final to initial volume of each fluid element. If the fluid is nonhomogeneous, \mathcal{U} and \mathcal{S} are also functions of the initial coordinates x_i .

The thermal dissipation function per unit initial volume is derived from Eq. (12.30) as follows. The thermal conductivity

$$k = k(J, T, x_i) \quad (13.2)$$

remains isotropic and is a function of J , T , and x_i . The Cartesian thermal resistivity is

$$\lambda_{ij} = \delta_{ij}/k. \quad (13.3)$$

By substituting this value in the covariant thermal resistivity (12.38) we obtain

$$\Lambda_{ij} = \frac{1}{Jk} \frac{\partial \bar{x}_\mu}{\partial x_i} \frac{\partial \bar{x}_\mu}{\partial x_j}. \quad (13.4)$$

The thermal dissipation function per unit initial volume (12.30) is therefore

$$\mathcal{D}^T = \frac{1}{2} \frac{T}{Jk} \frac{\partial \bar{x}_\mu}{\partial x_i} \frac{\partial \bar{x}_\mu}{\partial x_j} \dot{S}_i \dot{S}_j \quad (13.5)$$

in terms of the contravariant entropy flux \dot{S}_i .

In order to derive the dissipation due to the fluid viscosity for a Newtonian fluid we consider the stress components σ_{ij} in terms of the velocity gradients in the \bar{x}_i space. They are

$$\sigma_{ij} = \eta_1 \left(\frac{\partial v_i}{\partial \bar{x}_j} + \frac{\partial v_j}{\partial \bar{x}_i} \right) + \eta_2 \delta_{ij} \frac{\partial v_l}{\partial \bar{x}_l} \quad (13.6)$$

where

$$\eta_1 = \eta_1(J, T, x_i), \quad \eta_2 = \eta_2(J, T, x_i)$$

are viscosity coefficients, functions of the local state variables J , T and the initial coordinates x_i . If there is no bulk viscosity we put

$$\frac{2}{3} \eta_1 + \eta_2 = 0. \quad (13.7)$$

The virtual dissipation due to the viscosity per unit initial volume is

$$T \delta s^{*V} = J \sigma_{i\mu} \partial \delta u_i / \partial \bar{x}_\mu = J \sigma_{i\mu} \partial x_j / \partial \bar{x}_\mu \delta a_{ij} \quad (13.8)$$

where

$$\delta a_{ij} = \partial \delta u_i / \partial x_j. \quad (13.9)$$

We may express the derivative $\partial x_i / \partial \bar{x}_j$ in terms of $\partial \bar{x}_i / \partial x_j$ by writing the affine transformation from dx_j into $d\bar{x}_i$ and solving the linear equations for dx_i . The result is similar to Eq. (7.8). We obtain

$$\partial x_i / \partial \bar{x}_j = C_{ij} / J, \quad (13.10)$$

where C_{ij} is the cofactor of $\partial \bar{x}_i / \partial x_j$ in the Jacobian J . Hence the virtual dissipation (13.8) becomes

$$T \delta s^{*V} = C_{\mu j} \sigma_{i\mu} \delta a_{ij} = T_{ij}^V \delta a_{ij}. \quad (13.11)$$

The physical significance of this expression is brought out by comparison with the virtual work (5.12). Obviously,

$$T_{ij}^V = C_{\mu j} \sigma_{i\mu} \quad (13.12)$$

is the Piola viscous stress, i.e., the Cartesian components of the viscous forces acting on areas initially equal to unity and normal to x_j .

Similarly, we may express the velocity gradients in Eq. (13.6) in terms of partial derivatives with respect to x_i . We note that $\dot{u}_i = v_i$ and write

$$\frac{\partial v_i}{\partial \bar{x}_j} = \frac{\partial \dot{u}_i}{\partial x_\nu} \frac{\partial x_\nu}{\partial \bar{x}_j} = \frac{C_{j\nu}}{J} \dot{a}_{i\nu}, \quad (13.13)$$

where

$$\dot{a}_{ij} = \partial \dot{u}_i / \partial x_j. \quad (13.14)$$

We substitute the value (13.13) into expression (13.6) and change j into μ , thus obtaining

$$\sigma_{i\mu} = (\eta_1/J)(C_{\mu\nu} \dot{a}_{i\nu} + C_{i\nu} \dot{a}_{\mu\nu}) + (\eta_2/J) \delta_{i\mu} C_{l\nu} \dot{a}_{l\nu}. \quad (13.15)$$

With this value, the Piola stress (13.12) becomes

$$T_{ij}^V = (\eta_1/J)(C_{\mu\nu} C_{\mu j} \dot{a}_{i\nu} + C_{\mu j} C_{i\nu} \dot{a}_{\mu\nu}) + (\eta_2/J) \delta_{i\mu} C_{\mu j} C_{l\nu} \dot{a}_{l\nu}. \quad (13.16)$$

This may be written as

$$T_{ij}^V = (\eta_1/J)(C_{l\nu} C_{lj} \delta_{i\mu} + C_{\mu j} C_{i\nu}) \dot{a}_{\mu\nu} + (\eta_2/J) C_{ij} C_{\mu\nu} \dot{a}_{\mu\nu}. \quad (13.17)$$

By putting

$$B_{ij}^{\mu\nu} = (\eta_1/J)(C_{l\nu} C_{lj} \delta_{i\mu} + C_{\mu j} C_{i\nu}) + (\eta_2/J) C_{ij} C_{\mu\nu}, \quad (13.18)$$

the stress (13.17) becomes

$$T_{ij}^V = B_{ij}^{\mu\nu} \dot{a}_{\mu\nu}, \quad \text{for } B_{ij}^{\mu\nu} = B_{\mu\nu}^{ij}. \quad (13.19)$$

Hence, Onsagers reciprocity relations $B_{ij}^{\mu\nu} = B_{\mu\nu}^{ij}$ are verified for T_{ij}^V . This is as should be because it is an invariant property, already verified by the Newtonian stresses (13.6) (Biot, 1976b).

The rate of dissipation per unit initial volume is obtained from Eq. (13.11) by replacing the variations by time derivatives. We obtain

$$T\dot{s}^{*V} = T_{ij}^V \dot{a}_{ij} = 2\mathcal{D}^V = B_{ij}^{\mu\nu} \dot{a}_{\mu\nu} \dot{a}_{ij}, \quad (13.20)$$

where \mathcal{D}^V is a quadratic form in \dot{a}_{ij} . Because of the reciprocity property (13.19), we may write

$$T_{ij}^V = \partial\mathcal{D}^V/\partial\dot{a}_{ij}. \quad (13.21)$$

The exergy per unit initial volume is

$$\mathcal{V} = \mathcal{V}(J, T, x_i); \quad (13.22)$$

it is a function of the Jacobian J , the temperature T , and the initial coordinates x_i . Considering \mathcal{V} as a function of J and \mathcal{S} , its variation is

$$\delta\mathcal{V} = \partial\mathcal{V}/\partial J \delta J + \theta \delta\mathcal{S}. \quad (13.23)$$

Obviously, the local equilibrium pressure is

$$P = \partial\mathcal{V}/\partial J \quad (13.24)$$

for a reversible slow deformation. This result corresponds to equation (12.6). We may also write

$$\delta\mathcal{V} = T_{ij}^E \delta a_{ij} + \theta \delta S, \quad (13.25)$$

where

$$T_{ij}^E = P \partial J/\partial a_{ij} \quad (13.26)$$

is the Piola stress for the elastic pressure P .

By applying the principle of virtual dissipation with arbitrary variations δu_i inside a domain Ω and proceeding as in the preceding section for the solid, we obtain the field equations

$$\rho \ddot{u}_i - \frac{\partial}{\partial x_j} (T_{ij}^E + T_{ij}^V) + \rho \frac{\partial \mathcal{G}}{\partial x_i} = 0, \quad (13.27)$$

$$\partial T/\partial x_i + \partial\mathcal{D}^T/\partial \dot{S}_i = 0, \quad (13.28)$$

where \mathcal{G} is the gravity potential, \mathcal{D}^T is given by Eq. (13.5), and ρ is the initial density. An auxiliary equation for \dot{s}^* is

$$T\dot{s}^* = 2(\mathcal{D}^V + \mathcal{D}^T). \tag{13.29}$$

Under the assumption that S_i may be used as a state variable, the Lagrangian equations have the same form as Eq. (12.53), where the values (13.20) and (13.5) are now substituted in Eq. (12.54) for the dissipation function.

For a non-Newtonian fluid, the viscous stress σ_{ij} is expressed as

$$\sigma_{ij} = F_1\delta_{ij} + F_2e'_{ij} + F_3e'_{ik}e'_{kj}, \tag{13.30}$$

where

$$e'_{ij} = \frac{1}{2}(\partial v_i/\partial \bar{x}_j + \partial v_j/\partial \bar{x}_i) \tag{13.31}$$

and F_1, F_2, F_3 are functions of the three invariants $e'_{ij}\delta_{ij}, e'_{ij}e'_{ij}, e'_{ij}e'_{jk}e'_{ki}$.

In the general case they are also functions of T and x_i if the fluid is nonisothermal and nonhomogeneous. A very simple proof of this formula has been given (Biot, 1976b). The Piola viscous stress T_{ij}^V in this case cannot generally be derived from a dissipation function as for the Newtonian case (13.21). However, it is given by the same formula (13.12) in terms of the stress τ_{ij} . The field equations are then the same as Eqs. (13.27) and (13.28). However, the Lagrangian equations become

$$\frac{d}{dt} \left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i} \right) - \frac{\partial \mathcal{T}}{\partial q_i} + R_i + \frac{\partial D^T}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i, \tag{13.32}$$

where

$$R_i = \int_{\Omega} \frac{T_0}{T} T_{\mu\nu}^V \partial a_{\mu\nu} / \partial q_i d\Omega,$$

derived from Eq. (13.11), is the generalized non-Newtonian viscous force and

$$D^T = \int_{\Omega} \frac{T_0}{T} \mathcal{D}^T d\Omega \tag{13.33}$$

is the thermal dissipation function.

A special case of practical interest is that of a viscous incompressible solid undergoing slow deformations under isothermal conditions ($T = T_0$). Inertial forces are negligible, and we put $\mathcal{T} = 0$. The material may be inhomogeneous, either continuous or composed of different adherent solids. The potential \mathcal{P} depends only on gravity, and its value is

$$\mathcal{P} = \int_{\Omega} \rho \mathcal{G}(\bar{x}_i) d\Omega. \tag{13.34}$$

The dissipation function D depends only on the viscosity. By assuming Newtonian viscosity and putting $T = T_0$, we derive

$$D = \frac{1}{2} \int_{\Omega} B_{ij}^{\mu\nu} \dot{a}_{\mu\nu} \dot{a}_{ij} d\Omega. \quad (13.35)$$

The displacement field u_i is represented by generalized coordinates q_i as

$$u_j = u_j(q_1, q_2, \dots, x_l). \quad (13.36)$$

The dissipation function (13.35) is then a quadratic form

$$D = \frac{1}{2} \sum_{ij} b_{ij}(q_i) \dot{q}_i \dot{q}_j, \quad (13.37)$$

where the coefficients b_{ij} are functions of the generalized coordinates q_i . The Lagrangian equations become

$$\partial \mathcal{P} / \partial q_i + \partial D / \partial \dot{q}_i = Q_i. \quad (13.38)$$

The generalized driving forces Q_i are obtained by putting $\theta = 0$ in the surface integral (12.50), where f_i are the forces at the boundary per unit initial area.

XIV. Lagrangian Equations of Heat Transfer and Their Mechanical Interpretation, and a Mass Transfer Analogy

The particular case of pure heat conduction is obtained by considering a rigid solid ($\varepsilon_{ij} = 0$). An important feature here is that the *heat fluence* H_i becomes a state variable. The *heat content*, or energy per unit volume, is then

$$\mathfrak{u} = h = -\partial H_i / \partial x_i. \quad (14.1)$$

The total exergy of the domain Ω is now

$$V = \int_{\Omega} \mathcal{V} d\Omega, \quad \mathcal{V} = \int_0^h \theta/T dh, \quad (14.2)$$

where \mathcal{V} is a function of h . The dissipation function is

$$D = \frac{T_0}{2} \int_{\Omega} \frac{\lambda_{ij}}{T^2} \dot{H}_i \dot{H}_j d\Omega. \quad (14.3)$$

The thermal time history of the domain is determined by the fluence field H_i in terms of a finite number of generalized coordinates whose evolution is governed by the Lagrangian equations

$$\partial V/\partial q_i + \partial D/\partial \dot{q}_i = Q_i. \tag{14.4}$$

The thermal generalized force Q_i is obtained as a particular case of Eq. (12.50) by putting $\delta u_i = 0$ so that

$$Q_i = - \int_A \frac{\theta}{T} \frac{\partial H_j}{\partial q_i} n_j dA. \tag{14.5}$$

It is worth noting the physical significance of these equations. The purely thermal exergy \mathcal{V} represents the work to be accomplished mechanically by thermobaric transfer to bring a unit volume of solid to a given temperature. The heat is transferred by a heat pump from the thermal well at a temperature T_0 to the solid at a different temperature T . Similarly, the generalized thermal force (14.5) is the work accomplished mechanically in order to inject heat at the boundary by the same heat pumping process. On the other hand, the dissipation function (14.3) represents the rate of loss of mechanical availability of the thermal energy due to thermal conduction. Thus the Lagrangian equations (14.4) for heat conduction are given a purely mechanical interpretation as related to an availability balance.

An important formal simplification is immediately evident in the linear theory where θ is small and $T \cong T_0$. In this case $1/T_0$ is eliminated from the equations as a common factor. It was found that the factor $1/T_0$ may also be eliminated in the general nonlinear case. This is shown by applying the principle of virtual dissipation with arbitrary variations inside the domain Ω . This leads to

$$\int_{\Omega} \left(\frac{\theta}{T} \delta h + \frac{T_0}{T^2} \lambda_{ij} H_i \delta H_j \right) d\Omega = 0. \tag{14.6}$$

After integration by parts using the relation $\partial(\theta/T)\partial x_i = -(T_0/T^2) \partial\theta/\partial x_i$ and taking out the factor T_0/T^2 , we obtain

$$\int_{\Omega} \left(\frac{\partial\theta}{\partial x_i} + \lambda_{ij} \dot{H}_j \right) \delta H_i d\Omega = 0. \tag{14.7}$$

Another integration by parts then yields

$$\int_{\Omega} (\theta \delta h + \lambda_{ij} \dot{H}_j \delta H_i) d\Omega = - \int_A \theta \delta H_i n_i dA, \tag{14.8}$$

which is the variational principle derived earlier (see Biot, 1970). It leads to the Lagrangian equations (14.4) with a thermal potential V , a dissipa-

tion function D , and a generalized thermal force Q_i , which are now expressed as

$$V = \int_{\Omega} d\Omega \int_0^h \theta dh, \quad D = \frac{1}{2} \int_{\Omega} \lambda_{ij} \dot{H}_i \dot{H}_j d\Omega,$$

$$Q_i = - \int_A \theta \frac{\partial H_j}{\partial q_i} n_j dA. \quad (14.9)$$

Applications of this Lagrangian approach to heat transfer were developed in great detail in a monograph (Biot, 1970). The Lagrangian equations for conduction and simultaneous convection in an incompressible fluid of prescribed motion were also obtained. The heat flux in this case is

$$\dot{H}_i = J_i + v_i h, \quad (14.10)$$

where v_i is the velocity of the medium. The dissipation function is now written

$$D = \frac{1}{2} \int_{\Omega} \lambda_{ij} J_i J_j d\Omega. \quad (14.11)$$

This result may be derived directly (Biot, 1970) or also as a particular case of the general treatment of Section XI when restricted to pure heat transfer for a given velocity field of the fluid.

Attention should be called to special formulations such as that of *associated fluence fields*, which lead to the use of scalar temperature fields as unknowns instead of H_i , and the treatment of boundary heat transfer to a moving fluid using the concept of a trailing function (Biot, 1970). The latter eliminated the inconsistencies of standard methods based on local heat transfer coefficients. Collective analysis by Lagrangian equations is ideally suited to the unified treatment of heat transfer in mixed systems constituted by solids and moving fluids.

A highly useful concept that was derived from the Lagrangian formulation is that of *penetration depth*, which yields immediately the heat fluence due to sudden temperature rise at the boundary. It can be used as a basic tool simplifying the formulation of very complex problems.

Application of the Lagrangian equations has brought simplification and physical insight in many problems of heat transfer (Lardner, 1963, 1967; Prasad and Agrawal, 1972, 1974; Chung and Yeh, 1975; Yeh and Chung, 1977).

Many types of finite element methods may also be derived directly from the Lagrangian equations. For example, we may treat as generalized coordinates the fluence vectors located at the vertices of a grid, using linear or polynomial interpolations of these values to represent the complete

field. The method is systematic and should be highly accurate, because heat flux continuity is preserved (see Section XXVI).

It should also be noted that the Lagrangian equations are derived directly from the principle of virtual dissipation, using the dissipation function as a basic invariant, without requiring any prior knowledge of the field differential equations. This is in contrast with formal methods based on functional space theories. In addition, the variational principle yields directly the field differential equations in any coordinate system. The invariance of the variational Lagrangian formulations also brings to light unifying fundamental properties of the governing equations (Lonngren and Hsuan, 1978).

The Lagrangian variational equations of heat transfer are completely isomorphic to those of pure isothermal mass transfer (Biot, 1970). The heat fluence field H_i is simply replaced in all equations by the mass fluence M_i . Field and Lagrangian equations for nonlinear problems of mass transfer are thus readily obtained, as exemplified by the case of a moving boundary (Senf, 1981).

XV. Deformable Solids with Thermomolecular Diffusion and Chemical Reactions

As another example we shall consider the deformation of a nonhomogeneous solid, which contains a number of substances in solution. Thermal and molecular diffusion of the substances are induced by the deformation as well as their concentration and thermal gradients. Simultaneous chemical reactions between the dissolved substances may also occur. For simplicity we shall neglect the inertial forces and assume creeping deformation. The energy \mathcal{U} and entropy \mathcal{S} per unit initial volume are obtained by integrating Eqs. (6.2) and (6.3) along an arbitrary path. Although they are formulated for a single reaction, the results are readily generalized to multiple reactions ξ_ρ , as was done for the value (6.11). We thus obtain

$$\mathcal{U} = \mathcal{U}(\varepsilon_{ij}, \xi_\rho, M^k, T, x_l), \quad (15.1)$$

$$\mathcal{S} = \mathcal{S}(\varepsilon_{ij}, \xi_\rho, M^k, T, x_l) \quad (15.2)$$

as functions of the deformation ε_{ij} , the chemical coordinates ξ_ρ , the masses M^k added by diffusion, the temperature T , and the initial coordinates x_i . The latter dependence represents the inhomogeneity. From

Eq. (15.2) we may obtain T as a function of \mathcal{S} , ε_{ij} , ξ_ρ , M^k , and x_i . Thus the exergy

$$\mathcal{V} = \mathcal{U} - T_0 \mathcal{S} \quad (15.3)$$

per unit initial volume becomes a function of these variables. In a gravity field $\mathcal{G}(\bar{x}_i)$ the mixed collective potential of a solid occupying the initial domain Ω is

$$\mathcal{P} = \int_{\Omega} [\mathcal{V} + (m_0 + m)\mathcal{G}(\bar{x}_i)] d\Omega, \quad m = - \sum_k \frac{\partial M_i^k}{\partial x_i}, \quad (15.4)$$

where m_0 is the initial mass per unit initial volume and m is the mass added by the contravariant fluences M_i^k . We recall that \dot{M}_i^k is the mass flux of the dissolved substance k through a deforming solid area initially equal to unity and initially normal to the x_i axis. From Eqs. (6.11) and (15.3) we obtain

$$\delta \mathcal{V} = \tau_{ij} \delta \varepsilon_{ij} + \sum_k \phi_k \delta M^k + \theta \delta \mathcal{S} - \sum_\rho A_\rho \delta \xi_\rho. \quad (15.5)$$

This result extends the value (12.18) to the solid with molecular diffusion and chemical reactions.

The virtual dissipation is due only to the chemical reactions and the thermomolecular diffusion. It has a form similar to Eq. (8.25).

$$T \delta S^* = \sum_\rho \mathcal{R}_\rho \delta \xi_\rho + \sum_k \frac{\partial \mathcal{D}^{\text{TM}}}{\partial \dot{M}_i^k} \delta M_i^k + \frac{\partial \mathcal{D}^{\text{TM}}}{\partial \dot{S}_i} \delta S_i, \quad (15.6)$$

where \dot{M}_i^k and \dot{S}_i are now contravariant fluxes. The affinity \mathcal{R}_ρ is a function of ξ_ρ , ε_{ij} , M^k , T , and x_i . The dissipation function \mathcal{D}^{TM} for thermomolecular diffusion is a quadratic form in \dot{M}_i^k and \dot{S}_i whose coefficients are functions ξ_ρ , ε_{ij} , M^k , T , and x_i .

We now apply the principle of virtual dissipation with arbitrary variations, $\delta \xi_\rho$, δu_i , δM_i^k , δS_i inside the domain Ω of the solid. Proceeding as for the solid in Section XII we derive the field equations

$$\frac{\partial}{\partial x_j} \left(\tau_{\mu\nu} \frac{\partial \varepsilon_{\mu\nu}}{\partial a_{ij}} \right) - (m_0 + m) \frac{\partial \mathcal{G}}{\partial \bar{x}_i} = 0, \quad (15.7)$$

$$\partial \varphi_k / \partial x_i + \partial \mathcal{D}^{\text{TM}} / \partial \dot{M}_i^k = 0, \quad (15.8)$$

$$\partial T / \partial x_i + \partial \mathcal{D}^{\text{TM}} / \partial \dot{S}_i = 0, \quad (15.9)$$

$$-A_\rho + \mathcal{R}_\rho = 0, \quad (15.10)$$

where φ_k is the mixed convective potential (9.21). The symmetric structure and simplicity of these equations is worth noting in view of the

complexity of the physics. We may consider ξ_ρ , u_i , M_i^k , and S_i as the field unknowns, describing the evolution of the state of the system. However if the contribution from s^* is significant in determining the state of the system we may add an auxiliary equation such as Eq. (11.21) for the rate of dissipation or proceed as in Sections XI and XII by introducing a pseudo-energy fluence \mathcal{F}_i^\dagger in the field equations.

By neglecting s^* in first approximation we may describe the system in terms of generalized coordinates q_i as

$$u_j = u_j(q_1, q_2, \dots, x_l), \tag{15.11}$$

$$M_j^k = M_j^k(q_1, q_2, \dots, x_l), \tag{15.12}$$

$$S_j = S_j(q_1, q_2, \dots, x_l), \tag{15.13}$$

$$\xi_\rho = \xi_\rho(q_1, q_2, \dots, x_l). \tag{15.14}$$

By applying the principle of virtual dissipation with arbitrary variations δq_i , we derive the Lagrangian equations

$$\partial \mathcal{P} / \partial q_i + R_i + \partial D^{\text{TM}} / \partial \dot{q}_i = Q_i, \tag{15.15}$$

where

$$R_i = \int_\Omega \frac{T_0}{T} \sum_\rho \mathcal{R}_\rho \frac{\partial \xi_\rho}{\partial q_i} d\Omega \tag{15.16}$$

is similar to Eq. (11.36) and represents the generalized chemical dissipative force or affinity. The dissipation function for thermomolecular diffusion is

$$D^{\text{TM}} = \frac{1}{2} \int_\Omega \frac{T_0}{T} \mathcal{D}^{\text{TM}} d\Omega \tag{15.17}$$

and the generalized driving force

$$Q_i = \int_A \left(f_j \frac{\partial u_j}{\partial q_i} - \sum_k \varphi_k \frac{\partial M_j^k}{\partial q_i} n_j - \theta \frac{\partial S_j}{\partial q_i} n_j \right) dA \tag{15.18}$$

is due to forces f_j applied at the boundary per unit initial area and to thermodynamic forces of the environment on the open system. This expression contains the particular case [Eq. (12.50)] derived above.

For the case where chemical reactions are not far from equilibrium, the evolution is quasi-reversible, and we may introduce a chemical dissipation function

$$D^{\text{ch}} = \frac{1}{2} \int_\Omega \frac{T_0}{T} \mathcal{D}^{\text{ch}} d\Omega \tag{15.19}$$

where \mathcal{D}^{ch} is a quadratic form in $\dot{\xi}_\rho$ such that

$$\mathcal{R}_\rho = \partial \mathcal{D}^{\text{ch}} / \partial \dot{\xi}_\rho. \quad (15.20)$$

In this case the Lagrangian equations (15.15) become

$$\partial \mathcal{P} / \partial q_i + \partial D / \partial \dot{q}_i = Q_i, \quad (15.21)$$

where

$$D = D^{\text{ch}} + D^{\text{TM}} \quad (15.22)$$

is the total dissipation function. Note the formal identity of (15.21) with (13.38) for the creeping viscous solid.

XVI. Thermodynamics of Nonlinear Viscoelasticity and Plasticity with Internal Coordinates and Heredity

A general theory of linear viscoelasticity based on the Lagrangian equations of irreversible thermodynamics was established (Biot, 1954, 1955, 1956a, 1958). Its characteristic feature is the use of the concept of internal coordinates to represent heredity properties. The same Lagrangian formulation provides a natural extension to nonlinear viscoelasticity (Biot, 1976b). We shall consider the linear case in a subsequent section dealing with general linear phenomena and present here the thermodynamic theory of nonlinear viscoelasticity.

In order to formulate the stress-strain relations of the solid we apply a finite homogeneous deformation defined by six strain components ε_{ij} to a solid element that is initially a cube of unit size. The six strain components may be defined by any of the various ways described in Section V. As already pointed out, they are not necessarily tensor components. The six stress components τ_{ij} are corresponding forces applied to the faces of the solid element and defined by the principle of virtual work. Obviously the solid element represents a domain Ω as considered in Sections XII and XV, where ε_{ij} plays the role of generalized coordinates q_i while τ_{ij} plays the role of generalized forces Q_i applied externally to the system. In addition to external degrees of freedom represented by ε_{ij} , there may be internal ones represented by internal coordinates q_s , for which there are no external driving forces ($Q_s = 0$).

Such will be the case if, for example, the solid contains substances in solution that react chemically. Internal coordinates may also correspond to internal fluence fields due to thermomolecular diffusion if the material possesses a microstructure of inhomogeneities.

Nonlinear viscoelasticity may be defined by the property that the system is quasi-reversible, i.e., that the irreversibility is represented by a dissipation function that is a quadratic form in the time derivatives of the generalized coordinates. The stress-strain relations are then obtained by writing the Lagrangian equations of the system. We write the exergy of the solid element as

$$V = V(\varepsilon_{ij}, \mathcal{S}, q_s), \tag{16.1}$$

where \mathcal{S} is the entropy of the solid element and q_s represents a very large number of internal coordinates. The dissipation function

$$D = D(\dot{\varepsilon}_{ij}, \dot{\mathcal{S}}, \dot{q}_s) \tag{16.2}$$

is a quadratic form in $\dot{\varepsilon}_{ij}$, $\dot{\mathcal{S}}$, and \dot{q}_s . The Lagrangian equations of the element are

$$\partial V / \partial \varepsilon_{ij} + \partial D / \partial \dot{\varepsilon}_{ij} = \tau_{ij}, \tag{16.3}$$

$$\partial V / \partial \mathcal{S} + \partial D / \partial \dot{\mathcal{S}} = \theta, \tag{16.4}$$

$$\partial V / \partial q_s + \partial D / \partial \dot{q}_s = 0. \tag{16.5}$$

By referring to Eq. (8.31), we note that because of the assumption of quasi-reversibility, \dot{s}^* is negligible; hence this equation, integrated over the domain Ω of the element, shows that \mathcal{S} is the surface integral of the fluence S_i at the boundary. Hence \mathcal{S} is a state variable whose conjugate generalized force is θ . As a consequence, $T d\mathcal{S}$ represents the amount of heat provided reversibly to the solid element. Equations (16.5) are linear in \dot{q}_s . They may be integrated for q_s , which then become functionals

$$q_s = \mathcal{F}_s[\varepsilon_{ij}(t), \mathcal{S}(t)] \tag{16.6}$$

of $\varepsilon_{ij}(t)$ and $\mathcal{S}(t)$. When these functionals are substituted into Eqs. (16.3) and (16.4), these equations provide the stress-strain relations for nonlinear thermoviscoelasticity. Note that this result takes into account the temperature change and heat injection at the rate $T\dot{\mathcal{S}}$, thus yielding a heredity of the specific heat.

Plasticity may be handled in the same way (Biot, 1976b). However in this case the deformation is not quasi-reversible, and we may not assume the existence of a dissipation function. The internal coordinates for a plastic material are represented by dislocation slips q_{ij}^s . The double subscript defines the orientation of the dislocation and the slip direction. For simplicity we assume constant temperature $T = T_0$. The exergy

$$V = V(\varepsilon_{ij}, q_{ij}^s) \tag{16.7}$$

is a function of the deformation and the internal coordinates. The virtual dissipation is

$$T_0 \delta s^* = R_{ij}^s \delta q_{ij}^s, \quad (16.8)$$

where R_{ij}^s is the dissipative force acting on the dislocations. It may be expressed as a nonlinear rate function

$$R_{ij}^s = R_{ij}^s(\epsilon_{ij}, \dot{\epsilon}_{ij}, q_{ij}^s, \dot{q}_{ij}^s). \quad (16.9)$$

The corresponding Lagrangian equations

$$\partial V / \partial \epsilon_{ij} = \tau_{ij}, \quad (16.10)$$

$$\partial V / \partial q_{ij}^s + R_{ij}^s = 0 \quad (16.11)$$

represent the stress-strain relations for plastic deformation with internal coordinates q_{ij}^s and heredity. Comparison with Eq. (15.16) shows that R_{ij}^s is the tensor equivalent of the affinity.

Strain hardening is represented by freezing an increasing number of internal coordinates q_{ij}^s as the deformation proceeds. For a material that becomes weaker as the deformation increases, the opposite procedure is used by releasing an increasing number of internal coordinates. This property may be assimilated to internal failures. It is of particular interest for fiber composites.

For a viscoelastic continuum we may also derive field equations from the variational principle (Biot, 1976b). The result is entirely similar to Eqs. (15.7) and (15.9). However for a solid that is not centrosymmetric we must take into account possible coupling terms of the type of $\dot{\epsilon}_{ij} \dot{S}_\mu$ and $\dot{q}_s \dot{S}_\mu$ in the dissipation function. This leads to a coupling between the temperature gradient and the rate of deformation. These more general results are easily obtained by straightforward application of the variational procedures described above.

XVII. Dynamics of a Fluid-Saturated Deformable Porous Solid with Heat and Mass Transfer

The principle of virtual dissipation has been used to develop the field and Lagrangian equations for the dynamics of a porous solid with fluid saturation of the pores and heat transfer by convection and conduction. We shall follow the procedures developed earlier for the isothermal non-inertial case (Biot, 1972) and later for the nonisothermal dynamic case (Biot, 1977b).

For the noninertial case the problem is similar to that of a solid with a single substance in solution, and in many ways it may be considered as a particular case of the one treated in Section XV. However in the present

case we shall also take into account the inertial forces due to the motion of the porous frame and the motion of the fluid relative to the frame. We start with a unit initial volume of the material, initially of total mass m_0 . As the material is deformed, the exergy per unit initial volume is

$$\mathcal{V} = \mathcal{V}(\varepsilon_{ij}, m, T, x_i), \tag{17.1}$$

where ε_{ij} are the six strain components as defined in Section V, and

$$m = -\partial M_i / \partial x_i \tag{17.2}$$

is the mass of fluid added in the pores per unit initial volume. The contravariant fluence M_i is the mass of fluid that has been flowing through a material surface of the porous frame initially equal to unity and initially normal to x_i . A material point of the solid frame initially of coordinates x_i is displaced to a point of coordinates $\bar{x}_i = x_i + u_i$. If the porous material, which is approximated as a continuum, is inhomogeneous, \mathcal{V} is also a function of the initial coordinates x_i . Using procedures similar to those in Section XV, we may evaluate the entropy \mathcal{S} of the element in terms of ε_{ij} , m , T , and x_i . Hence we express \mathcal{V} replacing T by \mathcal{S} as one of the state variables. We write

$$\mathcal{V} = \mathcal{V}(\varepsilon_{ij}, m, \mathcal{S}, x_i), \tag{17.3}$$

with the property analogous to Eq. (15.5):

$$\delta \mathcal{V} = \tau_{ij} \delta \varepsilon_{ij} + \sum_k \phi \delta m + \theta \delta \mathcal{S}, \tag{17.4}$$

where $\theta = T - T_0$. The fluid pressure p_f in the pores in the present case is equal to the injection pressure, which was denoted by p_k for the case of a substance in solution. The corresponding injection enthalpy $\bar{\varepsilon}_f$ and injection entropy \bar{s}_f are given by Eqs. (2.2) and (2.4) as

$$\bar{\varepsilon}_f = \int_{p_0 T_0}^{p_f T} \left(\frac{dp_f'}{\rho_f'} + T' d\bar{s}_f' \right), \quad \bar{s}_f = \int_{p_0 T_0}^{p_f T} d\bar{s}_f', \tag{17.5}$$

where p_f' , ρ_f' , T' , and \bar{s}_f' are the pressure, density, temperature, and specific entropy of the fluid along the path of thermobaric transfer from a supply cell of fluid at the pressure p_0 and temperature T_0 . The convective potential is

$$\phi = \bar{\varepsilon}_f - T \bar{s}_f, \tag{17.6}$$

and the mixed collective potential is now

$$\mathcal{P} = \int_{\Omega} [\mathcal{V} + (m_0 + m)\mathcal{G}(\bar{x})] d\Omega, \tag{17.7}$$

where \mathcal{G} is the gravity potential.

We may write the rate of dissipation per unit initial volume as

$$T\dot{s}^* = 2\mathcal{D}, \quad (17.8)$$

where the dissipation function

$$\mathcal{D} = \frac{1}{2} C_{ij}^M \dot{M}_i \dot{M}_j + C_{ij}^S \dot{M}_i \dot{S}_j + (T/2) \Lambda_{ij} \dot{S}_i \dot{S}_j \quad (17.9)$$

is a quadratic form in \dot{M}_i and \dot{S}_i with coefficients functions of the local state variables ε_{ij} and T and the initial coordinates x_i . The contravariant entropy flux is

$$\dot{S} = \bar{s}_i \dot{M}_i + \dot{H}_i/T. \quad (17.10)$$

It embodies the convective heat transfer due to \dot{M}_i and the heat flux \dot{H}_i due to conduction. For $\dot{M}_i = 0$ the dissipation is due entirely to heat conduction and the dissipation reduces to the term $\frac{1}{2} T \Lambda_{ij} \dot{S}_i \dot{S}_j$ already obtained above (12.30) with a covariant thermal resistivity Λ_{ij} . For $\dot{H}_i = 0$ the dissipation function involves only \dot{M}_i and leads to Darcy's law generalized to a nonisotropic deformable medium.

In order to evaluate the inertial forces, we consider the momentum of the masses of solid and fluid of an element initially of unit volume and mass m_0 . This momentum is

$$\mathcal{M}_i = (m_0 + m) \dot{u}_i + \dot{M}'_i J, \quad (17.11)$$

where \dot{M}'_i is the mass flux of pore fluid relative to the solid frame per unit final area in the space \bar{x}_i . The Jacobian (7.11) is the volume J of the element. We may express \dot{M}'_i in terms of the contravariant mass flux \dot{M}_i using relations (7.9) and (7.11):

$$\dot{M}'_i = J' \dot{M}_j \frac{\partial \bar{x}_i}{\partial x_j} = \frac{1}{J} \dot{M}_j \frac{\partial \bar{x}_i}{\partial x_j} \quad (17.12)$$

Hence

$$\mathcal{M}_i = (m_0 + m) \dot{u}_i + \dot{M}_j \partial \bar{x}_i / \partial x_j. \quad (17.13)$$

Because the element of volume J is not of constant mass, the resultant of all inertial forces is $\partial \mathcal{M}_i / \partial t$ plus an additional term due to the rate of flow of momentum out of J . If we neglect the square of the relative velocity of the pore fluid then the resultant of the inertial forces is

$$\mathcal{F}_i = \partial \mathcal{M}_i / \partial t + \partial (\dot{u}_i \dot{M}_j) / \partial x_j. \quad (17.14)$$

The virtual work of the inertial forces for the porous solid, when we vary δu_i and δM_i , is

$$\sum_i I_i \delta q_i = \int_{\Omega} \mathcal{F}_i \delta u_i d\Omega + \int_{\bar{\Omega}} \ddot{u}_i \delta M_i' d\bar{x}_1 d\bar{x}_2 d\bar{x}_3, \quad (17.15)$$

where $\bar{\Omega}$ is the domain Ω in the coordinates \bar{x}_i .

In evaluating the second integral we have assumed that the acceleration of the fluid particles may be approximated as \ddot{u}_i . On the other hand, in variational form (7.12) is written

$$J \delta M_i' = \partial \bar{x}_i / \partial x_j \delta M_j. \quad (17.16)$$

Hence (7.15) becomes

$$\sum_i I_i \delta q_i = \int_{\Omega} (\mathcal{F}_i \delta u_i + \ddot{u}_i \partial \bar{x}_i / \partial x_j \delta M_j) d\Omega. \quad (17.17)$$

By varying δu_i and δM_i inside the domain Ω and applying the principle of virtual dissipation, we proceed as in Sections XII and XV. This leads to the field equations

$$\frac{\partial}{\partial x_j} \left(\tau_{\mu\nu} \frac{\partial \varepsilon_{\mu\nu}}{\partial a_{ij}} \right) - (m_0 + m) \frac{\partial \mathcal{G}}{\partial \bar{x}_i} = \mathcal{F}_i, \quad (17.18)$$

$$\partial \varphi / \partial x_i + \partial \mathcal{D} / \partial \dot{M}_i = -\ddot{u}_j \partial \bar{x}_j / \partial x_i, \quad (17.19)$$

$$\partial T / \partial x_i + \partial \mathcal{D} / \partial \dot{S}_i = 0, \quad (17.20)$$

where $\varphi = \partial \mathcal{V} / \partial m + \mathcal{G} = \phi + \mathcal{G}$, $\tau_{\mu\nu} = \partial \mathcal{V} / \partial \varepsilon_{\mu\nu}$, and $a_{ij} = \partial u_i / \partial x_j$. The equations are for the field components M_i and S_i . If we wish to take into account the entropy produced s^* as contributing to the state variables we add the auxiliary equations (17.8).

Lagrangian equations are also obtained directly from the principle of virtual dissipation by describing the fields u_i , M_i , and S_i in terms of generalized coordinates, as in Eqs. (15.11), (15.12), and (15.13), assuming S_i to be a state variable as an approximation. The Lagrangian equations are written

$$I_i + \partial D / \partial \dot{q}_i + \partial \mathcal{P} / \partial q_i = Q_i, \quad (17.21)$$

with the generalized inertial force

$$I_i = \int_{\Omega} \left(\mathcal{F}_j \frac{\partial u_j}{\partial q_i} + \ddot{u}_\mu \frac{\partial \bar{x}_\mu}{\partial x_j} \frac{\partial M_j}{\partial q_i} \right) d\Omega, \quad (17.22)$$

the dissipation function

$$D = \frac{1}{2} \int_{\Omega} \frac{T_0}{T} \mathcal{D} d\Omega, \quad (17.23)$$

and the generalized driving force at the boundary A

$$Q_i = \int_A \left(f_j \frac{\partial u_j}{\partial q_i} - \varphi \frac{\partial M_j}{\partial q_i} n_j - \theta \frac{\partial S_j}{\partial q_i} n_j \right) dA. \quad (17.24)$$

The forces f_j are applied at the boundary per unit initial area.

A semilinear theory of deformation of porous solids was also developed for the particular case where linear dependence is assumed between fluid pressure and microscopic volume changes while bulk deformations remain nonlinear (Biot, 1973c).

The problem of fluid flow through a rigid porous solid with heat transfer was also discussed in detail (Biot, 1978), including phase changes from vapor to liquid and multiple diffusion channels due to surface adsorption.

The results lead to a large variety of possible applications in geothermal and aquifer problems with heat and fluid flow including associated subsidence.

XVIII. Linear Thermodynamics near Equilibrium

Perturbations of a system near equilibrium are described by small changes of the state variables. We denote by θ the first-order increase of the initial uniform temperature T_0 . Other first-order perturbations are M^k , the mass increase of each molecular species per unit volume due to convection, the entropy \mathcal{S} , and the reaction coordinates ξ_ρ with initial zero values. The affinities also vanish at equilibrium, and their perturbations A_ρ are first-order quantities.

There are two important simplifications in the linear theory. First consider the linearized value of the first-order entropy obtained from Eq. (2.3),

$$\mathcal{S} = \sum_k \bar{s}_{0k} M^k + h/T_0, \quad (18.1)$$

where h is the heat acquired per unit volume and \bar{s}_{0k} is the initial value of the injection entropy in the initial equilibrium state. Since \mathcal{S} and M^k are state variables, the *heat injected* h is also a state variable.

Another simplification, which is a consequence of the first, is the *use of the thermobaric potential* ψ_k *instead of the convective potential* φ_k . For example, we may write Eq. (15.5) for the more general case of a solid, in differential form, as

$$d\mathcal{V} = \tau_{ij} d\varepsilon_{ij} - \sum_\rho A_\rho d\xi_\rho + \sum_k \psi_k dM^k + (\theta/T_0) dh, \quad (18.2)$$

where dh is now a state variable. The heat fluence H_i defined by

$$h = -\partial H_i / \partial x_i \quad (18.3)$$

is now also a state variable. By introducing the constant factor $1/T_0$ we may use as state variable the thermal entropy s^T . We write

$$s^T = h/T_0 = -\partial S_i^T / \partial x_i, \quad S_i^T = H_i/T_0, \quad (18.4)$$

with a thermal entropy fluence S_i^T . These quantities were introduced in the earlier developments of the theory (Biot, 1956b). Finally, we may of course use the total entropy fluence

$$S_i = \sum_k \bar{s}_{0k} M_i^k + S_i^T. \quad (18.5)$$

The fact that it is a first-order state variable is also a consequence of Eq. (8.31), namely,

$$\mathcal{P} = -\partial S_i / \partial x_i + s^*. \quad (18.6)$$

Since the entropy produced s^ is now of the second order, it may be neglected in a first-order description of the state of the system.*

Another point of importance in the linear theory is the dual role played by the energy \mathcal{U} and entropy \mathcal{P} . This may be illustrated in the simple case of linear thermoelasticity (Biot, 1956b, 1981). For this case the linear equations of state are

$$\tau_{ij} = C_{ij}^{\mu\nu} \varepsilon_{\mu\nu} - \beta_{ij} \theta, \quad (18.7)$$

where $C_{ij}^{\mu\nu}$ are the isothermal moduli of linear elasticity. The energy and entropy per unit volume are obtained by applying Eqs. (6.2) and (6.3) for the particular case $d\xi = dM^k = 0$. They become

$$d\mathcal{U} = \tau_{ij} d\varepsilon_{ij} + dh, \quad (18.8)$$

$$d\mathcal{P} = dh/T. \quad (18.9)$$

By using the equations of state (18.7) in (6.7), the value (6.4) of dh becomes

$$dh = T\beta_{ij} d\varepsilon_{ij} + c d\theta, \quad (18.10)$$

where c is the heat capacity per unit volume at constant strain, which we shall assume constant. We integrate the values (18.8) and (18.9) along a path, first for $\theta = 0$ and then for $d\varepsilon_{ij} = 0$. Keeping only first- and second-order terms, we derive

$$\mathcal{U} = \frac{1}{2} C_{ij}^{\mu\nu} \varepsilon_{ij} \varepsilon_{\mu\nu} + T_0 s^T, \quad (18.11)$$

$$\mathcal{P} = s^T - \frac{1}{2} (c\theta^2/T_0^2), \quad (18.12)$$

with

$$T_0 s^T = h = T_0 \beta_{ij} \varepsilon_{ij} + c\theta. \quad (18.13)$$

We see that s^T is a first-order state variable, but it does not represent the correct entropy to the second order. The thermoelastic potential or exergy becomes (Biot, 1981)

$$\mathcal{V} = \mathcal{U} - T_0 \mathcal{S} = \frac{1}{2} (C_{ij}^{\mu\nu} \varepsilon_{ij} \varepsilon_{\mu\nu} + c\theta^2/T_0). \quad (18.14)$$

It is interesting to note that in this expression the first-order terms drop out. Hence the entropy plays here a dual role, first as a linearized state variable s^T and second as a value \mathcal{S} that includes second-order terms.

A general discussion of the linear theory is particularly fruitful in Lagrangian form. Small perturbations from equilibrium may be described by expressing the fluence and displacement fields as linear functions of generalized coordinates q_i . For example, we may represent material point displacements as

$$u_j = \sum_i u_{ji}(x_i) q_i, \quad (18.15)$$

where $u_{ji}(x_i)$ are fixed displacement fields. Fluence fields M_j^k and S_j as well as ξ_ρ are represented similarly. Application of the principle of virtual dissipation then yields the linear Lagrangian equations for the perturbations q_i . They are

$$\frac{d}{dt} \left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i} \right) + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i, \quad (18.16)$$

with a kinetic energy

$$\mathcal{T} = \frac{1}{2} \sum_{ij} m_{ij} \dot{q}_i \dot{q}_j, \quad (18.17)$$

a dissipation function

$$D = \frac{1}{2} \sum_{ij} b_{ij} \dot{q}_i \dot{q}_j, \quad (18.18)$$

and a mixed collective potential

$$\mathcal{P} = \frac{1}{2} \sum_{ij} a_{ij} \dot{q}_i \dot{q}_j. \quad (18.19)$$

The constant coefficients are symmetric:

$$m_{ij} = m_{ji}, \quad b_{ij} = b_{ji}, \quad a_{ij} = a_{ji}, \quad (18.20)$$

while \mathcal{T} and D are positive definite.

Note that the generalized coordinates constitute a complete and accurate representation of the physical system and are not essentially "trial functions." This can be seen by using as generalized coordinates values of the fields at the vertices of a grid system of finite elements sufficiently small so that macroscopic laws are still valid while fluctuations at the molecular scale do not yet enter into play (see Section XXVI below).

The Lagrangian equations (18.16) thus govern and unify a vast domain of linear physics obeying a single universal mathematical formalism. In particular, in the absence of inertial and gravitational forces we may write

$$\partial V/\partial q_i + \partial D/\partial \dot{q}_i = Q_i, \tag{18.21}$$

$$\partial V/\partial q_s + \partial D/\partial \dot{q}_s = 0, \tag{18.22}$$

where q_s are a large number of internal coordinates, while Q_i are external driving forces. Consider the case where the equilibrium is stable. Then V is also nonnegative. We then solve Eqs. (18.22) for q_s and substitute these values into Eq. (18.21). The forces Q_i are then expressed as (Biot, 1954)

$$Q_i = \sum_j Z_{ij} q_j, \tag{18.23}$$

with

$$Z_{ij} = Z_{ji} = \sum_s D_{ij}^s \frac{p}{p + r_s} + D_{ij} + D'_{ij} p, \tag{18.24}$$

where D_{ij}^s , D_{ij} and D'_{ij} are nonnegative symmetric matrices and $r_s \geq 0$. The quantity p must be interpreted as $p = i\omega$ for the case where q_i varies proportionally to the harmonic function of time $\exp(pt)$.

For a nonperiodic dependence on time starting at $t = 0$ in a quiescent system, it is easy to show that Z_{ij} may be interpreted as an operator where

$$\frac{p}{p + r} f(t) = e^{-rt} \int_0^t e^{r't'} \frac{df}{dt'} dt', \quad pf(t) = \frac{df}{dt}. \tag{18.25}$$

This interpretation is completely general provided we introduce generalized Dirac functions (Biot, 1970).

The linear Lagrangian equations (18.21) and (18.22) were applied to derive the stress-strain relations of linear viscoelasticity with heredity (Biot, 1954, 1955, 1956a). By proceeding as in the more general nonlinear case in Section XVI, we consider the driving forces Q_i to represent stresses τ_{ij} applied to a unit cube of solid, and ε_{ij} to represent the associated response q_i . Equations (18.23) in this case are written

$$\tau_{ij} = \hat{C}_{ij}^{\mu\nu} \varepsilon_{\mu\nu}, \tag{18.26}$$

with the operators

$$\hat{C}_{ij}^{\mu\nu} = \sum_s D_{ij}^{s\mu\nu} \frac{p}{p + r_s} + D_{ij}^{\mu\nu} + D'_{ij}{}^{\mu\nu} p. \quad (18.27)$$

These operators satisfy the symmetry properties $\hat{C}_{ij}^{\mu\nu} = \hat{C}_{\mu\nu}^{ij} = \hat{C}_{ji}^{\nu\mu} = \hat{C}_{ij}^{\nu\mu}$. They are the same as the symmetry relations satisfied by the elastic moduli in classical linear elasticity. They also formally coincide with the elastic moduli obtained for various cases of geometric symmetry, such as isotropy, cubic symmetry, etc. As a consequence, a principle of *viscoelastic correspondence* was obtained (Biot, 1954, 1955, 1956a, 1958) whereby all formulas of linear elasticity are immediately applicable to linear viscoelasticity by simply replacing the elastic moduli by the operators (18.27).

Another important application of linear thermodynamics is to porous media including viscoelastic behavior of the solid component. The stresses τ_{ij} and the fluid pore pressure p_f are considered as driving forces Q_i , while the response q_i is the bulk solid strain ε_{ij} and the volume of fluid ζ which has entered the pores. Its value is $\zeta = m/\rho_f$, where m is the mass of fluid added in the pores per unit initial volume of the bulk material and ρ_f is the fluid density. By applying the general solution (18.23) we obtain the stress-strain relations (Biot, 1962)

$$\tau_{\mu\nu} = \hat{A}_{ij}^{\mu\nu} \varepsilon_{ij} + \hat{M}_{ij} \zeta, \quad (18.28)$$

$$p_f = \hat{M}_{ij} \varepsilon_{ij} + \hat{M} \zeta, \quad (18.29)$$

where the operators $\hat{A}_{ij}^{\mu\nu}$, \hat{M}_{ij} , and \hat{M} are of the type (18.27). Note that the heredity properties are due not only to viscoelasticity of the solid itself but also involve interactions of a very general relaxation type between the fluid and the solid, such as fluid squirting in microcracks and between grains, microthermoelasticity, mutual solubility, adsorption, and surface diffusion as well as chemical reactions.

A principle of viscoelastic correspondence is also valid for porous media whereby all formulas of the purely elastic theory are valid for the viscoelastic case if one simply replaces the elastic coefficients by the corresponding operators of the stress-strain relations (18.28) and (18.29) (Biot, 1962).

The linear thermodynamic theory has also been applied to piezoelectric crystals with thermal dissipation (Mindlin, 1961, 1974) by adding suitable electrostatic terms.

XIX. Linear Thermodynamics of a Solid under Initial Stress

The theory of small perturbations of a system initially in thermodynamic equilibrium is quite general and is applicable to the case where the system is in equilibrium in an initial state of stress. However the state of initial stress must be taken into account in the evaluation of the thermodynamic functions. The mechanics of initially stressed continua including elastic and viscoelastic properties was treated extensively in a monograph (Biot, 1965b). The theory was later extended on the basis of thermodynamics to include thermomolecular diffusion and chemical reactions (Biot, 1977c).

We shall present a summary of this completely general case. Attention is called to its formal applicability to porous media under initial stress insofar as we may identify seepage with thermomolecular diffusion. The problem of porous solids under initial stress was also treated earlier in a somewhat different context (Biot, 1963).

The initial Cartesian stress components are denoted by S_{ij} . It is important to note that the system may lie in a gravity field, so that equilibrium does not imply uniformity of the initial injection pressure p_{0k} . As a consequence, the initial values \bar{s}_{0k} , \bar{e}_{0k} , and ψ_{0k} of the injection entropy, the injection enthalpy, and the thermobaric potential may vary from point to point. The initial equilibrium temperature T_0 is of course uniform. When the system is disturbed from equilibrium, the stress becomes

$$\tau_{ij} = t_{ij} + S_{ij}. \tag{19.1}$$

The stress is defined here as in Section V on the basis of virtual work and may be nontensorial, so that t_{ij} is the increase of τ_{ij} per unit initial area. The thermobaric potential becomes

$$\psi_k = \psi_{0k} + \Delta\psi_k. \tag{19.2}$$

The perturbation involves a small displacement field u_i of the solid corresponding small strain components

$$e_{ij} = \frac{1}{2}(a_{ij} + a_{ji}), \quad a_{ij} = \partial u_i / \partial x_j. \tag{19.3}$$

An important point here is that the linear strain components (19.3) are not sufficient to establish a linearized theory under initial stress. Actually we must develop the actual strain ε_{ij} to the second order. We shall write

$$\varepsilon_{ij} = e_{ij} + \eta_{ij}, \tag{19.4}$$

where η_{ij} is a second-order quantity in a_{ij} . For example, in the case (5.5), we obtain

$$\eta_{ij} = \frac{1}{2}(e_{i\mu}\omega_{\mu j} + \varepsilon_{j\mu}\omega_{\mu i} + \omega_{i\mu}\omega_{j\mu}), \quad (19.5)$$

and in the two-dimensional case (5.7)

$$\begin{aligned} \eta_{11} &= \frac{1}{2}a_{21}^2, & \eta_{22} &= -\frac{1}{2}a_{21}(2a_{12} + a_{21}), \\ \eta_{12} &= \frac{1}{2}a_{21}(a_{22} - a_{11}). \end{aligned} \quad (19.6)$$

The perturbation from equilibrium is described by the displacement field u_i of the medium, the masses M^k of various substances acquired by diffusion per unit initial volume, small chemical reactions ξ_ρ , and temperature increments θ . As already pointed out, in the case of the general linearized theory we may use instead of θ the quantity $s^T = h/T_0$ as a state variable, where h is the heat acquired per unit initial volume. According to Eq. (18.4), we also introduce the thermal entropy fluence S_i^T as a state variable. Another simplification is also to use the thermobaric potential ψ_k instead of ϕ_k . We shall first evaluate the exergy \mathcal{V} per unit initial volume. Its differential (18.2) for the solid under initial stress is

$$d^{\mathcal{V}} = (t_{ij} + S_{ij}) d\varepsilon_{ij} - \sum_{\rho} A_{\rho} d\xi_{\rho} + \sum_k (\psi_{0k} + \Delta\psi_k) dM^k + \theta ds^T \quad (19.7)$$

or

$$d^{\mathcal{V}} = d^{\mathcal{W}} + S_{ij} d\varepsilon_{ij} + \sum_k \psi_{0k} dM^k, \quad (19.8)$$

where

$$d^{\mathcal{W}} = t_{ij} d\varepsilon_{ij} - \sum_{\rho} A_{\rho} d\xi_{\rho} + \sum_k \Delta\psi_k dM^k + \theta ds^T \quad (19.9)$$

The exergy \mathcal{V} is a function of ε_{ij} , ξ_{ρ} , M^k , and s^T . Because $S_{ij} d\varepsilon_{ij} + \sum_k \psi_{0k} dM^k$ is an exact differential, $d^{\mathcal{W}}$ is also an exact differential. Furthermore we may consider a_{ij} as independent state variables. In a linear theory we need evaluate \mathcal{V} only to the second order, hence we may replace ε_{ij} by e_{ij} in the value of $d^{\mathcal{W}}$. We write

$$d^{\mathcal{W}} = t_{ij} de_{ij} - \sum_{\rho} A_{\rho} d\xi_{\rho} + \sum_k \Delta\psi_k dM^k + \theta ds^T. \quad (19.10)$$

Integration yields the quadratic form

$$\mathcal{W} = \mathcal{W}(e_{ij}, \xi_{\rho}, M^k, s^T) \quad (19.11)$$

in e_{ij} , ξ_{ρ} , M^k , and s^T with the property

$$t_{ij} = \partial^2 W / \partial e_{ij}, \quad -A_p = \partial^2 W / \partial \xi_p, \quad \Delta \psi^k = \partial^2 W / \partial M^k, \quad \theta = \partial^2 W / \partial s^T. \quad (19.12)$$

The potential energy in the gravity field is

$$G = \int_{\Omega} \left(m_0 + \sum_k M^k \right) \mathcal{G}(\bar{x}_i) d\Omega, \quad (19.13)$$

where $\mathcal{G}(\bar{x}_i)$ is the gravity potential at the displaced point $\bar{x}_i = x_i + u_i$ and m_0 is the initial density. We develop $\mathcal{G}(\bar{x}_i)$ to the second order in u_i and write

$$\mathcal{G}(\bar{x}_i) = \mathcal{G}_0 + \mathcal{G}_i u_i + \frac{1}{2} \mathcal{G}_{ij} u_i u_j, \quad (19.14)$$

with

$$\mathcal{G}_0 = \mathcal{G}(x_i), \quad \mathcal{G}_i = \partial \mathcal{G}(x_i) / \partial x_i, \quad \mathcal{G}_{ij} = \partial^2 \mathcal{G}(x_i) / \partial x_i \partial x_j. \quad (19.15)$$

Hence to the second order except for a constant

$$G = \int_{\Omega} \left[m_0 \mathcal{G}_i u_i + (\mathcal{G}_0 + \mathcal{G}_i u_i) \sum_k M^k + \frac{1}{2} m_0 \mathcal{G}_{ij} u_i u_j \right] d\Omega. \quad (19.16)$$

We now apply the principle of virtual dissipation (9.19). With the value (19.8) of $d^{\circ} \mathcal{V}$ it becomes

$$\begin{aligned} & \sum_i I_i \delta q_i + \int_{\Omega} \left(\delta^{\circ} W + S_{ij} \delta e_{ij} + \sum_k \psi_{0k} \delta M^k \right) d\Omega + \delta G + T_0 \delta S^* \\ &= \int_A \left[(f_i + \Delta f_i) \delta u_i \right. \\ & \quad \left. - \sum_k (\psi_{0k} + \Delta \psi_k + \mathcal{G}_i + \mathcal{G}_i u_i) n_i \delta M_i^k - \theta n_i \delta S_i^T \right] dA, \end{aligned} \quad (19.17)$$

where Δf_i is the increment of forces f_i per unit initial area at the boundary S_i^T is the thermal entropy fluence (18.5).

When applied to the initial state of equilibrium under initial stress, the variational principle (19.17) yields

$$\begin{aligned} & \int_{\Omega} \left(S_{ij} \delta e_{ij} + \sum_k \psi_{0k} \delta M^k + m_0 \mathcal{G}_i \delta u_i \right) d\Omega \\ &= \int_A \left[f_i \delta u_i - \sum_k (\psi_{0k} + \mathcal{G}_0) n_i \delta M_i^k \right] dA. \end{aligned} \quad (19.18)$$

We now subtract equation (19.18) from (19.17) and obtain

$$\begin{aligned} & \sum_i I_i \delta q_i + \delta \mathcal{P} + T_0 \delta S^* \\ &= \int_A \left[\Delta f_i \delta u_i - \sum_k (\Delta \psi_k + \mathcal{G}_i u_i) n_i \delta M_i^k - \theta n_i \delta S_i^T \right] dA \end{aligned} \quad (19.19)$$

where

$$\mathcal{P} = \int \left(\mathcal{W} + S_{ij} \eta_{ij} + \mathcal{G}_i u_i \sum_k M^k + \frac{1}{2} m_0 \mathcal{G}_{ij} u_i u_j \right) d\Omega \quad (19.20)$$

plays the role of an *incremental mixed potential* already encountered in the quoted monograph (Biot, 1965b) for the less general case. The variational principle (19.19) represents the particular form of the principle of virtual dissipation for a system under initial stress. In a uniform gravity field $\mathcal{G}_{ij} = 0$, and \mathcal{G}_i is a constant equal to the acceleration of gravity. The virtual work of the inertial forces is

$$\begin{aligned} \sum_i I_i \delta q_i = \int_{\Omega} \left[\left(m_0 \ddot{u}_i + \sum_k m_{0k} a_i^k \right) \delta u_i \right. \\ \left. + \sum_k m_{0k} (\ddot{u}_i + a_i^k) \delta u_i^k \right] d\Omega, \end{aligned} \quad (19.21)$$

where m_{0k} is the initial mass of substance k per unit volume of solid and a_i^k its acceleration relative to the solid. We denote by δu_i^k the virtual displacement of the substance associated with δM_i^k . We have in the linear case

$$a_i^k = \ddot{M}_i^k / m_{0k}, \quad \delta u_i^k = \delta M_i^k / m_{0k}. \quad (19.22)$$

With these values, (19.21) may be written in the form

$$\sum_i I_i \delta q_i = \int_{\Omega} \left[\frac{d}{dt} \left(\frac{\partial \mathcal{E}}{\partial \dot{u}_i} \right) \delta u_i + \sum_k \frac{d}{dt} \left(\frac{\partial \mathcal{E}}{\partial \dot{M}_i^k} \right) \delta M_i^k \right] d\Omega, \quad (19.23)$$

where

$$\mathcal{E} = \frac{1}{2} m_0 \dot{u}_i \dot{u}_i + \sum_k \dot{u}_i \dot{M}_i^k + \frac{1}{2} \sum_k \frac{\dot{M}_i^k \dot{M}_i^k}{m_{0k}} \quad (19.24)$$

is the kinetic energy per unit volume.

Finally we must evaluate the virtual dissipation. In the linearized theory we may assume the validity of Onsager's principle. Hence the dissipation is derived from a dissipation function. We write

$$T_0 \delta S^* = \int_{\Omega} \left(\frac{\partial \mathcal{D}}{\partial \dot{\xi}_\rho} \delta \dot{\xi}_\rho + \frac{\partial \mathcal{D}}{\partial \dot{M}_i^k} \delta \dot{M}_i^k + \frac{\partial \mathcal{D}}{\partial \dot{S}_i^T} \delta \dot{S}_i^T \right) d\Omega, \quad (19.25)$$

where

$$\mathcal{D} = \mathcal{D}^{\text{ch}} + \mathcal{D}^{\text{TM}}. \quad (19.26)$$

The first term \mathcal{D}^{ch} is a quadratic form in $\dot{\xi}_\rho$ and represents the dissipation due to chemical reactions. The second term represents the dissipation due

to thermomolecular diffusion. It is a quadratic form in \dot{M}_i^k and \dot{S}_i^T analogous to (17.9) with constant coefficients.

We now substitute the values (19.9), (19.20), (19.23), and (19.25) into the variational principle (19.19) and vary u_i , ξ_ρ , M_i^k , and S_i^T arbitrarily inside the domain. Proceeding as before in the nonlinear problems (Sections XI, XII, XV), using integration by parts, we obtain the field equations

$$\frac{d}{dt} \left(\frac{\partial \mathcal{E}}{\partial \dot{u}_i} \right) - \frac{\partial}{\partial x_j} \left(t_{ij} + S_{\mu\nu} \frac{\partial \eta_{\mu\nu}}{\partial a_{ij}} \right) + \Delta K_i = 0, \quad (19.27)$$

$$\frac{d}{dt} \left(\frac{\partial \mathcal{E}}{\partial \dot{M}_i^k} \right) + \frac{\partial}{\partial x_i} \Delta \Psi_k + \frac{\partial \mathcal{D}}{\partial \dot{M}_i^k} = 0, \quad (19.28)$$

$$\partial T / \partial x_i + \partial \mathcal{D} / \partial \dot{S}_i^T = 0, \quad (19.29)$$

$$-A_\rho + \partial \mathcal{D} / \partial \dot{\xi}_\rho = 0, \quad (19.30)$$

where

$$\Delta K_i = m_0 \mathcal{G}_{ij} u_j + \mathcal{G}_i \sum_k M^k, \quad (19.31)$$

$$\Delta \Psi_k = \Delta \psi_k + \mathcal{G}_i u_i. \quad (19.32)$$

The quantity $\Delta \Psi_k$ represents the increase of a mixed thermobaric potential $\psi_k + \mathcal{G}$ at the displaced point, as already considered in earlier work (Biot, 1963) for the initially stressed porous solid. The unknowns in the field equations are u_i , ξ_ρ , M_i^k , and S_i^T . They determine the state of the system to the first order as functions of time.

Lagrangian equations are also obtained directly from the principle of virtual dissipation (19.20). Using representations of the fields u_i , ξ_ρ , M_i^k , and S_i^T as linear functions of generalized coordinates q_i of the type (18.15), we derive

$$\frac{d}{dt} \left(\frac{\partial \mathcal{T}}{\partial \dot{q}_i} \right) + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = Q_i, \quad (19.33)$$

where

$$\mathcal{T} = \int_\Omega \mathcal{E} \, d\Omega \quad (19.34)$$

is the total kinetic energy and

$$D = \int_\Omega \mathcal{D} \, d\Omega \quad (19.35)$$

is the dissipation function. The generalized driving force is

$$Q_i = \int_A \left(\Delta f_j \frac{\partial u_j}{\partial q_i} - \sum_k \Delta \Psi_k \frac{\partial M_j^k}{\partial q_i} n_j - \theta \frac{\partial S_j^T}{\partial q_i} n_j \right) dA. \quad (19.36)$$

Note that it is an incremental quantity defined by the increments Δf_j , $\Delta \Psi_k$, and θ at the boundary A . The values of \mathcal{T} , D , and \mathcal{P} are quadratic forms with constant coefficients, formally the same as (18.17), (18.18), and (18.19).

The Lagrangian equations (18.16) and (19.33), with or without initial stress, are identical, as they should be, because they both govern the same fundamental physics of perturbations of a thermodynamic system near equilibrium. The difference lies in the particular evaluation of \mathcal{P} and Q_i for each case. A difference also appears in the nature of the equilibrium state, which may be stable or unstable, as will be discussed in the next section.

As already mentioned, the theory is directly applicable to fluid saturated porous media under initial stress. The only modification is in the kinetic energy, which is written

$$\mathcal{E} = \frac{1}{2} m_0 \dot{u}_i \dot{u}_i + \sum_k \dot{u}_i \dot{M}_i^k + \frac{1}{2} \sigma \sum_k \frac{\dot{M}_i^k \dot{M}_i^k}{m_{0k}}, \quad (19.37)$$

where σ is a factor taking into account the distribution of the microvelocity field of the fluid in the pores. The same microvelocity field is also taken into account in the evaluation of the dissipation function associated with the viscous fluid seepage (Biot, 1963).

A further generalization of the concept of generalized inertial forces is obtained by the introduction of *viscodynamic operators* (Biot, 1962, 1976b).

XX. Linear Thermodynamics and Dissipative Structures near Unstable Equilibrium

Thermodynamic equilibrium may be stable or unstable. There are many cases in nature where the equilibrium is unstable. In particular this may be the case for systems under initial stresses, which may be due to gravity or externally applied forces. Such systems are governed by the linear Lagrangian equations (18.16). They exhibit important physical properties of a very general nature, which do not seem to have been recognized. One of these is the appearance of regular spatial distribution of the unstable perturbations that may be called dissipative structures and *are not bifurcations*. *The erroneous notion that such structures require the system to*

be nonlinear and far from equilibrium has been propagated by some currently fashionable schools.

Another important property of linear instability is its *nonoscillatory character*. The properties of such unstable systems near equilibrium may be derived in complete generality by the linear Lagrangian equations (18.16) after putting $Q_i = 0$, i.e., assuming no perturbations of the applied mechanical or thermodynamic forces at the boundary. The instability is governed by the Lagrangian equations

$$\frac{d}{dt} \left(\frac{\partial \mathcal{F}}{\partial \dot{q}_i} \right) + \frac{\partial D}{\partial \dot{q}_i} + \frac{\partial \mathcal{P}}{\partial q_i} = 0 \quad (20.1)$$

or, explicitly,

$$\sum_j (m_{ij} \ddot{q}_j + b_{ij} \dot{q}_j + a_{ij} q_j) = 0. \quad (20.2)$$

Solutions of these equations are of the type $\exp(pt)$ where the p are characteristic roots of the system. The roots p are either real or complex conjugate and the system is stable if the real part of each root is negative. However if there are roots with positive real parts the system is unstable. A fundamental theorem has been established that states that unstable roots are all real, hence that the *instability is always nonoscillatory* (Biot, 1965b, 1974). To show this, we consider a root p and its complex conjugate p^* . The roots satisfy the equations

$$\sum_j (p^2 m_{ij} q_j + p b_{ij} q_j + a_{ij} q_j) = 0, \quad (20.3)$$

$$\sum_j (p^{*2} m_{ij} q_j^* + p^* b_{ij} q_j^* + a_{ij} q_j^*) = 0. \quad (20.4)$$

We multiply Eqs. (20.3) by q_i^* and Eqs. (20.4) by q_i and add the results. Taking into account the symmetry properties $m_{ij} = m_{ji}$, $b_{ij} = b_{ji}$, and $a_{ij} = a_{ji}$, we obtain

$$\sum_{ij} (p^2 m_{ij} + p b_{ij} + a_{ij}) q_j q_i^* = 0, \quad (20.5)$$

$$\sum_{ij} (p^{*2} m_{ij} + p^* b_{ij} + a_{ij}) q_j q_i^* = 0. \quad (20.6)$$

The difference of these two equations yields

$$(p - p^*) \left[(p + p^*) \sum_{ij} m_{ij} q_j q_i^* + \sum_{ij} b_{ij} q_j q_i^* \right] = 0. \quad (20.7)$$

By their physical nature the kinetic energy \mathcal{T} and dissipation function D , as represented by the quadratic forms (18.17) and (18.18), are positive definite. Hence

$$\sum_{ij} m_{ij} q_j^* q_i > 0, \quad \sum_{ij} b_{ij} q_j^* q_i > 0. \quad (20.8)$$

If the solution is unstable,

$$p + p^* > 0, \quad (20.9)$$

and Eq. (20.7) cannot be verified unless $p = p^*$, i.e., unless the root is real.

Thus near unstable equilibrium the perturbations in the linear range are nonoscillatory and proportional to increasing exponentials. Note that this includes dynamical systems with inertial forces.

Another property is derived by assuming an unstable solution with real p . Equation (20.5) shows that in this case we must have

$$\sum_{ij} a_{ij} q_i q_j < 0. \quad (20.10)$$

Hence no instability is possible if $\mathcal{P} = \frac{1}{2} \sum_{ij} a_{ij} q_i q_j$ is positive definite. This constitutes a fundamental stability criterion.

An important example of linear instability is provided by a layer of viscous medium resting on a rigid base and surmounted by another viscous medium of higher density. Due to gravity forces, the system is under initial stress. The interface is unstable and shows a wavy structure of given wavelength and amplitude growing exponentially with time (Biot, 1965b) as illustrated in Fig. 1. *The appearance of such dissipative structures in linear thermodynamics near equilibrium is quite general. In the context of geophysics and the formation of salt domes, such structures have been analyzed in detail (Biot and Odé, 1965; Biot, 1966).*

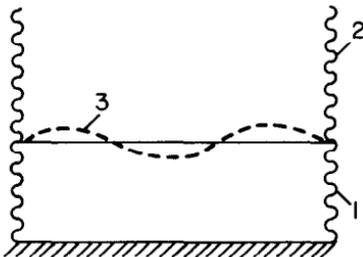


FIG. 1. Viscous layer (1) surmounted by a denser viscous layer (2) under gravity. Unstable waviness of increasing amplitude (3) appears at the interface.

XXI. Thermoelastic Creep Buckling

Physical insight into the thermodynamics of systems near a state of unstable equilibrium is provided by the case of a *purely thermoelastic continuum under initial stress*. As a simple example, consider a straight elastic rod initially under axial compression. It will tend to buckle. If the thermal conductivity is very small, the buckling load will be determined by the adiabatic elastic coefficients. On the other hand, if thermal conductivity is very large, the buckling load will be determined by the isothermal elastic coefficients. Hence we may distinguish between *isothermal and adiabatic buckling*. In the case where the axial load is between the isothermal and adiabatic value the thermal conduction will determine the rate at which the buckling instability appears. According to the general theorem of the previous section, the buckling that includes the effect of the inertial forces will be nonoscillatory, and all buckling modes will exhibit exponentially increasing amplitudes. If the axial load barely exceeds the isothermal value, the buckling amplitude will increase slowly and constitute a form of creep motion. In this case, the rate of creep is limited and dominated by the thermal conduction. We are dealing here with an example of creep instability that does not involve any viscosity and is entirely of thermodynamic nature. When we increase the axial load the rate of buckling increases until it is dominated by the inertial forces and becomes a dynamic buckling. By idealizing the case for a massless material we see that creep buckling will occur between two critical buckling loads, a lower one for isothermal buckling and a higher one for adiabatic buckling for which the rate of buckling becomes infinite. In the range between these two loads the massless rod exhibits a finite rate of creep. These effects were brought to light in some earlier work and discussed in the context of a complete analogy with the buckling of a porous elastic medium saturated with a massless fluid (Biot, 1963, 1964). The two phenomena are isomorphic and belong to the same underlying theory of instability of linear thermodynamic systems governed by the general Lagrangian equations (18.16). In the thermoelastic case, the dissipation function is due to thermal diffusion, whereas in the case of a porous medium it is due to viscous forces generated by fluid seepage between pores obeying Darcy's law.

The phenomenon was analyzed in more detail in later work in the context of general three-dimensional thermoelasticity. In particular, it was pointed out that for an isolated system the instability may be considered as occurring because the *unstable state of equilibrium corresponds to a minimum value of the entropy* of the whole system (Biot, 1973a, 1974).

XXII. Lagrangian Formulation of Bifurcations

By their very nature, the generalized coordinates may be used to describe *departures from a given time-dependent evolution of a system*. For example, we may write the displacement field of a solid as

$$u_i = u_i(q_1, q_2, \dots, x_l, t), \quad (22.1)$$

where $q_1 = q_2 = \dots = 0$ corresponds to a given time-dependent evolution. Note that in principle the dependence may be chosen arbitrarily, so that the case $q_i = 0$ does not necessarily represent a solution of the equations of evolution. The principle of virtual dissipation is applicable to this more general case, where variations δq_i are applied to any state of the system as frozen at a particular instant t . Hence Lagrangian equations may be derived that govern the departures from a given arbitrary evolution as measured by the generalized coordinates q_i .

Of considerable interest is the case where $q_i = 0$ represents a solution of equations governing the system and corresponds to an actual physical evolution. It is immediately evident that the Lagrangian equations in this case provide a clue to solutions that represent *branching or bifurcations* away from the case $q_i = 0$. In particular, this provides a powerful method of testing the stability of a given evolution. There are many advantages associated with the Lagrangian formulation. One is the possibility of studying *finite departures* from a given evolution in contrast to linearized methods of infinitesimal perturbations. Another is that a finite number of generalized coordinates may be used, with resulting simplification in the numerical or analytical treatment.

To be mentioned also is the probing of the accuracy of a given solution by testing the magnitude of possible departures.

XXIII. Generalized Stability Criteria for Time-Dependent Evolution Far from Equilibrium

The Lagrangian equations may be applied to provide very general stability criteria for the time-dependent physical evolution of a system that is not near equilibrium and for which linear thermodynamics is not applicable. In order to illustrate the method we consider the case of a system for which the inertial forces are negligible. Putting $I_i = 0$, the Lagrangian equations (10.4) become

$$\partial\mathcal{P}/\partial q_i + R_i = Q_i, \quad (23.1)$$

where R_i is a generalized dissipative force and Q_i the generalized driving forces. Such equations govern (for example) coupled thermomolecular diffusion and chemical reactions in a gravity field. We denote by

$$q_i = \varphi_i(t) \quad (23.2)$$

a time-dependent solution; a perturbed solution is given as

$$q_i = \varphi_i(t) + \Delta q_i, \quad (23.3)$$

where Δq_i is a small perturbation. The driving force Q_i is given and maintained unperturbed. Substitution in Eqs. (23.1), neglecting higher-order terms, yields

$$\sum_j \frac{\partial^2 \mathcal{P}}{\partial q_i \partial q_j} \Delta q_j + \Delta R_i = 0. \quad (23.4)$$

The perturbed dissipative force is

$$\Delta R_i = \sum_j \left(\frac{\partial R_i}{\partial q_j} \Delta q_j + \frac{\partial R_i}{\partial \dot{q}_j} \Delta \dot{q}_j \right). \quad (23.5)$$

The linear differential equations (23.4) in Δq_i determine the time-dependent evolution of the perturbations Δq_i . The coefficients of these equations are generally functions of time. If the perturbations Δq_i tend to zero with time the evolution is stable. The mathematical theory of linear differential equations provides stability criteria for the solutions of the perturbation equations (23.4). When considered in the context of irreversible thermodynamics, special stability criteria may be obtained.

Consider, for example, the steady-state evolution already discussed (Biot, 1976b). We write the perturbation equations (23.4) in the form

$$\sum_j \mathcal{A}_{ij} \Delta q_j + \sum_j \mathcal{B}_{ij} \Delta \dot{q}_j = 0, \quad (23.6)$$

where

$$\mathcal{A}_{ij} = \frac{\partial^2 \mathcal{P}}{\partial q_i \partial q_j} + \frac{\partial R_i}{\partial q_j}, \quad \mathcal{B}_{ij} = \frac{\partial R_i}{\partial \dot{q}_j}.$$

In addition, we assume that the system is quasi-reversible. In this case the dissipative forces are derived from a dissipation function

$$D = \frac{1}{2} \sum_{ij} b_{ij}(q_i) \dot{q}_i \dot{q}_j, \quad (23.7)$$

which is a positive quadratic form in \dot{q}_i with coefficients b_{ij} depending on q_i . We derive

$$R_i = \partial D / \partial \dot{q}_i, \quad \mathcal{B}_{ij} = b_{ij} = b_{ji}, \quad (23.8)$$

and Eqs. (23.6) become

$$\sum_j \mathcal{A}_{ij} \Delta q_j + \sum_j b_{ij} \Delta \dot{q}_j = 0. \quad (23.9)$$

By multiplying these equations by Δq_i and adding the results, we obtain

$$\sum_{ij} \mathcal{A}_{ij} \Delta q_i \Delta q_j + \sum_{ij} b_{ij} \Delta q_i \Delta \dot{q}_j = 0. \quad (23.10)$$

We note that for a steady state evolution b_{ij} is constant. Hence we may write

$$\sum_{ij} b_{ij} \Delta q_i \Delta \dot{q}_j = \frac{d}{dt} (\Delta D), \quad (23.11)$$

with the positive quadratic form

$$\Delta D = \frac{1}{2} \sum_{ij} b_{ij} \Delta q_i \Delta q_j. \quad (23.12)$$

Equation (23.10) is now

$$\sum_{ij} \mathcal{A}_{ij} \Delta q_i \Delta q_j + \frac{d}{dt} (\Delta D) = 0. \quad (23.13)$$

If we assume \mathcal{A}_{ij} to be a positive definite matrix, i.e., if

$$\sum_{ij} \mathcal{A}_{ij} \Delta q_i \Delta q_j > 0, \quad (23.14)$$

then Eq. (23.13) shows that ΔD must decrease with time. Because it is positive definite, the values of Δq_i must also tend to zero. Hence the inequality (23.14) constitutes a fundamental stability criterion.

If the inequality (23.14) is not verified, instability may arise. It may be due to the negative nature of $\partial^2 \mathcal{P} / \partial q_i \partial q_j$, in which case it is analogous to the instability of a linear system near equilibrium considered in Section 20. The instability may also be due to the negative nature of $(\partial R_i / \partial q_j + \partial R_j / \partial q_i)$, which arises essentially from the nonequilibrium state of evolution. Such a case of instability was illustrated by the example of an embedded viscous layer (Biot, 1976b), as recalled in more detail in the next section. In addition, in this example $\mathcal{A}_{ij} = \mathcal{A}_{ji}$, which implies that the instability is nonoscillatory.

The stability criterion (23.14) differs fundamentally from those presently in vogue (Glansdorff and Prigogine, 1971) by its generality and simplicity as well as by the physical insight provided.

XXIV. Creep and Folding Instability of a Layered Viscous Solid

Consider a solid viscous layer embedded in a large solid viscous medium of much lower viscosity. We assume incompressible media. A strain rate is imposed upon this system corresponding to uniform compressive strain parallel to the axis of the layer. For example, it may be compressed by two rigid frictionless planes normal to the layer, whose distance decreases with time. Obviously if the geometry is perfect, the layer will remain straight and be uniformly compressed. However, it is known (Biot, 1965b, 1976b) that the evolution is unstable, and if there are small initial perturbations of the geometry, they will grow and develop into a sinusoidal buckling of wavelength

$$L = 2\pi h \sqrt[3]{\eta/6\eta_1}, \tag{24.1}$$

where h is the layer thickness, η_1 its viscosity, and η the viscosity of the embedding medium. The result was verified experimentally. The regular pattern of wavelength L is obviously a dissipative structure due to an unstable state of evolution away from equilibrium. It has important implications in geology.

In the context of the general stability theory in the previous section, the folding represents a perturbation of a state of evolution. The unperturbed state of evolution is a uniform compression where the layer remains perfectly straight. We have assumed isothermal deformation and neglected gravity forces. The Lagrangian equations of creeping motion of the solid in this case become extremely simple. They are

$$\partial D / \partial \dot{q}_i = 0, \tag{24.2}$$

where D is a quadratic form in \dot{q}_i with coefficients depending on q_i . With $\mathcal{P} = 0$, the stability criterion is given by Eq. (23.14). It can be shown that it is not verified in this case for perturbations Δq_i from the uniform compression. The instability and Eq. (24.1) for the buckling wavelength have also been derived by this method of perturbation of the Lagrangian equations (Biot, 1976b).

Another example is provided by the internal folding of a stack of viscous layers of alternately high and low viscosity. When the system is

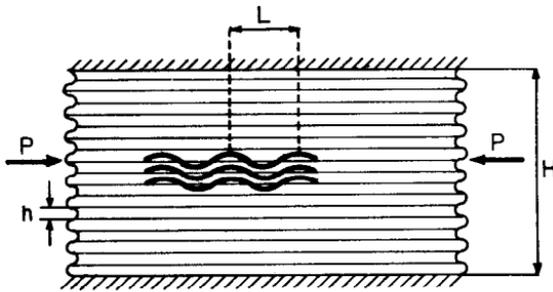


FIG. 2. Stack of alternate layers of large and small viscosity between rigid planes subject to a compression P . Note the appearance of internal folding of wavelength L .

compressed in the direction of the layers, an internal folding develops as shown in Fig. 2, with a wavelength

$$L = 1.9 \sqrt{hH}, \quad (24.3)$$

where h is the thickness of the more viscous layers and H the total thickness of the stack (Biot, 1965a, 1967).

These instability problems may also be considered from the standpoint of bifurcation, as discussed in Section XXII. In this case the uniform compression is represented by a steady state where the generalized coordinates are known functions of time $q_i^s = \varphi_i(t)$. Any deviation from this steady state may then be represented by new generalized coordinates q_i that represent departures from the steady state. We then evaluate the dissipation function D in terms of q_i^s and q_i . It will be a function that is linear and quadratic in \dot{q}_i with coefficients functions of q_i^s and q_i . The Lagrangian equations are of the same form as Eq. (24.2) with coefficients that may now be functions of time. We note that they express *minimum dissipation* under the constraint $q_i^s = \varphi_i(t)$.

A final remark is in order here in connection with Helmholtz's theorem, which states that under creeping flow conditions a viscous fluid tends to a stable steady-state flow (see Lamb, 1932, p. 619). This is not in contradiction with our results, because Helmholtz's theorem applies only to a fluid of uniform viscosity. This is not the case for an embedded layer or a stack of layers with two different viscosities.

XXV. Coupling of Subsystems and the Principle of Interconnection

In many problems, we deal with complex systems made up of separate components that differ from each other by their physical nature. Each of

these components or subsystems may be analyzed separately, and Lagrangian equations may be obtained that govern its behavior. The analysis of each subsystem may usually be achieved by *simple methods adapted to its particular physical nature* in terms of a small number of generalized coordinates that determine the field distribution of mass and energy fluence, material displacements, and reaction coordinates. The evolution of each subsystem (s) is governed by Lagrangian equations

$$I_i^{(s)} + R_i^{(s)} + \partial \mathcal{P}^{(s)} / \partial q_i = Q_i^{(s)\text{int}} + Q_i^{(s)\text{ext}}, \quad (25.1)$$

where $Q_i^{(s)\text{int}}$ are the driving forces on the subsystems at a coupling interface while $Q_i^{(s)\text{ext}}$ are the driving forces external to the combined system. We may add Eqs. (25.1) for all subsystems. In this process the interfacial forces $Q_i^{(s)\text{int}}$ may be grouped in pairs where they are equal and opposite in sign at each interface. Hence

$$\sum_s Q_i^{(s)\text{int}} = 0 \quad (25.2)$$

and

$$\sum_s I_i^{(s)} + \sum_s R_i^{(s)} + \sum_s \frac{\partial \mathcal{P}^{(s)}}{\partial q_i^s} = \sum Q_i^{(s)\text{ext}}. \quad (25.3)$$

We thus obtain unified Lagrangian equations for the combined system from which *interfacial forces have been eliminated*.

The method constitutes a generalization of a process of elimination of interfacial forces in classical mechanics by the method of virtual work.

We note that in this classical context it is nothing but the expression of the *third law of mechanics whereby action is equal and opposite to reaction*. Its extension to thermodynamic forces is evident from expression (9.17), in which the entropy and mass fluences are continuous at the boundary while the outward normal directions n_i of the subsystems are equal and opposite at the interface.

A special remark is in order for mechanical systems that are not adherent at interfaces. In this case the interfacial virtual work vanishes only if there is no friction. However, in the context of the more general thermodynamic formulation we may consider the solids to be adherent by considering that one of the surfaces is constituted by a thin, deformable, adherent skin where the shear deformation generates the friction forces and entropy production. *By this artifice, Coulomb friction may be included in the general formulation*.

The principle of interconnection is applicable to a wide variety of problems. It was discussed in the particular context of heat transfer (Biot, 1970). There are also a number of problems that have been treated in the past without realizing that the methods involved are particular cases of

such a broad unifying principle. For example, in aeronautical structural analysis and aeroelasticity during the years 1942–1945 it became common practice to consider normal modes of subsystems as generalized coordinates and interconnect the subsystems by *modal synthesis*.

Another example is in classical mechanics, where Lagrangian equations are obtained for the motion of rigid solids in a perfect incompressible fluid (see Lamb, 1932, p. 160). These equations may be derived by using the interconnection principle. Lagrangian equations are obtained separately for the motion of the solids and that of the fluid due to generalized interfacial forces that are equal and opposite. By interconnection, dynamical equations are obtained for the solids that embody implicitly the dynamics of the surrounding fluid.

Many more general problems suggest themselves here. Among others we may cite those of interaction between elastic solids and compressible fluids with or without viscosity.

XXVI. Completeness of the Description by Generalized Coordinates. Resolution Threshold and Lagrangian Finite Element Methods

The present treatment of irreversible thermodynamics emphasizes the description of a complex system as an assemblage of cells. From a fundamental viewpoint, the size of these cells may be extremely small while remaining above a *resolution threshold*, below which the statistical average definition of temperature and entropy breaks down and fluctuations enter into play. The cells are finite in number and determined by a finite number of generalized coordinates, which, as pointed out earlier (Biot, 1970), provide a complete physical description from the macroscopic viewpoint. As a consequence, the corresponding Lagrangian equations also *describe rigorously* the evolution of the system.

It is important to note that use of continuum models is an extrapolation, beyond the validity of physical laws, which introduces spurious difficulties in terms of completeness in the context of the mathematical concepts of measure, continuous sets, and functional space theories. Recent work by Woods (1981) has demonstrated the *lack of physical validity of much of the current fashionable formalism of continuum mechanics and thermodynamics*.

The Lagrangian equations also provide the foundation of a large variety of finite element methods where the state of finite cells is described by

generalized coordinates as values of scalar and vector fields at grid vertices, linear or quadratic interpolation providing values in the cells in terms of these generalized coordinates. The corresponding Lagrangian equations for the discrete variables are then obtained directly *without prior knowledge of the field differential equations*.

XXVII. Lagrangian Equations in Configuration Space. Internal Relaxation, Order-Disorder Phenomena, and Quantum Kinetics

The concept of threshold minimum size of cells, as described above for physical space, may be extended to subspaces in the abstract multidimensional configurational thermodynamic space (Biot, 1982b). For example, we may consider the translational and vibrational degrees of freedom of gas molecules as constituting distinct subspaces with their own entropy and temperature. The state of an assembly of such subsystems is then determined by mass and energy fluence between them. Following the same procedures as used for cells in physical space, completely general Lagrangian equations of evolution may be obtained with exchanges represented by internal fluence coordinates. In particular, this approach is applicable to internal relaxation effects in gases.

This procedure with Lagrangian equations and internal coordinates is also implicit in the general thermodynamic theory of relaxation and heredity in viscoelasticity (Biot, 1954).

The concept of subspace cells may be extended to quantum levels with their own temperatures and entropy. The kinetics of exchanges obeyed by fluence coordinates is then obtained from transition probabilities in quantum kinetics and statistics.

The same procedure may also be used for order-disorder phenomena in metal alloys where the order-disorder state is described by internal fluence coordinates.

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